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Stem Cells and Metallothionein - A Review

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ABSTRACT

Stem Cells are capable of self renewal and can differentiate into other lineages upon induction with specific growth factors and proteins. Mesenchymal stem cells obtained from various sources like adipose tissue, umbilical cord, bone marrow, umbilical cord blood have been reported to have stem cell characteristic features laid down by International Society for Cellular Therapy. Research so far deals with the differentiation and self renewal properties of stem cells, which needs to be understood further. Metallothionein, is a metal binding protein isolated from equine renal cortex and shown to be present in nearly all of our cells, with differential expression of it's isoforms. Apart from metal binding properties, this protein expression is deregulated in a variety of diseases and other treatment conditions. With respect to cancer biology, this protein expression is studied in almost all cancer types and results indicate pivotal role of this protein in cancer. Certain cancers are associated with up-regulation while some types are associated with down-regulation. The localization of this protein has also reported to change between actively proliferating and normal cells. Given the importance of this protein in cancer biology, the role of this protein in stem cell renewal as well as differentiation is poorly understood. This review discusses about stem cells, - its type and differentiation; metallothioenein – expression, function, review about different cancer types, role in angiogenesis and plausible role of this protein in the self renewal and differentiation of stem cells.

Key Words: Stem cells, Metallothionein, Differentiation, Self renewal, Apoptosis

STEM CELLS

In 1960s, mesenchymal stem cells were first identified as plastic adherent, non-haematopoietic stromal cells in bone marrow with osteogenic potential. Initially they were named as colony forming units and later they were renamed as mesenchymal stem cells (MSCs) as they can readily differentiate into adipocytes and osteoblasts (Pittenger et al., Science, 1999) [1]. Subsequently, differentiation to other lineages like ectoderm and endoderm has also been reported. Since then, MSCs have been isolated from many other tissues like adipose tissue, umbilical cord, umbilical cord blood, umbilical cord Wharton's Jelly, synovial membrane and tooth pulp. In general, stem cells are classified based on their source of origin as embryonic stem cells and tissue specific / adult stem cells. Recently, Shinya Yamanaka reported of creating pluripotent stem cells from terminally differentiated fibroblasts [2-12]. Stem cells are also classified based on their differentiation potential - totipotent (early progeny of the zygote up to the eight cell stage of the morula), pluripotent (Inner cell mass of embryo, epiblast), multi/oligopotent (Fetal tissues, membranes, placenta and adult stem cells), bipotent (lymphoid or myeloid stem cells) or unipotent (Muscle stem cells) [13, 14].

Characteristic features of MSCs

Ideally MSCs are isolated and identified based on their ability to adhere to static surface; preferably plastic coated with elements which support anchoring of cells and this is considered gold standard method still [15]. Another method of identifying and purifying the MSC population is by sorting of cells via Fluorescence activated cell sorting method. This is done by raising monoclonal antibodies against certain cell surface proteins. These surface markers are said to vary in their expression pattern and are donor-, isolation- and passage-dependent [16]. However there is consensus that MSC do not display CD11b, CD31, CD34, CD45, CD117 and HLA-DR. Positive expression of markers identified so far is: CD13, CD29, CD44, CD73, CD90, CD105, CD166,

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STRO-1, and Sca-1[17, 18, 19]. Several other methods such as membrane filtration, magnetic beads sorting, capillary electrophoresis, and differential centrifugation have also been employed among other emerging technologies to isolate these cells [20, 21].

MSCs also show multi-potential differentiation ability. Research has shown that MSCs have inherent property to differentiate into cells of mesoderm lineage, forming bone (osteocyte), fat (adipocyte) and cartilage (chondrocyte) cells upon induction [22]. These are the minimal criteria to define the isolated populations of cells as mesenchymal stem or stromal cells as described by the International society for Cellular Therapy (ISCT) in 2006 [16].

Self-renewal and differentiation

Self-renewal may be defined as the ability of cells that sustain the capacity of cells to remain in quiescent or undifferentiated state. It can be influenced by presence or absence growth factors such as Leukemia Inhibitory Factor (LIF), Fibroblast Growth Factors (FGFs), Wnt family of proteins, Sox2 and Oct4 among others. Commitment or differentiation of mesenchymal stem cells, inherently towards mesodermal lineage, as well as cells towards ectodermal and endodermal lineage is a tightly and temporally controlled process guided by microenvironment and culture conditions [23]. These can be regulated in order to enhance the differentiation capacity of MSCs by various methods using biological, biochemical and mechanical approaches [24, 25, 26].

Mesodermal differentiation

Differentiation of MSCs to form bone, fat or cartilage is inherent and can readily be observed upon induction by culturing MSCs with transforming growth factors β1 and β2 (TGF-β1&2), bone morphogenic protein (BMP)2, 4, 6, 12 and 13. To mimic the bone development in vitro; cells are cultured in the presence of β-glycerophosphate and ascorbic acid-2-phosphate, BMPs, Wnts, dexamethasone which would result in increased alkaline phosphatase activity and calcium deposits and are positive for von Kossa staining. Chondrocytes or cells forming cartilage can be obtained in vitro by culturing cells in high seeding density as pellet or micromass form, in the presence of Insulin-Transferrin-Selenium (ITS), linoleic acid, selenious acid, pyruvate, ascorbate 2-phosphate, dexamethasone and transforming growth factor-β III (TGF-βIII). At the end of differentiation period, cells tend to accumulate proteoglycans and type II collagen. To obtain fat cells or mature adipocytes, cells are cultured with dexamethasone, insulin, isobutyl methyl xanthine (IBMX), and indomethacin. The resulted cells are able to produce lipid droplets which can be revealed by addition of oil red stain and expression of Adipocyte-specific genes Peroxisome Proliferator Activated Receptor gamma (PPAR-γ), Adipocyte protein 2 (ap2) and Liporotein Lipase (LPL) genes [17, 27, 28].

Ectodermal differentiation

Despite of mesodermal origin, MSCs have the ability to differentiate into non mesodermal lineage such as neurons and glial cells. Neuronal or glial cells can be obtained upon exposure to cocktails of growth factors like Hepatocyte Growth Factor (HGF), fibroblast growth factor (FGF), epidermal growth factor (EGF), neurogenin-1, forskolin, cAMP, β- Mercaptoethanol (BME), Nerve Growth Factor (NGF), Insulin, Retinoic Acid, Valproic Acid, BME, hydrocortisone, Glial cell line derived Neurotrophic Growth Factors (GNDF), Brain-Derived Neurotrophic Factors (BDNF), 5-Azacytidine, isobutyl methylxanthine (IBMX), and indomethacin among others either alone or in combination [29]. Cerebrospinal fluid (CSF) has also been implicated in culture condition to induce neuronal phenotype and function [30].

Endodermal differentiation

Likewise, MSCs of various sources have shown to differentiate into endodermal cell types such as hepatocytes, insulin producing beta cells and renal cells. Trans-differentiation into hepatocytes is a two-step process involving differentiation and maturation [31]. In the presence of EGF, bFGF and nicotinamide, MSCs differentiate into hepatocytes and exposure to oncostatin M, dexamethasone and ITS+ (Insulin, Transferrin, Selenium) premix will form mature hepatocytes which can be confirmed by expression of markers like albumin, α-fetoprotein and nuclear factor 4 α (HNF-4α). Insulin producing β-cells can be successfully obtained by induction with growth factors, i.e. Acitvin A, sodium butyrate, taurine and nicotinamide. However cells obtained other than mesodermal lineage are yet to be translated in clinical practice due to low efficiency of functional capacity [32].

Though the above mentioned reports have been discussed about the isolation, differentiation and clinical usage of stem cells, research in this field needs more input, particularly with respect to differentiation and clinical application. Metallothionein, is a metal binding protein, expressed in most of the cells and tissues, have a major role in cell division, apoptosis and homeostasis of zinc and copper [33]. Numerous reports were about the role of metallothionein in cancer research [34]. Regarding stem cells, role of metallothionein in self renewal and differentiation needs to be identified.

METALLOTHIONEIN

Margoshes and Valley isolated metallothionein (MT) as a metal binding protein from equine renal cortex. Subsequently many types of MT have been discovered [33]. MT is known to present in all eukaryotes and in some prokaryotes, and

possesses a high degree of homology [35]. Characteristic features of this protein include absence of aromatic amino acid and histidine; presence of highly conserved cysteine residues (cys-x-cys, cys-x-y-cys, or cys-x-cys-cys) in the sequence (where x and y are amino-acids other than cysteine), and the presence of high metal content and a low molecular weight 6-7kDa. It has a high affinity for group I b and II b metals and is found to be a major zinc binding intracellular protein. Zinc and cadmium binds with thiolate clusters and form tetrahedral geometry, where as copper forms trigonal geometry. MT protein contains two domains: N-terminal (beta domain) region with 9 cysteine residues, bind 3 divalent or 6 monovalent ions while the C-terminal (alpha domain) region with 11 cysteine residues, bind 4 divalent or 6 monovalent ions. The two domains are connected by a hinge region composed of a conserved lys-lys segment [36-44]. The MT genes encoding at least 11 MT-1 genes (MT-1A, 1B, 1E, 1F, 1G, 1H, 1I, 1J, 1K, 1L, 1X); MT2A, MT3 and MT4 are clustered in the q13 regions of human chromosome number 16 [45]. In mice only one copy of each of MT1, 2, 3, 4 are present within a 60kb region on chromosome 8 [46]. MT-I and II are almost expressed in all tissues, whereas MT-III is restricted to central nervous system and male reproductive organs [47]. MT-IV is expressed only in stratified epithelial cells [47].

EXPRESSION OF METALLOTHIONEIN

The expression of metallothionein was found to be at constitutive levels in most cells but vary with cell type. The expression of different isoforms of MT was found to be regulated differently. The *cis* and *trans* acting factors were involved in the regulation of MT. DNA methylation of *cis* acting elements appears to play a role in the regulation and induction of MT genes in different cell types. The level of *trans* acting factor plays a role in the differential regulation and induction of MT genes in response to heavy metals. Low level, basal level as well as induced level of MT mRNA and protein is controlled by the cis acting DNA elements that are located upstream in the 5' region of the MT gene. The classical TATA boxes and the initiator regions (InR) form the promoter regions of MT-I and MT-II. They recruit the transcription factor II-D (TFIID) as a part of the pre initiation complex. Apart from the promoter region, they contain a metal responsive element (MRE), which is also essential for all levels of MT induction. But the MREs act in association with a zinc responsive transcription factor, termed as metal transcription factor-1 (MTF-1). Anti-oxidant Responsive Element (ARE) sequence is also present in adjacent to the MREs. Apart from these, a GC box (consensus sequence GGGGCGGGG), which respond to Sp1 transcription factor is also located in the promoter region of MT [48].

FUNCTIONS OF METALLOTHIONEIN:

Metallothionein, which is known to be induced by a variety of factors like heavy metals, glucocorticoids, cytokines, UV rays, hypoxic conditions, oxidative stress, cancer and, play different roles like - acting as metallochaperones to transport metal ions; in maintaining the concentrations of intracellular free zinc and copper ions; in acting as anti-oxidant, scavenging the free radicals; in the detoxification of heavy metals; and in the protection against various stress conditions. In short, metallothionein acts as a primary defense mechanism in the cells in order to protect against various harmful conditions [49].

MT and CANCER

Cellular localization of MT have been reported to be cytoplasmic in non-pathological tissues while in actively proliferating cells, MT localization varies with respect to cell cycle such as in nucleus in the S and G2 phase. This indicates that the altered MT level could correspond to abnormal cell division. Role of MT in proliferation, apoptosis, and invasion in cancer biology have been well studied using biopsy samples or cultured cancer cells. These reports indicate that increase in MT gene as well as protein expression, in actively proliferating normal cells, cancer cells of kidney, breast, lung, nasopharynx, salivary gland, ovary, testes, urinary bladder, leukemia and non-Hodgkin's lymphoma. Decreased MT expression has been reported in human hepatic, prostate and thyroid cancers. Apart from this, reports indicate that MT expression can be used as biomarker to identify the tumor stage [34] [Figure 1].

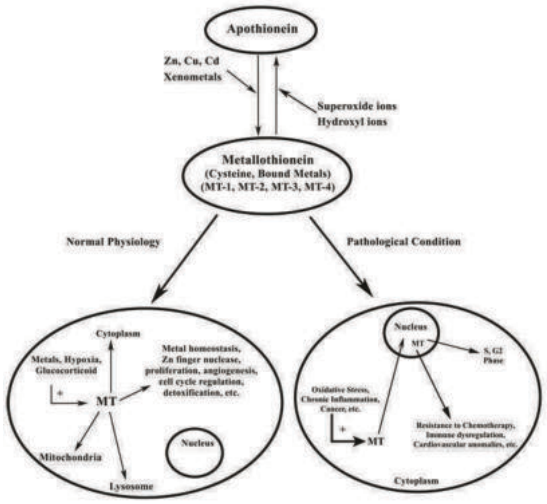

Figure 1: General overview of Metallothioneins (MTs). Thionein can exist in two forms intracellularly as Apothionein (inactive, unbounded, Cytoplasmic) and Metallothionein (Active, bounded, Cytoplasmic & Nuclear). This transition from Apo- to Metallo- and vice versa is a reversible process. Upon activation, it exerts many physiological functions such as metal homeostasis, gene expression, cell cycle regulation etc.

ENDODERMAL CARCINOMAS AND MT:

Hypermethylation of MT promoter region have been reported in papillary thyroid tissue when compared to normal thyroid tissue, which is associated with down regulation of MT in papillary and follicular thyroid carcinoma. When compared with healthy control tissue, laryngeal tissue biopsies show significant increased expression of MT. Regarding lung cancer, strong MT expression was reported in non-small-cell squamous cell carcinoma and adenocarcinoma while decrease in small-cell lung carcinoma, when compared with healthy control tissue. Reports indicate increased nuclear and cytoplasmic expression of MT in malignant and reactive cells in oral and pharyngeal squamous cell carcinoma. In esophagus carcinoma, MT negative tumors showed decreased lymph node metastases and distant organ metastases when compared with MT positive tumors. Increase in MT expression has been reported in gastric cancers and gastric dysplasia lesions but the levels are unrelated to tumor grade, stage or survival. Nuclei/cytoplasmic expression of MT have been reported in colorectal carcinomas. In hepatic cancer, MT expression is increased in surrounding healthy cells and reactive cells when compared with tumor cells. Regarding pancreatic carcinoma, studies reported that out of 75 patients, 59% showed negative expression and 41% were MT positive. In positive cases, MT expression was localized in cytoplasm and levels were correlated to metastasis and shorter survival. In bladder and ovarian cancer, increased MT staining was associated with tumor stage and grade, reduced survival. There is no association between MT expression and estrogen or progesterone receptor status in ovarian cancer [34] [Figure 2 & 3].

MESODERMAL CARCINOMAS AND MT:

Significant inverse correlation has been reported between MT expression and patient survival in renal cancer. In prostate cancer, increased MT level indicate an improved prognosis. Prostate cancer cells both in in vitro and in vivo show very low expression of MT levels when compared with healthy cells. In contrast, in case of uterine cancer increase in MT expression correlated with higher tumor grade, poor survival and increased tumor cell proliferative capacity [34] [Figure 2 & 3].

ECTODERMAL CARCINOMAS AND MT:

Number of studies reported that MT levels were associated with tumor grade, recurrence rate as well as poor survival in malignant invasive ductal breast carcinomas and MT expression is inversely correlated with estrogen and progesterone receptor status. Regarding skin cancer, mixed results were reported for MT expression. Weinlich et al., (2007) [50] reported that increased MT expression is correlated with poor survival while Suzuki et al., (2003) [51] reported that increased MT expression is protective in initial stages of skin carcinogenesis. In CNS, increase in MT expression is found to be therapeutically important as it is believed to protect non-malignant astrocytes and neurons from radiation induced apoptosis, thereby increasing the survival [34] [Figure 2 & 3].

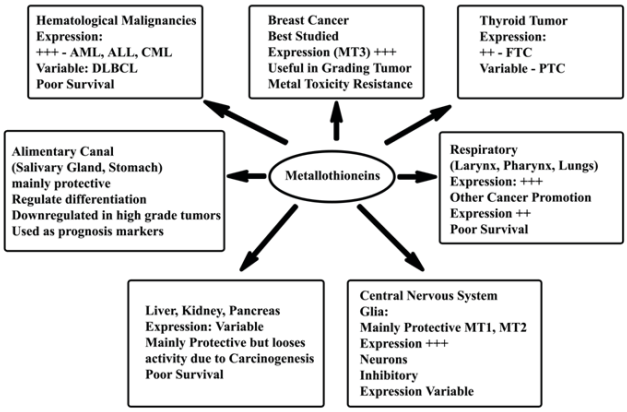

Figure 2: An overview of role of Metallothioneins in various neoplasms and malignancies.

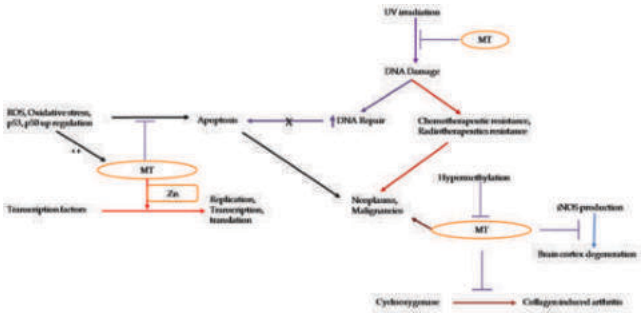

Figure 3: Mechanism of action of metallothioneins (MTs) in physiology and pathology. MTs upon induction by various metals and oxidative stress, translocate from cytoplasm to the nucleus and starts transcription of anti-apoptotic and survival genes by donating the metals, zinc for example, to zinc dependent transcription factors, thus inhibiting apoptosis. However, the same mechanism can lead to abnormal proliferation of cells even in the presence of oxidative stress thereby transforming cells into neoplastic or precancerous cells. MTs also reduce DNA damage caused by UV irradiation and augments DNA repair mechanisms. Conversely, it induces chemo- and radio- therapeutics resistance in the given cell giving them a niche to grow as malignant cell. MTs, on the other hand down regulates/ inhibit iNOS production thus protecting brain cortex degeneration. Also, MTs exert its protective role by inhibiting Cyclooxygenase which causes collagen induced arthritis. Nevertheless, hyper-methylation in the MT genes can diminish its protective activity and thus become a promotor or enhancer of malignant transformation of cells.

REGENERATIVE EFFECTS OF MT:

MT expression during cell cycle varies considerably. In G0 and G1, MT is localized primarily in cytoplasm, while in S and G2 phase, they are seen in nucleus and finally in G2/M, MT expression is cytoplasmic. Apart from this, reports indicate that nuclear expression of MT has a role in cell growth. Augmenting reports indicate that MT can activate transcription factors, metallo-enzymes and cyclin D by which it exerts its function during regeneration and tissue repair. Anti-inflammatory cytokines, growth factors, neutrophils and their receptors like IL-10, TGF-β & its receptor, FGF & its receptor, vascular endothelial growth factor (VEGF), NGF, NT-3-5, brain-derived neurotrophic factor (BDNF) and glial cell line derived neurotrophic factor (GDNF) were reported to be activated by MT [34].

ANGIOGENESIS AND MT:

Metastasis of cancer requires growth of new blood vessels, supply of oxygen and nutrients to tumor cells. The process of angiogenesis involves degradation of endothelial basement membrane, migration of endothelial cells to perivascular stroma and capillary sprouting. *De novo* synthesis and expression levels of number of growth factors like FGF, TGF-β and VEGF are known to be induced by MT. These factors are known to have a role in angiogenic process. Number of reports indicates relationship between MT and angiogenesis. In MT deficient mice, following the CNS injury, expression of angiogenic factors decreases when compared with that of normal. MT deficiency also inhibits proangiogenic effects of IL-6. *In vivo* expression of MT in endothelail cells at the site of angiogenesis and down regulation of MT in those cells inhibit cell proliferation and migration; *in vitro* network formation as well *in vivo* angiogenesis, have been reported. Also reports indicate that MT down regulation arrest cells in G1 phase. Together these reports indicate that MT has a role in angiogenesis [34].

Stem cells differentiation and Metallothionein:

Dohi et al., (2005) [52] reported that MT-2 expression was increased at both mRNA and protein level during the course of osteoblastic differentiation of MSCs. They further reported that MT-1 & 2 mRNA levels were very high during 48h after addition of dexamethasone and it declined to basal level. The osteoblastic markers alkaline phosphatase (ALP) and osteocalcin mRNA levels increased steadily from day 1 to day 14. Addition of antisense oligonucleotides against MT – 1& 2 mRNA during the first two days of differentiation in the presence of dexamethasone, decreased the ALP and osteocalcin level after day 14. They reported that early expression of MT mRNA and protein has a role towards osteoblastic differentiation of MSCs. MT as a zinc storage protein inside the cell, might play a role in differentiation process, by controlling the availability of zinc inside the cell. MT may also directly involve in controlling the differentiation process by interacting with other transcription factors. In 2011, Lin et al., [53] reported that addition of zinc in the differentiation process of dental pulp stem cells towards odontoblasts, agumented the differentiation process. Though they have not confirmed the report by inhibiting MT expression, this report cannot be ruled out regarding the role of MT in differentiation process.

DISCUSSION

Plausible roles of MT in the self-renewal and differentiation of Stem Cell:

MT, Cell cycle and Apoptosis:

Reports indicate that MT localization varies during cell cyle and with cell stage. MT has been reported to be present in cytoplasm in non pathological tissues, whereas in actively proliferating tissues, MT localizes in nucleus. In S and G2 phase, nuclear localization of MT has been reported [34]. Stem cells in their self renewal state can continuously divide. In such case, it will be note worthy to study about the expression, localization as well as role of MT in stem cells. MT has been reported to have role in apoptosis. Particularly when cardiomyocytes from MT transgenic mice are exposed to doxorubicin, MT suppresses apoptosis via inhibition of cytochrome c release from mitochondria and caspase – 3 [54]. Reports also indicate that zinc directly regulates caspase -3 activities [55]. Tumor suppressor gene p53 needs zinc in order to maintain the active structure. Replacement of zinc with cadmium, disrupts its function. Physical interactions between MT and p53 have been reported [56, 57]. Another mitogenic transcription factor NF-κB was also reported to be deregulated in cancer cells. Reports indicate that MT can interact with p50 subunit of RelA/NF-κB. This interaction stabilizes the DNA binding activity of NF-κB which in turn activates expression of several mitogenic genes [58]. Other reports indicate that MT can physically interact with the protein PKCμ, which has dual role in prostate cancer depending upon androgen status. PKCμ expression is repressed in androgen-independent prostate cancer, whereas it is enhanced in androgen dependent prostate cancer. MT is said to directly interact with lysine residue (612) at ATP binding site of PKCμ, which is responsible for its enzymatic activity. This indicates that interaction of MT with PKCμ can decrease its enzymatic activity. This may be a reason for decreased activity of PKCμ in androgen-dependent prostate cancer. However it is note worthy to find out the interaction between MT and androgen [59]. The above reports indicate that MT might have a role in stem cell renewal as well as differentiation. This area of research needs more attention to find out the role of MT in regulating differential genes involved in self renewal as well as differentiation [Figure 4].

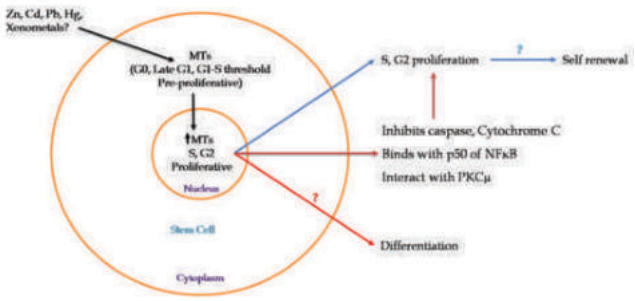

Figure 4: Do metallothioneins have any putative role in stem cell biology? A plausible area of research in the field of regenerative medicine.

CONCLUSION

In a multicellular organism like humans, daily wear and tear process is a common phenomenon. To maintain the cell homeostasis, every organ harbors a small quiescent population of cells termed as stem cells which serve as a reservoir of organ specific progenitor cells. These cells have the ability to both self-renew and give rise to differentiated cells and gain specialized function. Stem cells are reported to be present in various organs and tissues. Stem cell isolation, culture, differentiation and clinical application have been reported by various laboratories. Stem cells have the ability to self renew and differentiate. Research needs more input in understanding the balance between self renewal and differentiation. Though various growth factors and chemicals have been used for maintaining the above mentioned state, role of metallothionein has not been reported in detail. Metallothionein is a metal binding protein, which plays active role in cell division, cancer and apoptosis. This protein is reported to be activated by various agents like metals, growth factors, x-rays, etc. Most of the growth factors and chemicals used in differentiation of stem cells have the ability to activate metallothionein expression. Proteins like p53, NF-κB and PKC have been reported to interact with metallothionein. These proteins have role in cell cycle and apoptosis. Given the interaction of metallothionein and these proteins, role of metallothionein in stem cell renewal and differentiation cannot be ruled out. This area of research would be helpful in understanding the self renewal and differentiation. By altering the expression of metallothionein, either self renewal or differentiation can be improved, which would yield better population of cells for clinical translation.

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Compliance with Ethical Standards

Conflict of Interest: The authors have no competing interests to declare.

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On the Potential of Phytochemical Remedy for Envenomation and the Consequent Endocrinopathy, with a Note on Conservation – A Case Study of Venom Informatics

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Abstract

Envenomation is a serious neglected health issue at the global level that affects millions of people every year. It is highly prevalent among farmers and rural natives and is mainly due to the bite from snakes, spiders, frogs, dogs, wasps, bees, ants, etc. Many plants with antidote potential grow around our backyard without proper recognition and, unfortunately, several of them are under threat of extinction due to human interference and other environmental factors. The sustainable utilization of those antidote herbs can benefit as a life saver to the needy patients. The herbs can also be farmed and used commercially for the pharmaceutical application and incorporated with biotechnology and bioinformatics with a vision of synthesizing antidote drugs with less or no side effects. The objective of the present work is to create awareness among the public for the wise use of wild and local herbs, and their sustainable utilization with a computational case study on laboratory experiments done in two traditional plant based antidotes, selected from literature. The investigation is focused on *Daboia russelii* venom neutralization via *in silico* approach which can significantly reduce the time, expense, labour and samples taken. Our approach will add to the conventional non-specific polyvalent anti-snake venom (ASV) with more specific plant-based antidotes.

Keywords: Antidote, Envenomation, Herbal Medicines, Sustainable Utilization, Venom Informatics

1. Introduction

The term "envenomation" describes the process by which venom is injected into animals and or men by the bite or sting of a venomous species [1]. Millions of envenomation occurs every year. Precise statistical data in this regard are not available since majority of the morbidity/mortality rate is under-reported by either the hospitals or the local healers or the reported data may be fragmentary[2]. Among the animal bites, the most important are from snakes and up to five million people are affected at the global level by snake bites alone. An estimated approximately 2.4

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million people are bitten by venomous snakes and 94,000-125,000 deaths per year are annually reported with an additional 4 00,000 amputations and other severe health consequences [3]. South Asia is one of the regions where the highest burden of mortality and morbidity due to snake bites occur, especially in the Indian subcontinent. More than 200,000 snake bite cases, with more than 35,000-50,000 deaths, are reported in India [3, 4, 5]. Most of these venomous bites that lead to human lethality are due mainly to the "Big Four" venomous snakes, *viz*. *Naja naja* (Spectacled cobra), *Bungarus caeruleus* (Common krait), *Daboia russelii* (Russell's viper) and *Echis carinatus* (Saw scaled viper). In Kerala, India, most snake bite deaths are due to *Daboia russelii* as it delivers the highest dose of venom to the victims in a single bite.

Among the many manifestations of envenomation is endocrinopathy. Case studies, with special reference to bite of Russell's viper, have reported severe hypofunction of pituitary gland accompanied by problems in secretion of insulin and thyroxine[6, 7, 8]. An experimental study in rat model, using venoms of four species of snakes from Saudi Arabia, revealed that testosterone levels were either normal or stimulatory with acute treatment or inhibitory with chronic treatment. Cortisol levels were normal at acute treatment but showed a gradual rise reflecting the stress imposed on the animals. The effects on insulin and thyroxine were similar to those of testosterone level showing normal or stimulatory effect with acute treatment followed by decreased levels of hormones with chronic treatment[9].

The severity will be in high risk if the victim is far from medical facilities, as well as the allergic reactions due to the modern polyvalent anti-sera treatments. The insufficient facility to store antivenoms and the lack of timely treatments increase the risk. The current treatment modalities such as polyvalent anti-snake venom (ASV) and antibiotics are very expensive and also produce adverse effects.

Nature has been a healing agent which has been recognized for centuries. The Western Ghats, one of the "hottest hot-spots" of Biodiversity[10, 11, 12], passing through the entire stretch of Kerala, and continued on the North as well as South, is enriched with a plethora of fauna and flora having diverse therapeutic properties. Traditional knowledge and scripts have used this rich source of medicinal plants for treating several curable and incurable diseases. Local traditional healers, especially the tribal communities, have amazing practical expertise in the traditional primary healthcare. Now-a-days, scientists are focusing on traditional ethnomedicinal and alternative therapy-based treatments since these are free from side-effects and cost-effective compared to the allopathic treatments including polyvalent antivenoms and antibiotics. Many plants with antidote properties found around our surroundings, including gardens and back-yards, are potent drugs for many insect and animal bites. The sustainable and proper utilization of these medicinal herbs can be primary aids for venomous bites and thus as a life saver to the victims. The current global changes and the human activities have made the valuable plants getting vanished. In addition to this, the increasing research interests in the analysis and evaluation study of phytochemicals are having a critical role in the significant reduction of availability of medicinal plants. The need for maintaining the resources of *Mother Nature* has to be taken into consideration for the well-being of life. The modern scientists are curiously investigating the scope of bringing the potential of medicinal herbs into a single drug-like capsule for its easy availability and administration.

Venom Informatics, a systematic Bioinformatics approach is one in which the venom data are stored in electronic repositories which can be used to analyse, interpret and predict the molecular level drug-toxin interaction using various advanced Computational Biology and Bioinformatics tools and software. With the aid of those Bioinformatics databases and software, the primary analysis, ADME (Absorption, Distribution, Metabolism and Excretion) and evaluation study for a particular biological activity at molecular level can be predicted for *in vivo*/*in vitro* experiments with the goal of reducing the huge collection of plant resources at primary level of analysis, time, expense and labour efforts taken to identify the best leads. The present work is based on such practices with a case study on two plant based antidotes, *Hemidesmus indicus* and *Strychnos nux vomica* identified from a review article [13]. The experimentally isolated and characterized metabolites such as 2-hydroxy-4-methoxybenzoic acid from the root of *Hemidesmus*

indicus and Caffeic acid from the seed of *Strychnos nux vomica,* which have undergone i*n vitro* and *in vivo* studies in experimental animals[14, 15] were used in our *in silico* molecular docking analysis lab to confirm the predictability of the computational software.

2. Materials and Methods

The selected secondary metabolites from the specified plants, *Hemidesmus indicus* and *Strychnos nux vomica,* were subjected to molecular docking studies against the potential target venom protein, Phospholipase A_2 (PLA_2) of Russell's viper. The molecular docking was performed using the commercial molecular software, Discovery Studio 4.0 (BIOVIA, USA) on the Microsoft Windows 8 operating system. It is a suite of software for simulating small molecule and macromolecule systems[16]. The ligand molecules were subjected to pre-docking steps such as molecular preparation and energy minimization to optimize the molecular stability using the software. The analysis of protein-ligand interaction, and thus the biological activity, was also computed using the simulation software.

2.1 Ligand Identification and Optimization

The antidote property showing secondary metabolites, 2-hydroxy-4-methoxybenzoic acid obtained from *Hemidesmus indicus* and Caffeic acid from *Strychnos nux vomica* were selected based on the perusal of literature[13] in which the extracted metabolites have shown significant molecular effect in neutralizing the toxicity of Russell's viper[14, 15]. The three-dimensional structures of the small molecules from the respective plants were selected from the open access chemical database, PubChem with the compound identifiers CID: 75231 and 689043, respectively[17, 18]. The downloaded ligand molecules were prepared and optimized using the protocols, Ligand Preparation and Ligand Minimisation in the Discovery Studio 4.0. It generates possible orientation of ligands as conformers. All the generated isomers of the ligand molecules were subjected to docking process to predict the best lead isomer from the receptor-ligand complexes.

2.2 Target Identification, Validation and Optimization

The 3D structure of the target protein was searched based on the group II snake venom secretory PLA_2 of *Daboia russelii* as it is well-studied among snake venom proteins. From the list of X-ray crystallographic structures classified under Hydrolase enzyme, the protein with PDB ID 1TH6 was retrieved from the Protein Data Bank. The protein was selected based on the good resolution at 1.23 A° and Ramachandran plot. The protein consists of a single chain with 121 amino acid residues featured with 71 helices, 8 sheets and 42 loops/coils. The active site1 with functional residues Histidine 48, Aspartic acid 49 and Lysine 69 have been defined as binding sites. Prior to docking, the validated target protein was allowed to protein purification, preparation and minimization steps to globally optimize the protein structure to attain the stable confirmation using the Discovery Studio software.

2.3. Computational Molecular Docking

Molecular docking studies were conducted to evaluate the binding affinity of the selected ligand molecules to the target protein. The docking procedure was carried out using the force field, CHARMm-based CDocker algorithm. It is a grid-based molecular docking refinement method that generates maximum random conformations of protein-ligand complexes through High Temperature Molecular Dynamics. The docking parameters were kept as default. The docked poses listed as Hits were ranked according to the least CDocker energy which is calculated on the basis of internal ligand strain energy (-ve CDocker energy) and receptor-ligand interaction energy (-ve CDocker Interaction energy). The interaction energies calculated the non-bonded interactions such as Vander Waal's and electrostatic energies between two sets of atoms. Here, the highest value with –ve CDocker energy and –ve CDocker Interaction energy were considered as the favourable scores having least energies. All docked poses were further subjected to calculate the Binding Energy protocol to predict the best hit with least binding energy. The binding energy implies the stability of the receptor-ligand binding affinities. The filtered pose with least energies were further screened on the basis of number

of hydrogen bonds which implies the stability of the molecular interaction. The filtered best poses were then subjected to ADME, Mutagenicity and Carcinogenicity tests to predict the best non-toxic lead molecule.

3. Results and Discussion

It was observed that the least energy scores of -ve CDocker energy and -ve CDocker Interaction energy with 58.3086 kCal/mol and 64.3222 kCal/mol, respectively, have shown the least binding energy value (564.483 kCal/mol) among the hits obtained from the 1TH6 and 2-hydroxy-4-methoxybenzoic acid docked complexes (Table 1). The hydrogen bond interactions (Figure 1) with residues Lysine 69 with a bond distance of 2.00515 A° show the ligand as a significant antagonist of viper venom protein PLA_2. The other interaction residues are Glycine 32 with 5.54918 A° and Tryptophan 31 with 5.54918 A°. Similarly, the Caffeic acid has shown the best pose with the least binding energy (-309.016 kCal/mol) where -ve CDocker and -ve CDocker Interaction energies are 45.0078 kCal/mol and 47.0702 kCal/mol, respectively, with PLA_2 (Table 2). The interaction residues (Figure 2), Lysine 69 with a hydrogen bond distance of 1.96024 A° and Glycine 33 with 1.90193 A° also show antagonistic/inhibitory property to reduce the neurotoxic venom. It is also noted that Lysine 69 is the key residue that is having a significant role in inhibiting the venom PLA_2 activity. The ADME, Carcinogenicity and Mutagenicity tests predicted (Table 3) that 2-hydroxy-4-methoxybenzoic acid is less toxic with

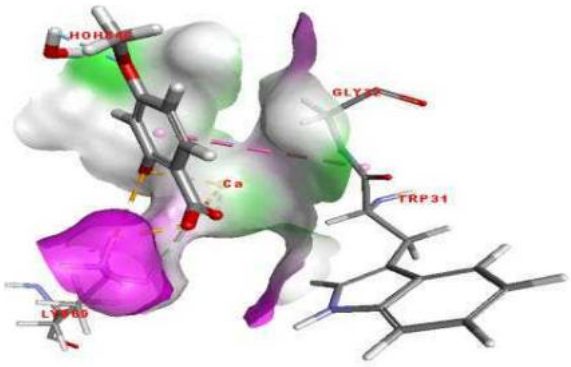

Figure 1. Selected docked pose and H-bond interactions of 2-hyroxy-4-methoxybenzoic acid with Russell's viper venom phospholipase A_2 in Discovery Studio software.

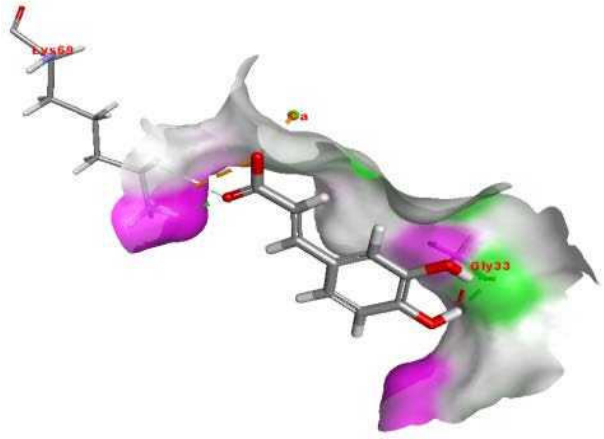

Figure 2. Selected docked pose and H-bond interactions of Caffeic acid with Russell's viper venom phospholipase A_2 in Discovery Studio software.

Table 1. Details of selected Hit molecule from *Hemidesmus indicus* against PLA_2 in Discovery Studio 4.0

Ligand	-CDocker Energy (Kcal/mol)	-CDocker IE (Kcal/mol)	BE (Kcal/mol)	Residues	H-bond Distance (A0)	No. of H-bonds	Potential Energy (Kcal/mol)	Van der waal's Energy (Kcal/mol)	Electrostatic Energy (Kcal/mol)
2-hydroxy-4-methoxy benzoic acid	58.3086	64.3222	-564.483	Lys69 Gly32 Trp31	2.00515 5.54918 5.54918	7	132.04488	2.06174	124.01204

Table 2. Details of selected Hit molecule from *Strychnos nux vomica* against PLA_2 in Discovery Studio 4.0

Ligand	-CDocker Energy (Kcal/mol)	-CDocker IE (Kcal/mol)	BE (Kcal/mol)	Residues	H-bond Distance (A0)	No. of H-bonds	Potential Energy (Kcal/mol)	Van der waal's Energy (Kcal/mol)	Electrostatic Energy (Kcal/mol)
Caffeic acid	45.0078	47.0702	-309.016	Lys69 Gly33	1.96924 1.90193	0	-21.50396	1.3162	-25.50056

Table 3. ADME, Mutagenicity and Carcinogenicity predictions of the selected ligand molecule from Discovery Studio 4.0

Ligands	Aqueous Solubility	BBB	Absorption Level	AlogP	Mutagenicity	Carcinogenicity
2-hydroxy-4-methoxy benzoic acid	4	3	0	1.201	0.000	0.000
Caffeic acid	4	3	0	1.443	0.964	0.027

no carcinogenic and mutagenic property when compared to Caffeic acid. Based on the interaction study and ADME prediction, 2-hydroxy-4-methoxybenzoic acid shows a significant neutralization effect when compared to Caffeic acid against Russell's viper venom phospholipase A_2.

4. Conclusions

The *in silico* approach used in the investigation has been validated and proves that the docking results are consistent with the laboratory experiments in animal models. Hence, the approach would strengthen the use of computational approach and analysis for an effective screening strategy and thereby conserve the potential plants for generations.

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Transient Gestational Exposure to Hexavalent Chromium (CrVI) Adversely Affects Testicular Differentiation: A Study in Rat Model

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Abstract

Chromium (Cr), an essential trace element, turns into an endocrine disruptor and male reproductive toxicant when its concentration in drinking water exceeds the safe limit. Improper disposal of effluents from more than 50 industries that use Cr contaminate the environment, in addition to occupational exposure of the workers. Testis has come to stay as a target for the reproductive toxicity of hexavalent Cr (CrVI), whereas its impact on fetal testicular differentiation remains elusive. We tested the hypothesis "*In utero* exposure to CrVI may alter the level of specific proteins controlling differentiation of testicular cell types". Pregnant Wistar rats were exposed to drinking water containing 50, 100 and 200 ppm potassium dichromate (CrVI) during gestational days 14 to 21, covering the period of fetal differentiation of testicular cells. Testes were collected on postnatal day 1 and subjected to light microscopic histological studies and immunohistochemical detection of cell-specific proteins. Testis of neonatal rats with gestational exposure to high doses of CrVI showed shrunken and dispersed tubules with fewer gonocytes, extensive vacuolization of seminiferous cord accompanied by damaged epithelium, and shrunken Leydig cells present in large interstitial spaces and loose compaction of cells when compared coeval control group. Immunosignals of androgen and estrogen receptor β increased, whereas those of estrogen receptor α, follicle stimulating hormone receptor, anti-Mullerian hormone, P_{450} aromatase, inhibin, c-fos and c-jun decreased. Immunosignals of steroidogenic acute regulatory protein and CYP11A1 increased, whereas 3β - hydroxy steroid dehydrogenase and CYP17A1 proteins decreased, indicating compromised steroidogenic function. Our findings support the proposed hypothesis and we conclude that gestational exposure to CrVI disrupts specific hormones and hormone receptors that control fetal differentiation of testicular cells. The detrimental effect of gestational exposure to CrVI on functional differentiation of testicular cells may have a bearing on testicular function at adulthood.

Keywords: Gonocytes, Leydig Cell, Sertoli Cell, Steroidogenesis, Testis

Abbreviations

AR, androgen receptor; **3-βHSD**, 3β-hydroxy steroid dehydrogenase; **17-βHSD**, 17β-hydroxy-steroid dehydrogenase; **CrIII**, trivalent chromium; **CrVI**, hexavalent chromium; **CYP11A1**, cytochrome P450 family 11 subfamily A member 1; **CYP17A1**, cytochrome P450 family 17 subfamily A member 1; E_2, 17β estradiol; **ERα**, estrogen receptor α; **ERβ**, estrogen receptor β; **FSH**, follicle stimulating hormone; **FSHR**, FSH receptor; **GD**, gestational day; **LCs**, leydig cells; **LH**, luteinizing hormone; **LHR**, LH receptor; **PND**, postnatal day; **SCs**, sertoli cells; **StAR**, steroidogenic acute regulatory protein; **T**, testosterone; **USEPA**, united states environment protection agency.

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1. Introduction

Endocrine disrupting chemicals (EDCs) are major causative factors of male infertility, both in animals and humans[1]. Increasing incidences of hypospadias, cryptorchidism, testicular germ cell cancer, and declining sperm count and fertility rates worldwide due to EDCs have raised apprehensions about environmental influence on male reproductive health[2-4]. Chromium (Cr), an essential trace element[5-8] is also one among the top ten heavy metal pollutants of the environment[9] and endocrine disruptor[10,11]. Recent reports have shown that Cr pollution is one of the top six toxic threats to the world[12]. It is used in more than 50 industries across the world with applications including tanneries, wood processing, chrome plating, welding, wax, paint, steel manufacturing, alloy, cast iron, ammunition, etc[13,14]. Its exponential usage in various industries worldwide and improper disposal of the effluent contaminate the environment, which has deleterious effect on human health, including reproduction[15]. CrVI, released from industries, is deposited in the landfills and waterways, and affects millions of people exposed to the polluted sites, who drink Cr-containing water[16]. It has been envisaged that approximately 74 million people in 7000 communities who drink tap water polluted with Cr across the world are at risk[17]. The concentration of Cr in drinking water supplied in different parts of USA has been reported to be higher than the safe limit[17-21] approved by US EPA i.e. 0.1 mg/L (0.1ppm)[21]. In many parts of India also, Cr concentration in drinking water is higher than the recommended safe level,[16,22,23] particularly in Ranipet (Tamil Nadu State, India), a flourishing tanneries site, which has total Cr in the range of 3.1 to 246 ppm in drinking water wells, whereas in Kanpur, another hub of tanneries (Uttar Pradesh State, India), it is between 1.05 and 35.34 ppm[24].

Chromium has become a potential threat to human reproductive health[25]. Increased incidences of birth and developmental defects among children born to mothers living around tanneries, chrome and leather industries in the developing world may attest the adverse effect of Cr on reproduction[16]. Abortion by 12 weeks in pregnant women employed in a dichromate manufacturing factory in Russia has been reported[26]. Exposure to CrVI decreased sperm counts and increased sperm abnormalities by disrupting germ cell arrangement and spermatogenesis in rat and humans[27]. Welders who work in stainless steel industry have poor sperm quality when compared to others[28,29]. Subfertility in 673 welders from Danish population in the same geographical area was reported and the study lead to the conclusion that 79% of wives of welders had increased rate of delayed conception[30]. Poor semen quality, sperm abnormalities and infertility in workers exposed to CrVI in mild steel welding industry was attributed to developmental problems including cancer in children[31]. Altered sex ratio with reduced male births due to paternal exposure to the metal fumes containing Ni and Cr has been reported in workers in an Italian mint[32].

Experimental studies performed in animal models pointed out that excess Cr may be a male reproductive toxicant. Direct effect of Cr on mammalian testis was predicted with the finding of its accumulation in the interstitial tissues of rat[33]. This view got entrenched by the finding of uptake of CrVI by the testis and its persistence in the tissue for a prolonged period in the form of CrIII in rat and mouse[34]. Edema of interstitial tissues, congestion of blood vessels and complete absence of spermatocytes in the seminiferous tubules have been found in rabbits administered 0.7 mg CrVI/kg body weight CrVI through oral route for six weeks[36]. Administration of 2 or 3 mg CrVI/kg body weight for 69 days to adult rats decreased sperm count and motility, and disrupted spermatogenesis with decreased late stage spermatids and germ cell number at stage VII, and altered activities of testicular enzymes sorbitol dehydrogenase, lactate dehydrogenase, λ-glutamyl transpeptidase and glucose-6-phosphate dehydrogenase[37]. Intraperitoneal (i.p.) injection of CrVI (0.5 mg/kg body weight) for five days a week for eight weeks led to testicular atrophy and reduced sperm counts and motility in rats, which could be reversed after eight weeks of reversal period[38,39]. Injections (i.p.) of 2 mg CrVI/kg body weight/day to adult rats for 15 days resulted in ultrastructural changes in testis, which included leakage of SC tight junctions in seminiferous tubules, cytoplasmic vacuolization and degeneration of mitochondria in the seminiferous epithelium and disruption of mitochondrial sheaths in the tail and mid-piece of spermatids[40,41]. Enlarged intercellular spaces, tissue loosening and significant loss of gametes into the lumen of seminiferous tubules, decreased sperm motility and number, and increased sperm abnormality were observed in adult rats treated CrVI (1 or 2 mg/kg body weight) for fifteen consecutive days[42].

Studies performed in our laboratory[43,44] on a non-human primate (*Macaca radiata*) model entrenched the male reproductive toxicity of sub-lethal doses of CrVI

(50, 100, 200, 400 ppm) administered through drinking water for a chronic period of six months. Adult monkeys exposed to different doses of CrVI experienced decreased sperm counts and forward motility from the second month onwards leading to azoospermia by the sixth month[43,46]. Ultrastructural studies on these monkeys revealed the presence of multi-nucleate hypertrophied germ cells undergoing degeneration in the lumen of testis and epididymis[45], which was attributed to oxidative stress in these organs[46]. Azoospermia in CrVI-treated monkeys was associated with free radical toxicity due to decreased specific activities of antioxidant enzymes, superoxide dismutase (SOD) and catalase (CAT), and the concentration of reduced glutathione in seminal plasma, which was reversed by supplementation of various doses of vitamin C (0.5, 1, 2 mg/L)[44]. The level of H_2O_2 in the seminal plasma/sperm of monkeys increased with increasing doses and duration of CrVI exposure[44]. While all these changes were reversed after 6 months of Cr-free exposure period, simultaneous supplementation of vitamin C prevented the development of Cr-induced oxidative stress[44]. Electron micrographs of testis of Cr-treated monkeys revealed premature release of spermatocytes and round spermatids into the lumen, which underwent degeneration beginning with hypertrophy; epididymis developed micro-canalization in an adaptive mechanism to avoid extravasation of sperm in monkeys exposed to Cr[45]. Abundance of basal cells, intraepithelial macrophages and lipofuscin (LF) material in these cell types of the epididymis increased in CrVI treated monkeys; the principal cells phagocytosed dead sperm from the lumen due to CrVI exposure and processed them partially into LF material[47].

It was further reported from our laboratory that swollen LCs with large vacuoles and lipid inclusions, swollen mitochondria with collapsed cristae and vacuoles in SER of prepubertal (PND30) and young adult (PND 60) rats born to mothers with gestational exposure to 50 ppm /100 ppm CrVI, whereas LCs in PND90 rats had normal organization[48]. Gestational or lactational exposure to CrVI led to temporal reversible changes in serum testosterone and estradiol titres in rats[48]. Recently, we reported atrophy of seminiferous tubules and interstitial edema with distorted tubular morphology and increased interstitial space in adult rats of mothers with gestational exposure to CrVI[10]. The above report also showed disruption of inter-SC tight junctions and SC-GC junctions leading to disruption of spermatogenesis and premature release of round spermatids into the lumen in sequel to decreased expression of *Ar* and *Fshr* and tight junction proteins occludin and claudin-11 in SCs.

An *in vitro* study has proved the adverse effect of Cr on differentiation and self-renewal mechanisms of spermatogonial stem cells (SSCs) and disruption of steroidogenic apparatus due to decreased expression of *Cyp11a1* and *3βHsd* and increased *Star* and *Cyp17a1* expression in TM3 LC lines challenged with various concentrations of CrVI; TM4 SC line challenged with CrVI showed decreased expression of tight junction signaling and cell receptor molecules like *Tjp1, Ocln, Vim*, and thus impaired secretory functions[49].

Testicular differentiation is a critical event during male sex development, beginning at GD14 with the appearance of seminiferous cords in rat[50] and is strictly regulated by proteins and hormones of testicular origin. However, the impact of excess CrVI on fetal testicular differentiation remains a grey area of research. Therefore, we hypothesized that *in utero* exposure to CrVI may affect the expression of specific proteins controlling differentiation of testicular cell types, which we put to test in this study.

2. Materials and Methods

2.1 Experimental Animals and Chemicals

The experiments in Wistar rats (*Rattus norvegicus*) were approved by the Institutional Animal Ethics Committee for studies on experimental animals (Ref: IAEC No. 03/013/08), which had a nominee of the Committee for Prevention of Cruelty and Safety to Experimental Animals (CPCSEA), Government of India, Ministry of Environment, Forests and Climate Change, New Delhi. The entire study was conducted in triplicate with rats in three separate batches. The female rats were divided into four groups: **Group 1, Control**: Pregnant rats which received regular normal drinking water. **Groups 2, 3 and 4 (CrVI-treated)**: Pregnant rats which received drinking water containing 50, 100 and 200 ppm $K_2Cr_2O_7$ respectively, from gestational day (GD) 14 to GD21, encompassing the critical window of fetal testicular differentiation[50]. These doses of Cr have been in practice in our laboratory for more than a decade based on dose-response studies performed in rat and monkey models[43,46,51]. Among the selected doses, 50 ppm is the minimum effective dose, 100 ppm is the half-maximal effective dose and 200 ppm is the maximum effective dose, which induced reproduc-

tive toxicity as assessed by serum hormones and spermatogenesis/sperm counts without any mortality in rats[10]. Doses lower than 50 ppm (12.5 and 25 ppm) did not produce any obvious change in reproductive physiology or hormonal profiles of experimental animals[43,46,51]. Since the objective of the study has been to test the reproductive toxicity of the metal, we did not test lower doses prescribed for 'No-observed adverse effect level (NOAEL)' for carcinogenic responses[52] in the present study. These doses are above the USEPA (2017) guideline for safe limit of Cr (0.1 ppm) in drinking water and comparable to Cr level in drinking water in many developing countries with Cr based industries[16,53]. Throughout the study, rats were fed standard rat pellet feed (Brooke Bond Lipton India Ltd.,Bengaluru) *ad libitum* and maintained under controlled temperature (25±1 °C) and photoperiod (12h Dark: 12h Light). The animals were dewormed with albendazole (10 mg/kg body weight, orally) one week before use. The estrous cyclicity of rats was checked by observing the vaginal smear, daily morning and evening under the microscope (Long and Evans, 1922). Adult male rats with proven fertility (stud) were dewormed and allowed to mate with the females (1:2) at late proestrous phase. Presence of vaginal plug in the morning confirmed successful mating and that day was considered as day '0' of pregnancy, and the conceptus was considered as one day old, 24 h later i.e., day 1 post-coitum (dpc) or gestaional day (GD 1). On PND1 the male pups were euthanized (3 pups in each group from three sets of animals i.e. a total of 9 pups in each group), testes were randomly dissected out and fixed in 4% para-formaldehyde solution for sectioning followed by immunohistochemical localization of various key proteins associated with testicular differentiation, whereas 10% neutral buffered formalin was used as fixative for histological analysis of testis.

2.2 Hematoxylin and Eosin Staining

Testes of newborn (PND1) rats were dissected and fixed in 10% neutral buffered formalin solution for 3 days. The tissues were embedded in paraffin and sectioned at 5 µm thickness, and prepared for Harris' hematoxylin and Eosin. The sections were mounted in Distyrene Plasticizer Xylene (DPX). The sections were examined in a Nikon Eclipse 80i microscope and photographs were obtained at 400x magnification using Network Internet System (NIS) -imaging and capturing software (Nikon Instruments, Tokyo, Japan).

2.3 Immunohistochemical Analysis

PND1 rat testes for immunohistochemistry were randomly selected after completion of treatment period from GD14 to GD21. Testes were fixed in 4% paraformaldehyde (Fisher Scientific, Mumbai, India) for 3 days, processed and embedded in paraffin at 58 °C, sectioned at 5 µm thickness and stored at room temperature until processed for immunostaining. The sections were deparaffinized by using xylene and rehydrated with different dilutions of alcohol in their descending percentages, then treated with 3% H_2O_2 in methanol to suppress endogenous peroxidase activity. Antigen retrieval was performed by heating the sections in citrate buffer (1:10 dilution in deionized water, pH 6.0) (Sisco Research Laboratories, Mumbai, India). The avidin-biotin peroxidase method was used for immunostaining[54]. The sections were incubated with 1% normal bovine serum albumin in TBS for 45 min to reduce nonspecific staining. Thereafter, the sections were kept for incubation overnight at 4 °C with specific primary antibodies (Santa Cruz Biotechnology, Santa Cruz, CA). The optimal working dilution of each antibody was determined by incubating sections with various concentrations of antibody ranging from (1:150 to 1:250 µL dilution). Following incubation with the primary antibody, the slides were washed in TBS (Tris Buffer Saline) and incubated with biotinylated secondary antibody anti-rabbit IgG or anti-goat IgG (1:300 µL) for 1 hour at room temperature, and then with avidin-biotin peroxidase (1:200 µL) (Vector Labs, Burlingame, CA) for 30 min. Further, the sections were exposed to 3, 3' diaminobenzidine tetra-hydrochloride (DAB) (Impact, Vector Labs, Burlingame, CA), counterstained with hematoxylin, and mounted with DPX (Sisco Research Laboratories, Mumbai, India).

The stained sections, after mounting, were observed in a Nikon Eclipse 80i microscope and photographed using NIS element software at 400x magnification. At least five 40x power fields were digitized for each sample with a NIS element software camera (Nikon Eclipse 80i microscope). The immunostained cells and the intensity of staining of each testicular subpopulation were considered to find the outcome in each group for analysis.

2.4 Statistical Analysis

All statistical analyses were performed using Prism (version 6.0; Graph Pad Software, San Diego, CA). For comparison of control and CrVI-treated (50 ppm, 100 ppm and 200 ppm) animals, one-way ANOVA followed by Newman Keuls post-test for multiple comparisons was used.

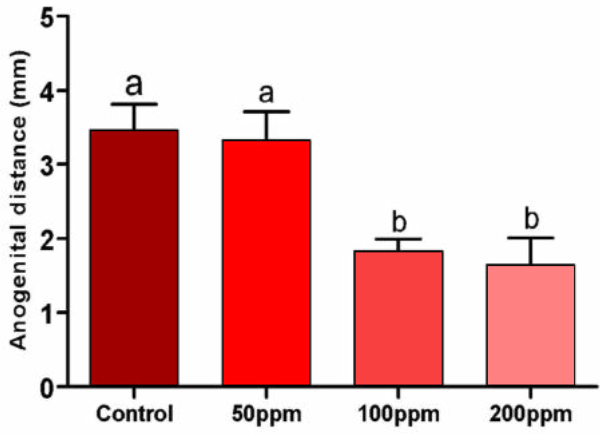

Figure 1. Impact of gestational exposure to CrVI on the AGD of neonatal rats. X-axis indicates doses of CrVI;the bar above each histogram denotes the SEM of five animals ; alphabets above each histogram indicate the statistical significance of difference between means;same alphabets in two means indicate no significance,whereas different alphabets indicate statistically significant difference at $p<0.05$ between the two means.

3. Results

3.1 Measurement of Anogenital Distance (AGD)

F_1 progeny of mothers exposed to drinking water containing 100 ppm and 200 ppm CrVI during GD14 to 21 had decreased AGD as compared to coeval control rats. The AGD of 50ppm CrVI treated male rats were comparable to the control (Figure 1).

3.2 Histological Changes

Testis of control rats showed normal arrangement of the spermatogenic cords with mononucleate gonocytes and spindle-shaped mesenchymal cells having normal distribution in interstitium (Plate 1A). F_1 progeny of mothers who consumed drinking water containing CrVI manifested various histopathological changes, which were exponential with increasing concentrations of the metal (Plate 1A-D). The F_1 progeny of mothers exposed to 50 ppm CrVI during gestational period showed unaltered histoarchitecture in general, except for loosening of tubular compaction and increased interstitial space (Plate 1B), whereas neonates of mothers exposed to 100 ppm CrVI showed shrunken tubules with damaged SCs with highly vacuolated cytoplasm and increased interstitial space (Plate 1C). The neonatal rats of mothers exposed to the highest concentration of (200ppm) CrVI exhibited marked disruption of spermatogenic cells with appearance of some multinucleate and vacuolated gonocytes (Plate 1D). The spermatogonial cells had increased heterochromatin in the 200 ppm CrVI treated neonatal rats.

3.3 Immunohistochemical Changes

AMH exhibited strong signal within the seminiferous tubule of control rat testis retrieved on PND1 (Plate 2A); consistent with the fact that SCs are its source, intense AMH signal was seen in and around these supportive cells. However, the signal intensity decreased in F_1 progeny of mothers exposed to 50 ppm, 100 ppm and 200 ppm CrVI during gestational period (Plate 2B,C,D)

Inhibin showed immunopositivity and strong signal of inhibin in seminiferous tubules (Plate 3A). Though the staining pattern in CrVI-treated pups bore resemblance to the testis of control rats, the signal intensity in 50 ppm, 100 ppm and 200 ppm CrVI-treated rats decreased significantly as compared to control (Plate 3B,C,D).

FSHR protein in F_1 neonatal rats showed strong immunostaining in control rats (Plate 4A), whereas a significant reduction in signal was observed in pups born to mothers who consumed drinking water containing CrVI during gestation (Plate 4B,C,D).

The LHR protein showed no immunopositive signal in the testis of F_1 neonatal rats of either control or CrVI treated group (Plate 5).

PND1 rat pups belonging to the control groups exhibited no conspicuous immunosignal of AR protein in the interstitium, peri-tubular myoid (PTM) cells and SCs of newborn control rat testis. Coeval rats born to mothers with gestational exposure to CrVI also showed very weak signal in the interstitium and PTM, especially in the group exposed to 200 ppm CrVI (Plate 6).

ERα protein exhibited strong signal in tubular compartment as well as in interstitial cells of control neonatal rat testis. On the other hand, F_1 progeny of mothers with gestational exposure to CrVI revealed decreased signal intensity in a dose-dependent manner, compared to coeval control in the order of control >50 ppm > 100 ppm > 200 ppm CrVI treated groups (Plate 7).

Neither control nor experimental rats with exposure to 50 ppm and 100 ppm CrVI showed any immunopositivity for ERβ. However, neonates born to mothers in 200 ppm group showed ERβ positivity in a few interstitial cells (Plate 8).

LCs of neonatal control rat testis showed immunopositivity of StAR protein, whereas F_1 progeny of mothers in 50 ppm, 100 ppm and 200 ppm CrVI treated groups exhibited increased signal intensity in SC cytoplasm along with LCs (Plate 9).

The control and F_1 neonates of mothers in 50 ppm CrVI treated group showed immunopositivity of CYP11A1 protein in LCs, and the intensity of the signal in both groups was comparable, whereas the signal intensity increased in 100 ppm and 200 ppm CrVI treated groups, not only in interstitial LCs but also in intraluminal compartment containing SC component. The shift in enzyme signal was more pronounced in SCs than interstitial LCs in the neonatal rats of mothers in 200 ppm CrVI group (Plate 10).

The interstitial LCs of neonatal control rats showed immunopositivity for 3βHSD protein, whereas F_1 progeny of mothers exposed to CrVI during gestational period exhibited diminished signal compared to coeval control in a dose-dependent manner. The intensity of the signal was in the order: control > 50 ppm > 100 ppm > 200 ppm (Plate 11).

The immunopositivity of CYP17A1 protein exhibited strong signal in the interstitium of control testis, which decreased in CrVI-treated rats. While decreased CYP17A1 signal intensity was observed in 50 ppm CrVI treated group, testicular cells of newborn rats of mothers in 100ppm and 200ppm CrVI treated groups did not show any immunopositive signal for CYP17A1 protein (Plate 12).

Immunostaining for P_{450} aromatase protein showed positivity in LCs and a weak signal within the seminiferous tubules of neonatal control rats and 50 ppm CrVI treated group. On the other hand, neonates of mothers with gestational exposure to 100 or 200 ppm CrVI exhibited no or very weak signal of aromatase, compared to coeval control (Plate 13).

The immunohistochemical localization of c-fos showed intense staining in the tubular compartment as well as LCs of control neonatal rat testis. The F_1 progeny of mothers with gestational exposure to CrVI exhibited diminished intensity in a dose-dependent manner, in the order: control > 50 ppm > 100 ppm > 200 ppm (Plate 14).

c-Jun protein, showed immunopositivity in the tubular and interstitial compartments of control rat testis, the intensity of which decreased in F_1 neonatal rats of mothers with gestational exposure to CrVI (Plate 15).

4. Discussion

The histological pictures clearly attest interruption in the testicular differentiation process in newborn F_1 progeny rats of mothers who consumed drinking water containing CrVI at concentrations higher than the safe limit prescribed by US EPA[21]. The changes that appeared in the seminiferous cords of fetal testis suggest that CrVI exposure during the critical window of differentiation interferes with the normal development of testicular structure.

Another important finding of the present study is that gestational exposure to CrVI may alter the male phenotypical characters in the progeny. This could be deduced from shortened AGD, a biomarker for male phenotype, which is longer in males than in females attesting its androgenic control[55]. AGD is known to be shortened in male rats exposed to numerous endocrine disruptors during prenatal period[56]. Puberty acceleration, sex differentiation and secondary sexual characters in rodents are marked by the AGD[57] which is under the control of androgens[58]. Thus, reduced AGD has been considered as a proxy indicator of decreased testosterone level[59]. The reduction of AGD in male rats with gestational exposure to flutamide, an anti-androgen, was attributed to subnormal androgen status[56]. Therefore, decreased AGD observed in the present study in new-born (PND1) rats of mothers exposed to CrVI during gestational period suggests that the heavy metal treatment has modified the androgen-dependent male phenotype. Our earlier report has shown sub-normal testosterone level in adult F_1 progeny of mothers with gestational exposure to CrVI[10]. Presumably, the F_1 neonatal male progeny rats of the present study might also have been in a state of skewed androgen status during the critical window of fetal testicular differentiation, resulting in reduced AGD.

Sexual differentiation, particularly masculinization programming window, is driven by anti-Mullerian hormone (AMH) and androgens secreted by fetal testis[60,61]. The earliest event in the testis differentiation beginning at GD14 in rat is the appearance of seminiferous cords within the gonadal ridge where the first appeared SCs undergo differentiation[62,63]; these fetal SCs secrete the essential male factor AMH which facilitates masculinization of the fetus by degenerating Mullerian duct[60] and, thus, ensure the development of male reproductive system under the direction of androgens[61]. Fetal SCs secrete AMH until birth, even after regression of Mullerian ducts[64,65]. Therefore, subnormal level of AMH detected in

experimental rat pups of the present study may suggest that gestational exposure to CrVI might interfere with sex differentiation process. Studies performed in our laboratory have clearly shown the predominance of female pups born to mothers with gestational exposure to CrVI[66,67]. The manifestation of LC hyperplasia and infertility have been reported in *Amh* knockout mice[68] indicating the role of AMH in regulating fetal LC function[69]. In the fetal testis, both AMH and testosterone coexist in higher concentrations[70]. Moreover, AMH is an impeccable marker for SC differentiation as its expression sharply drops during the perinatal and prepubertal period[71]. The hormone dependence of masculinization renders this process susceptible to disruption by factors interfering with hormone production[72]. Taken together, the findings of the present study, such as decreased AMH and diminution of androgen status evident from reduced AGD, and steroidogenic proteins (3βHSD and CYP17A1) and hormone receptors (LHR and FSHR) suggest that CrVI might have evoked an adverse effect on the fetal masculinization process by affecting differentiation of testicular cell types.

Another peptide hormone secreted from SCs is inhibin, first detected on GD14.5 in fetal rat[73], which selectively suppresses FSH secretion[74]. Fetal FSH stimulates SC proliferation, and secretion of AMH and inhibin[75]. Based on diminished level of inhibin in the F_1 newborn rats of mothers exposed to CrVI during gestational period, one may anticipate a possible shoot-up in FSH secretion and action on the testis. However, decreased FSHR noticed in the testis of the progeny of mothers with gestational exposure to CrVI in the present study goes against this suggestion. Thus, gestational exposure to CrVI, particularly during the male programming window, might have altered sexual differentiation by altering hormonal status and, thus, testicular function in F_1 rats.

Immunohistochemical studies on gonadotropin receptors revealed that the testis of newborn (PND1) rats express both *Fshr* and *Lhr* with the former being predominant. FSH interacts through its specific receptor on SCs, the number of which begins to rise by GD 20 in rodents[76]. *Fshr* mRNA is first detected at GD14.5 in SCs, and responds to FSH from GD15.5 onwards in rats[77,78]. SCs divide during the fetal and neonatal periods and cease to proliferate by PND17–18 in mice.[79] The proliferation of SCs is FSH-dependent during late fetal life in rats as decapitation or treatment with anti-FSH of rat fetuses at GD18.5 led to a decreased proliferation of SCs at GD20.5 and GD21.5, which was rescued by injections of FSH[51,80]. FSHR -/- mice had reduced number and proliferation index of SCs at birth suggesting that fetal FSH promotes the proliferation of SCs[81]. The FSH dependent proliferation of SCs during late fetal life has also been validated in the rats[80,82]. Thus, FSH and its receptor play a crucial role in the proliferation and functional differentiation of fetal SCs. Therefore, decreased level of FSHR noticed in F_1 progeny of mothers with gestational exposure to CrVI may be expected to have adverse effect on testicular differentiation by affecting the proliferation and functional differentiation of SCs. Histological pictures of the testis and secretory proteins of SCs of these animals may attest this suggestion.

The c-Fos and c-Jun are members of the AP-1 family of transcription factors (TFs) that stimulate the expression of genes in rat SCs[83]. *Fshr* gene in rat, mouse and sheep contain a number of important regulators including AP-1 site in the core promoter region[84]. Therefore, diminution of Fshr protein detected in the testis of neonates with prenatal exposure to CrVI may be linked to reduced level of c-Fos and c-Jun proteins. The reduction in Fshr may be attributed to defective SC proliferation and function in F_1 progeny of mothers exposed to CrVI during pregnancy.

Lhr in fetal LCs is first detected on GD 16.5, and significant amounts of LH are not seen until testosterone begins to decrease towards the end of gestation[85,86]. In addition, the male reproductive tract of *Lhr* knockout mice was similar to control animals at birth, supporting LH-independent production of testosterone[87]. The differentiation of FLCs does not require stimulation by LH[88,89] and, thus, lack of LH or LHR may not perturb FLC function or fetal gonadal development[90,91]. Since LH does not play role in steroidogenesis during fetal period, the unaltered level of LHR in the neonates due to CrVI exposure in the present study may not be of any significance.

The FLCs contain most of the steroidogenic proteins/enzymes such as StAR, CYP11A1, 3βHSD III and CYP17A1 except 17βHSD III which is located in SCs and converts androstenedione to testosterone[92,93]. During normal fetal development, intra-testicular testosterone level increases steadily from GD15.5 onwards with a peak on GD19.5 and subsequently declines on PND1[94]. In LCs, the translocation of cholesterol to the inner mitochondrial membrane is mediated by the transduceosome complex, an assembly of proteins including a marker trans-membrane protein StAR[95,96], to facilitate the conversion of cholesterol to pregnenolone by enzyme CYP11A1[97,98]. The augmented immunosignal of StAR and CYP11A1 and an

opposite trend in other components of steroidogenesis such as 3βHSD, CYP17A1 and P_{450} aromatase in the LCs of newborn rats of mothers exposed to CrVI during pregnancy indicate enzyme/protein specific interference. This might jeopardize steroidogenic activity in neonates with gestational exposure to CrVI. In addition, it is interesting to notice the shift of enzyme signal to the intraluminal compartment of the testis in pups of mothers with gestational exposure to CrVI, which appears to be a devise to cope up with the cellular stress generated due to CrVI toxicity. The attendance of StAR and CYP11A1 immunosignal in other than LCs in rats exposed to CrVI is consistent with the findings that expression of these proteins in SCs is a protective stress response[99, 100].

3βHSD and CYP17A1 enzymes of steroidogenic machinery catalyze conversion of pregnenolone to progesterone and progesterone to androstenedione, respectively[101,102]. Reduced immunodetection of 3βHSD and CYP17A1 clearly points out that gestational exposure to CrVI might have led to subnormal production of steroids. In addition, even the available substrate (pregnenolone) also might not have been utilized for the synthesis of progesterone and androstenedione since CrVI treatment had decreased the level of both 3βHSD and CYP17A1. Moreover, enhanced levels of StAR and CYP11A1 seen in CrVI treated pups might have been an attempt to counterbalance the decreased levels of 3βHSD and CYP17A1. Thus, our findings clearly indicate interference of CrVI at each level of steroidogenic pathway.

Fetal and neonatal testicular cells possess P_{450} aromatase, ERα and ERβ[103-106], which are known to regulate differentiation of testicular cells during late gestational period, and inhibit the number and activity of somatic and germ cells[107], Fetal and neonatal testes are estrogen sensitive, as the inactivation of ERα increased steroidogenesis, whereas ERβ inactivation enhanced development of the germ cell lineage in the male[107]. ERα knockout mice (ERαKO) showed increased testosterone production by the fetal testes as early as GD13.5[108]. The activity of FLCs increased by inactivation of the ERα gene causing hypertrophy of these cells and augmented expression of genes transcribing steroidogenic enzymes[108]. ErβKO mice showed increased number of gonocytes after birth due to boosted proliferation and decreased apoptosis.[109,110] Therefore, diminution of P_{450} aromatase and ERα, and augmented ERβ (200 ppm CrVI) in the rats exposed to might have also adversely affected the somatic and germ cells population, and functionality of FLCs by perturbing the expression of steroidogenic protein/enzymes, and thus cellular differentiation of fetal testis. Data on AR suggest that CrVI exposure did not modify this nuclear hormone receptor in any significant manner.

5. Conclusion

Taken together, the findings on enzymatic / non-enzymatic proteins of the steroidogenic apparatus, along with hormone receptors and peptide hormones AMH and inhibin, support our hypothesis so as to conclude that exposure of pregnant mothers to drinking water containing high concentration of CrVI much above the permissible safe level may disrupt the fetal endocrines controlling differentiation of the testis and male phenotype.

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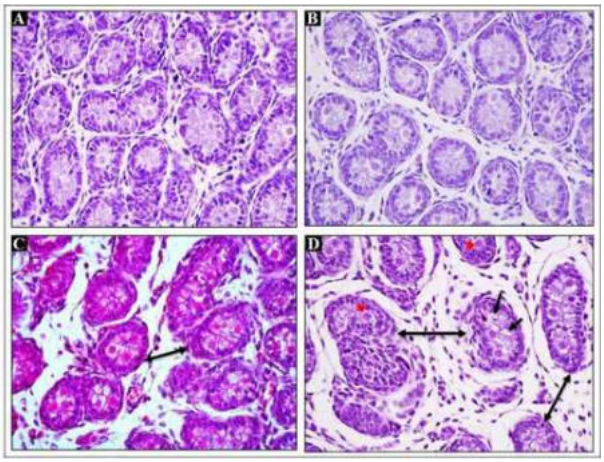
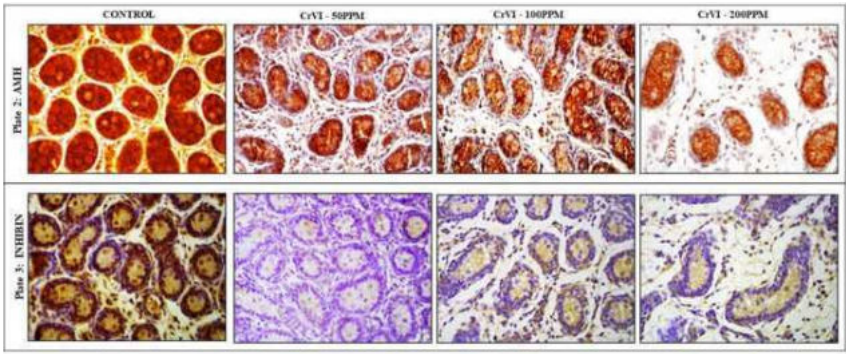
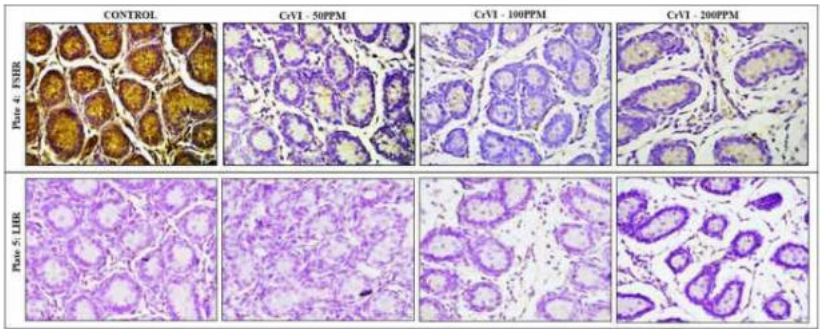


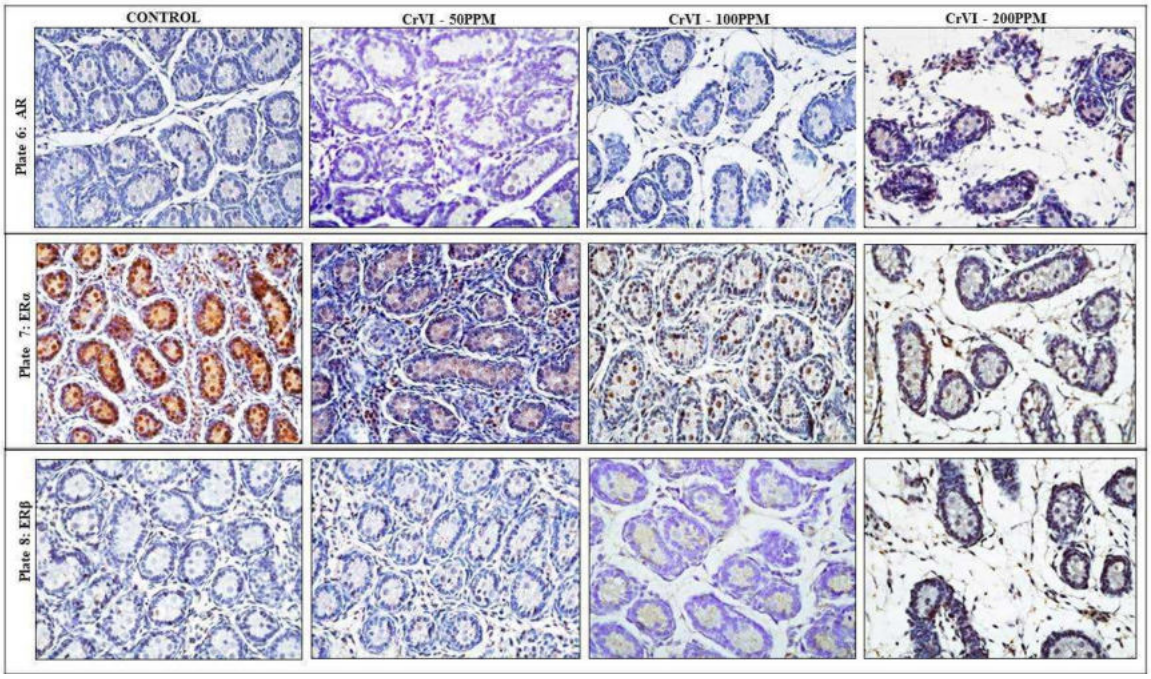
Plate 1. Testicular histology at PND1. (A) Testis of new born control rats showing seminiferous tubules with gonocytes surrounded by SCs around the periphery, and LCs present in the interstitial spaces. Testis of CrVI-exposed pups shows lack of compaction, and constricted tubules with large interstitial spaces (double-headed arrow). (B) Gestationally exposed to CrVI (50 ppm). Little if any change is indicated. (C & D) Testis of pups which had exposure to the higher doses of CrVI (100 & 200 ppm) exhibit reduced number of gonocytes. Gonocytes are located centrally in the seminiferous tubules due to vacuolization of SC cytoplasm (black single-headed arrow). Multinucleate gonocytes (red-forked arrow) are also visible in testes of pups whose mothers had exposure to 200 ppm CrVI. Hematoxylin and Eosin (H&E) staining. Original magnification: 400x.



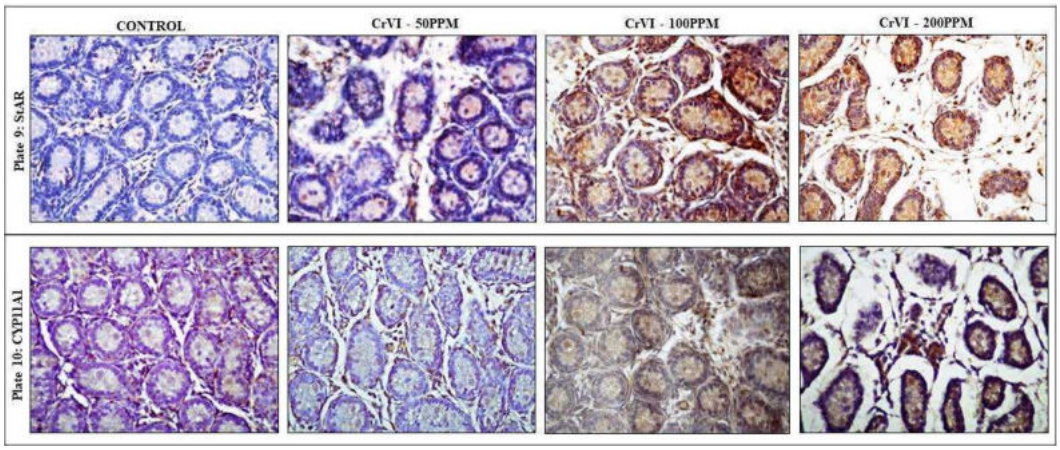
Plates 2-3. Immunohistochemical localization of AMH (Plate 2) and inhibin (Plate 3) proteins in testis of PND1 rats. The AMH protein shows strong immunostaining within the tubule of control rat testis **(A)** as compared to all groups treated with CrVI. The F_1 progeny of mothers with exposure to the high dose (200 ppm) CrVI show atrophied and constricted tubules (Plate 2). Inhibin protein shows strong immunopositivity in seminiferous tubules of control rat testis (A), whereas decreased intensity in all the treatment groups (B, C, D) as compared to control (Plate 3). Original magnification: 400x.



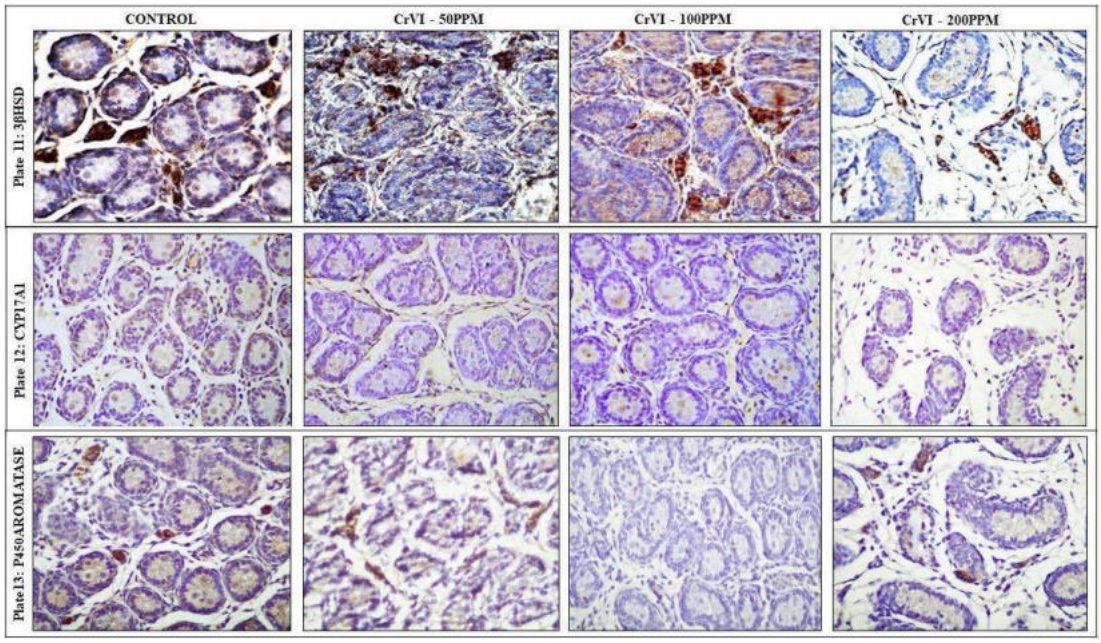
Plates 4-5. Immunostaining of FSHR protein shows intense signal in the SCs of control neonate testis (A) and very weak/no immunostaining in the testis of F_1 progeny rats of mothers with transient gestational exposure to CrVI (B, C, D) (Plate 4). LHR protein shows no immunosignal in LCs of either control or F_1 neonates of mothers exposed to 50 ppm, 100 ppm and 200 ppm CrVI (Plate 5). Original magnification: 400x.



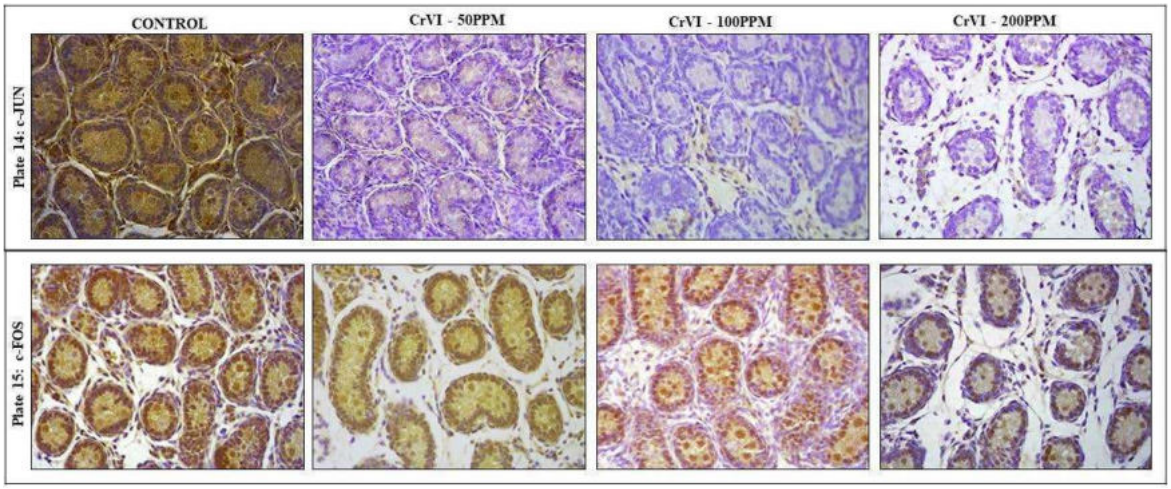
Plates 6-8. Neonate testis at PND1 immunostained for AR, ERα and ERβ. The AR signal shows intense staining in the interstitium, peri-tubular myoid (PTM) cells and weak/no staining in the SCs of neonatal testis of 200 ppm CrVI-treated rats as compared to coeval control, 50 ppm and 100 ppm CrVI-treated testis (Plate 6). The ERα immunostaining shows its presence in the tubular compartment as well as interstitial LCs in the testis of control rats. The changes in the immunohistochemical staining show a progressive decrease in a dose-dependent manner in CrVI treated pups (Plate 7). ERβ shows immunopositivity in testis, particularly in LCs, of F_1 progeny of mothers exposed to 200 ppm CrVI only (D) (Plate 8). Original magnification: 400x.



Plates 9-10. Immunohistochemical detection of steroidogenic protein StAR and CYP11A1 enzyme. The immunopositive signal of StAR protein appears in the LCs of control rats, whereas all CrVI treated neonates exhibit higher intensity as compared to coeval control. There is also a shift in the enzyme signal into the intra-luminal compartment containing SCs with mild staining in 50 ppm and maximally in 100 ppm and 200 ppm CrVI treated group (Plate 9). CYP11A1 shows immunopositivity in LCs of control and 50 ppm CrVI treated groups and are comparable; 100 ppm and 200 ppm CrVI treated groups exhibit increased signal intensity with shift in the enzyme signal into the intra-luminal compartment of seminiferous tubule (Plate 10). Original magnification: 400x.



Plates 11-13. Immunohistochemical detection of steroidogenic enzymes 3βHSD, CYP11A1 and P_{450} aromatase. Intense signal of 3βHSD appears in LCs of control rats (A) and progressively diminishes in intensity in pups with gestational exposure to 50 ppm, 100 ppm and 200 ppm CrVI (B,C,D) compared to control (Plate 11). The steroidogenic enzyme CYP17A1 shows immunostaining in the interstitium as well as in tubular compartments of control testis (A), marked decrease in signal intensity of 50 ppm CrVI treated rats (B) and no visible detection in F_1 progeny of mothers with gestational exposure to 100 ppm (C) and 200 ppm (D) CrVI (Plate 12). P_{450} aromatase protein shows strong intensity within seminiferous tubules and LCs of neonatal control rats and 50 ppm CrVI treated group; no signal is seen in the seminiferous tubules and LCs of 100ppm CrVI group, whereas 200 ppm treated group shows decreased intensity of aromatase in LCs only (D) compared to control (Plate 13). Original magnification: 400x.



Plates 14-15. Immunohistochemical detection of c-Fos and c-Jun proteins. c-Fos shows strong immunopositivity in the tubular and interstitial compartments of control rat (PND1) testis; however, testis of F_1 neonates with gestational exposure to 50 ppm, 100 ppm and 200 ppm CrVI shows progressively diminished signal (Photomicrograph 13). Strong c-Jun signal intensity appears in the tubular as well as interstitial compartments of control rat testis, and no signal in F_1 neonatal rats of 50 ppm, 100 ppm and 200 ppm CrVI exposure groups. (Plate 15). Original magnification: 400x.

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INVITRO REGENERATION OF A THREATENED MEDICINAL PLANT *PHYLLODIUM PULCHELLUM* L. DESV.

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ABSTRACT

An efficient in vitro regeneration protocol was developed Phyllodium pulchellum (L.) Desv. A threatened medicinal plant. The plants were regeneration from shoot tip and nodal explants. The highest number of shoots per explant was obtained on the medium supplemented with 1.5 mg/l BAP + IAA 0.5 mg/l from shoot tip explants (4.30±0.40) and nodal explants (4.06±0.31). The elongated shoots were successfully rooted on MS with NAA (α-naphthalene acetic acid) or IBA; 0.75 mg/l of NAA provided better response for rhizogenesis among them. For regenerated shoots rooting, MS medium supplemented with 0.75 mg/l NAA (α- naphthalene acetic acid) was most effective with maximum number (4.50±0.36 roots per plantlet) and length (2.76±0.15 cm per root) of roots respectively. Regenerated plantlets were successfully transferred into pots with soil and over 90% of them grew into healthy mature plants. This is the first report of direct organogenesis in P. Pulchellum with significantly high plantlet regeneration frequency.

KEYWORDS: Phyllodium Pulchellum, Threatened, Shoot Tip and Nodal, Plant Growth Regulator & Regeneration

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Original Article

INTRODUCTION

Phyllodium pulchellum (L.) Desv. (*Desmodium pulchellum* (L.) Benth.) is commonly known as Tamil – Vellalothi. It is a Subshrub 1(3) m; branchlets downy- pubescent to tomentose. *Leaves* 3-foliolate, to 15 m; leaflets ovate or elliptic-oblong, laterals less than half as long as the terminal, in equilateral, thin-coriaceous, appressed-pubescent above, tomentose below, base subacute, margin wavy, apex obtuse-acute; R*acemes* to 20 cm; *Stamens* monadelphous; vexillary one free above middle. *Ovary* 2 mm, pubescent; seeds ellipsoid or orbicular, 2 mm. Traditionally, decoction of dried leaves of *Desmodium pulchellum* is used in cold fever, malaria, enlargement of liver and spleen, rheumatism bone pains and swelling due to contusion or sprain. Decoction of charred roots used to reduce excessive menstrual flow. Leaves are also applied to ulcers and skin sores in hemorrhages. The whole plant is used in Chinese medicine to treat rheumatic fever, infant convulsions, toothache, and also to dissolve internal blood clots, and to aid digestion. The international union for conservation of natural and national resource has a long time ago listed *Phyllodium pulchellum* (L.) Desv., as a threatened species (Lopez, 2012). Some attempts were made recently for relative's species for *invitro* regeneration and conservation of plants (Thandar and Tun, 2015). The plant has been shown to ethanolic extract of barks may contribute to the reduction of blood glucose levels and can be useful in the management of diabetes (Noor *et al.,* 2013). The methanolic extract of the leaves of *Desmodium pulchellum,* were a biological active ingredient that are active for anti-diarrheal actions (Rahman *et al.,* 2013). The ethanolic extract of *D. gangeticum* can be used as a source of natural antioxidants with could serve as free radical inhibitors, scavengers or primary antioxidants (Venkatachalam and Muthukrishnan, 2012).

However, protocol for *in vitro* conservation of *P. pulchellum* has not yet been established and as such the present work was undertaken to study effects of culture media composition and temperature/light conditions on *in vitro* propagation and slow-growth conservation.

MATERIALS AND METHODS

Collection of Plant Materials

Shoot tip and nodal part of *Phyllodium pulchellum* were collected from the *Jambhuthu* hamlet is situated at Boda hill of Namakkal District, Tamil Nadu, India and identified in Botanical survey of India, Southern regional centre under the Voucher specimen number: BSI/SRC/5/23/2012-13/Tech-1795 & Serial No. 2.

Explant Source and Sterilization

The shoot tip and node of *P. pulchellum* were used as expalnts. These explants were washed first under running tap water for 30 minutes, then treated with 0.1% (V/V) aqueous solution of Tween-20 (Hi-media, Mumbai) for 15 min, followed by 5 to 6 washes with distilled water thoroughly. Explants were surface sterilized with bavistin 5% for 5 minutes to remove the fungal contamination. Then they were rinsed in autoclaved sterile distilled water twice or thrice and were then taken to the laminar air flow chamber where they were surface sterilized with 0.1% $HgCl_2$ for 3-5 minutes. They were again washed twice or thrice using sterile distilled water. After repeated rinsing (five times) with distilled water, the explants were ready to inoculate on the culture media. The surface-sterilized explants were aseptically cut into 1-2 cm segments and were carefully inoculated onto the MS culture media (Murashige and Skoog, 1962).

Culture Media and Culture Conditions

The culture media consisted of MS basal constituents, supplemented with different concentration BAP, Kn and IAA. The media were supplemented with 3% sucrose and 0.8% agar was used as the gelling agent. The pH was adjusted with a pH meter at 5.7 adjustment was done with 0.1 N HCI and 0.1 N NaOH and autoclaved at 121ºC, 15 lb pressure for 45 min. The cultures were maintained at 25 ± 2ºC, 16/8 hr (light/dark) photoperiod with a light intensity of 1500 lux at relative humidity (RH) of 60 - 70%.

Statistical Analysis

Total number of explants taken for observation 35 (each treatment consists of at least 7 explants and the experiments were repeated three times). Data were statistically analyzed, using SPSS Statistical Software package (Ver. 16.0). The mean comparisons were carried out by DMRT at a probability level of 5% ($p<0.05$).

RESULTS

Direct Regeneration

For direct regeneration of *Phyllodium pulchellum* shoot tip and node explants were used. Various plant growth regulators were used along with MS media, from that, BAP and IAA only give a high amount of response in multiple shoot induction, NAA only induced a high range of root formation.

Shoot Tip Explants

Studies were carried out to produce plantlets form shoot tip explants through direct organogenesis without intervention of callus. The results obtained are given in Table 1. BAP was used in concentration ranging from (0.5, 1.0,

1.5, 2.0 and 2.5 mg/l), with IAA concentration (0.5 mg/l) and KN concentration ranging from (0.5, 1.0, 1.5, 2.0 and 2.5 mg/l), with IAA concentration (0.5 mg/l). Maximum response and maximum number of shoots per explants were observed in 1.5 mg/l of BAP combination with 0.5 mg/l of IAA (4.30±0.40) was relatively minimum effective in which, number of shoot in BAP of 2.5 mg/l (0.93±0.25). The frequency of culture response was 62.85 and the mean shoots produced also high in 1.5 mg/l of BAP and 0.5 mg/l of IAA combination (Table 1 and Figure 1) and the various stages in the production of plantlets by direct organogenesis.

Nodal Explants

Direct organogenesis was also carried with nodal explants of *P. pulchellum*. The observations are given in Tables 2 and Figure 2. BAP, KN and IAA were used for direct organogenesis. The concentration ranging from BAP (0.5-2.5 mg/l), KN (0.5-2.5 mg/l) along with IAA (0.5 mg/l). Maximum response and maximum number of shoots per explants were observed in 1.5 mg/l of BAP combination with 0.5 mg/l of IAA (4.06±0.31) was relatively minimum effective in which, number of shoot in KN of 2.5 mg/l (0.96±0.21). More or less the pattern of response was similar to the shoot tip explants. However the frequency of culture response was 77.14 and the mean shoots produced also high in 1.5 mg/l of BAP and 0.5 mg/l of IAA combination. Comparison of shoot tip explants and nodal explants reveals that the nodal explants are relatively superior both in terms of percentage of response and number of shoots is produced from the explants.

ROOT INDUCTION FROM DIRECT REGENERATION

Auxins played multifarious role in rhizogenesis, which included division of meristematic cells, their elongation and differentiation into root primordial. The number of roots produced per shoot, root length and thickness varied with the concentration of auxin used in the medium. Root induction was carried out in well elongated shoots developed from nodal explants in *vitro* regeneration and culturing them on MS with 0.25 – 1.25 mg/l of NAA and IBA. In the present study, NAA (0.75 mg/l) was found to e most effective for rooting. Maximum number of root (4.50±0.36) were produced in 0.75 mg/l of NAA and mean root length was found to be 2.76±0.15 cm. Maximum number of roots (3.53±0.35) was produced in 1.0 mg/l of IBA and mean root length was 2.63±0.15 cm. best results of rooting were observed on the MS media supplemented with 0.75 mg/l of NAA with percentage of root induction in 66.33±3.78 (Table 3).

DISCUSSIONS

Earlier reports indicate that the superiority of BAP over other cytokines in shoot induction of *Dysolobium pilosum* shoot tip explants (Kalva *et al.,* 2015) and *Cassia angustifolia* regeneration *via* direct organogenesis is still BAP, KN and IAA (Iram *et al.,* 2015). Similar observation was made in *Andrographis paniculata* (Purkayastha *et al.,* 2008) and the efficiency of BA in multiple shoot induction in several aromatic and medicinal plants such as *Ocimum basilicum* (Sahoo *et al.,* 1997), *Withania somnifera* (Sen and Sharma, 1991) and *Hippophae rehnoides* (Purohit *et al.,* 2009). This was in consistent with other studies where BAP and IAA promoted the proliferation and multiplication of the shoots in number of plants (Randive, 2013; Remya *et al.,* 2013; Skala *et al.,* 2014).

Shoot multiplication of nodal segments of *Phyllodium pulchellum* was observed in present study, shoots were developed in MS medium with BAP and IAA. The results were obtained resembling to the shoot tip explants. Highest mean shoots was absorbed on 1.5 mg/l of BAP combination with 0.5 mg/l of IAA. Similar results were reported in *Pterocarpus marsupium* Roxb. axillary shoot proliferation on Murashige and Skoog's (MS) basal medium fortified with BAP (6–benzylaminopurine) and kinetin (Kn) singly or in combinations with auxins at different concentrations (Jaiswal *et*

al., 2015). The role of BAP in multiple shoot production through direct organogenesis and the combination of BAP and KN found to be effective in *Sarcostemma brevistigma* previously reported by Thomas and Shankar (2009). *In vitro* organogenesis was achieved through direct organogenesis on MS containing of BAP at 0.25 mg l-1 and NAA at 0.05 mg l-1 has been effective on shoot regeneration of *Lathyrus chrysanthus* Boiss. (Telci, 2012). Same results were reported that the genus *Desmodium gangeticum* (Vishwakarma *et al.,* 2009) Effectiveness of BAP in shoot regeneration from cotyledonary nodes has been reported in several other species of leguminaceae e.g. *Dalbergia tatifotia* Roxb. (Pradhan *et al.,* 1998), *Arachis hypogea* L. (Venkatachalam *et al.,* 1999, *Vigna* mungo (L.) Hepper (Ignacimuthu *et al.,* 1997) and *Acacia nitotica* subsp. *indica* Brenan (Dewan *et al.,* 1992). This result is contrasting with reports on leguminous species *Dalbergia sissoo* Roxb. and *Macrotyloma uniflorum* (Arya *et al.,* 2013; Bisht *et al.,* 2013) where BAP gave maximum shoot proliferation. The protocol employed in the present study for *in vitro* shoot induction of *Phyllodium pulchellum,* an important plant species from Boda malai, Tamil Nadu can be useful for conservation of the endemic plants.

CONCLUSIONS

This is the first report describing a protocol for organogenesis of *Phyllodium pulchellum*. It is concluded that direct *in vitro* protocol was developed for *P. pulchellum* which could be able to produce a large number of plant lets. The highest degree of shoot induction was found on MS basal medium with BAP + IAA medium combination in the respective explants were found to be best. The organogenesis and plant regeneration system developed in this study could be utilized in future for secondary metabolites production experiments.

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APPENDICES

Table 1: Influence of Different Concentration of Either Cytokinin (BAP and KN) Alone or in Combination with Auxin (IAA) on Direct Shoot Regeneration From Shoot Tip Explants of *Phyllodium Pulchellum*

Hormone Concentration mg/l (µg)		No of Explants Cultured	No. of Explants Responded	Frequency of Culture Response	No. of Shoot/Explants Mean ±SD
BAP					
0.5 (0.11)		35	11	31.42	1.33 ± 0.15^{hij}
1.0 (0.22)		35	15	42.85	2.06 ± 0.25^{de}
1.5 (0.34)		35	18	51.42	3.06 ± 0.25^{b}
2.0 (0.45)		35	12	34.28	1.80 ± 0.20^{efg}
2.5 (0.56)		35	9	25.71	0.93 ± 0.25^{jk}
KN					
0.5 (0.11)		35	8	22.85	1.00 ± 0.20^{jk}
1.0 (0.22)		35	10	28.57	1.73 ± 0.20^{efgh}
1.5 (0.32)		35	13	37.14	2.13 ± 0.15^{cde}
2.0 (0.43)		35	9	25.71	1.20 ± 0.20^{ijk}
2.5 (0.53)		35	6	17.14	0.86 ± 0.15^{k}
BAP+IAA					
0.5 (0.11)	0.5 (0.08)	35	15	42.85	2.53 ± 0.30^{c}
1.0 (0.22)	0.5 (0.08)	35	18	51.42	3.33 ± 0.20^{b}
1.5 (0.34)	0.5 (0.08)	35	22	62.85	4.30 ± 0.40^{a}
2.0 (0.45)	0.5 (0.08)	35	17	48.57	3.28 ± 0.38^{b}
2.5 (0.56)	0.5 (0.08)	35	12	34.28	2.47 ± 0.33^{cd}
KN+IAA					
0.5 (0.11)	0.5 (0.08)	35	8	22.85	1.45 ± 0.24^{ghi}
1.0 (0.22)	0.5 (0.08)	35	11	31.42	1.90 ± 0.11^{ef}
1.5 (0.32)	0.5 (0.08)	35	17	48.57	2.42 ± 0.24^{cd}
2.0 (0.43)	0.5 (0.08)	35	13	37.14	1.51 ± 0.15^{fghi}
2.5 (0.53)	0.5 (0.08)	35	10	28.57	1.19 ± 0.09^{ijk}

- Total number of explants taken for observation = 35 (each treatment consists of at least 7 explants and the experiments were repeated three times).
- Mean values followed by various letters are significantly different from each other at $P < 0.05$ level comparison (DMRT).

Table 2: Influence of Different Concentration of Either Cytokinin (BAP and KN) Alone or in Combination with Auxin (IAA) on Direct Shoot Regeneration From Nodal Explants of *Phyllodium Pulchellum*

Hormone Concentration mg/l (µg)	No of Explants Cultured	No. of Explants Responded	Frequency of Culture Response	No. of Shoot/Explants Mean ±SD
BAP				
0.5 (0.11)	35	13	37.14	1.45 ± 0.07^{gh}
1.0 (0.22)	35	17	48.57	2.32 ± 0.47^{d}
1.5 (0.34)	35	20	57.14	3.21 ± 0.32^{b}
2.0 (0.45)	35	15	42.85	1.64 ± 0.08^{fg}
2.5 (0.56)	35	11	31.42	1.39 ± 0.13^{gh}
KN				
0.5 (0.11)	35	10	28.57	1.09 ± 0.21^{hi}
1.0 (0.22)	35	13	37.14	1.65 ± 0.18^{fg}
1.5 (0.32)	35	15	42.85	2.00 ± 0.92^{def}

2.0 (0.43)		35	11	31.42	1.63±0.04^{fg}
2.5 (0.53)		35	9	25.71	0.96±0.21^{i}
BAP+IAA					
0.5 (0.11)	0.5 (0.08)	35	17	48.57	2.84±0.08^{c}
1.0 (0.22)	0.5 (0.08)	35	23	65.71	3.25±0.10^{b}
1.5 (0.34)	0.5 (0.08)	35	27	77.14	4.06±0.31^{a}
2.0 (0.45)	0.5 (0.08)	35	22	62.85	3.30±0.14^{b}
2.5 (0.56)	0.5 (0.08)	35	15	42.85	2.73±0.24^{c}
KN+IAA					
0.5 (0.11)	0.5 (0.08)	35	11	31.42	1.65±0.08^{fg}
1.0 (0.22)	0.5 (0.08)	35	13	37.14	2.06±0.14^{de}
1.5 (0.32)	0.5 (0.08)	35	23	65.71	2.97±0.24^{bc}
2.0 (0.43)	0.5 (0.08)	35	15	42.85	1.94±0.11^{ef}
2.5 (0.53)	0.5 (0.08)	35	12	34.28	1.34±0.15^{gh}

- Total number of explants taken for observation = 35 (each treatment consists of at least 7 explants and the experiments were repeated three times).
- Mean values followed by various letters are significantly different from each other at P < 0.05 level comparison (DMRT).

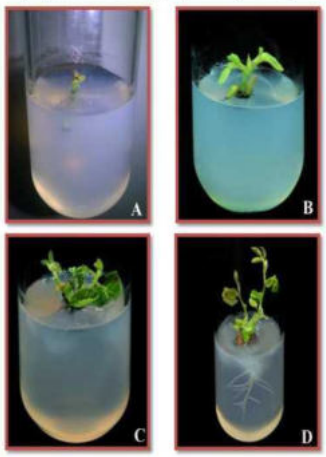
Table 3: Effect of Growth Regulator on Root Induction of *Phyllodium Pulchellum* L. Desv

Growth Regulators (mg/l)	Percentage of Root Inducted Mean±SD	No. of Roots/Shoots Mean±SD	Root Length (cm) Mean±SD
NAA			
0.25	35.66±1.52^{e}	2.36±0.11^{d}	0.60±0.20^{e}
0.50	48.33±3.05^{c}	3.46±0.35^{b}	1.76±0.15^{bc}
0.75	66.33±3.78^{a}	4.50±0.36^{a}	2.76±0.15^{a}
1.0	40.66±2.08^{de}	3.23±0.32^{b}	1.43±0.20^{cd}
1.25	29.00±2.00^{f}	2.30±0.26^{d}	0.56±0.25^{e}
IBA			
0.25	26.33±2.51^{f}	1.73±0.20^{e}	0.33±0.15^{e}
0.50	35.66±3.51^{e}	2.30±0.17^{d}	1.13±0.20^{d}
0.75	43.00±2.64^{d}	2.93±0.15^{c}	2.03±0.20^{b}
1.0	55.66±3.51^{b}	3.53±0.35^{b}	2.63±0.15^{a}
1.25	25.00±3.60^{f}	2.23±0.20^{d}	1.33±0.41^{d}

Mean values followed by various letters are significantly different from each other at

P < 0.05 level comparison (DMRT).

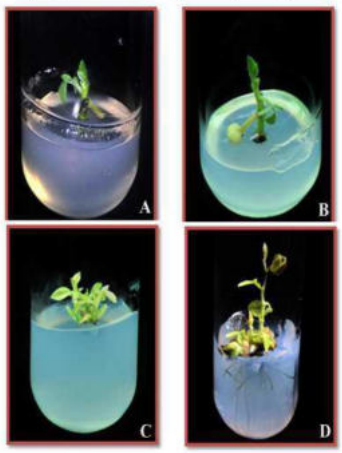
Direct Organogenesis from Shoot tip Explant of *Phyllodium pulchellum*



A) & B) Shoot initiation from nodal explants on MS medium + 1.5 mg/l of BAP combination with 0.5 mg/l of IAA.
C) Shoot induction on MS + BAP 1.5 mg/l + IAA 0.5 mg/l.
D) Shoot elongation a rooting on MS Medium with 0.75 mg/l of NAA.

Figure 1

Direct Organogenesis from Nodal Explant of *Phyllodium pulchellum*



A) & B) Shoot initiation from shoot tip explants on MS medium + 1.5 mg/l of BAP combination with 0.5 mg/l of IAA.
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Figure 2

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Preliminary Phytochemical Analysis of methanolic leaves extract of *Solanum pubescens* Willd.

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Abstract: *The present study was aimed to investigate the preliminary phytochemical screening of the leaves of Solanum pubescens is a shrub in solanaceae family. It's mainly found in Peninsular India and Sri Lanka. The plants are tribal's for the treatment of several diseases Brain disorders, liver disorders, diarrhoeal diseases and cancer disorders injury with classical signs of warmth, reddening pain, swelling and loss of function.The present study was carried out to investigate the Phytochemical analysis shows the presence of alkaloid, glycoside, Saponins, Phenolic compounds Tanins, flavonoids, and shows the absent protein and amino acid,*

Key Words: *Phytochemical constituents, Solanum pubescens and Alkaloid.*

1. Introduction

Solanum pubescens are well known as Usti in Telugu and Kattusundai in Tamil (India). Previously reported compounds from the plant were flavonol-3-o-methyl esters (Krishna Kumari, *et al,* 1985). The use of herbal preparations in the management of various forms of epilepsies is very common in many parts of the world. Epilepsy affects more than 50 million persons worldwide (White, 1999). The plants are tribal's for the treatment of Brain disorders, liver disorders, diarrhoeal diseases and cancer disorders injury with classical signs of warmth, reddening pain, swelling and loss of function. A medicinal plant is factually any plant which in one or more of its parts contains substances that can be used for therapeutic purposes or which have precursors for the synthesis of direct therapeutic agents. The Use of medicinal plant is increasing in many countries where 35% of drugs contain natural products (Sofowora, 1982). Plants synthesize a vast array of secondary metabolites that are important for human life. For therapeutic purpose, phytochemical investigation of plants is an interesting area of research, leading to the isolation of several new compounds. Therefore, in recent years research is more oriented towards folk medicine, searching for new leads for the development of better drugs against infectious diseases (Benkeblia, 2004) and other common ailments. It is the protective attempt by the organism to remove the injurious stimuli as well as initiate healing process for the tissues and considered to be the major cause of rheumatoid arthritis. Drugs currently used for management of pain and inflammatory conditions present toxic side effects on chronic administration. Therefore, attempts are being taken to study promising plants which may lead to develop newer or safer drugs (Fayaz, 1994). *Solanum pubescens* is a traditional medicine plant for the treatment of headache, menstrual pain, rheumatoid arthritis, tuberculosis, ulcers, etc (Sumalatha, *et al*., 2013) and it has been used in the treatment of whooping cough and of certain other diseases (Reddy, *et al*., 2006) Furthermore, it has been used in the treatment of hypoglycaemia and topical application for skin infections. Similarly, in scientific literature there are very few reports on evaluated pharmacological properties like Antidiabetic (Hemamalini, *et al*., 2012) hepatoprotective (Hemamalini, *et al.,* 2012) gastroprotective (Hemamalini, *et al*., 2011) anti-inflammatory (Niyogi, *et al.,* 2012) Anti-anxiety, Anti-depressants, My orelaxant and Antidiarrheal (Deepika, *et al*., 2013). It has not been extensively used in the traditional medicine may be for its bitterness which may acts as cytotoxic agent. Thus for, *Solanum pubescens* has not been explored for a through quantitative and qualitative phytochemical analysis. There are no reports on its complete phytochemical contents except a few indicating the existence of flavonoids and alkaloids in leaf extract (Anurag Bhargav, *et al*., 2012), (Krishna Kumari, *et al.,* 1985), (Krishna Kumari*, et al*., 1986) and (Krishna Kumari, *et al.,* 1985). Hence, it is imperative take up thorough phytochemical studies.

2. Materials and Methods

2.1 Morphological characters

Unarmed pubescent shrubs. Leaves to 12 x 7 cm, ovate-elliptic to deltoid, apex acute, base unequally truncate, membranous, margins entire to wavy; petiole to 8 cm, pubescent. Racemes axillary; peduncle to 5 cm, pubescent; pedicels 2 cm, pubescent; flowers blue; calyx lobes 6 mm, lanceolate, pubescent; corolla tube 5 mm, lobes 6

mm, lanceolate, pubescent; ovary 1.5 mm, style 1 cm, stigma capitate.

2.2 Collection of Plant material and extraction

Solanum pubescens were collected from Western Ghats, Sirumalai, Dindugal district, Tamilnadu. The healthy plant leaves were collected and washed thoroughly in distilled water. The leaves allowed drying in shade place for one week. Well dried leaf samples were powdered by soaking 100gm of dried powder in 200ml of methanol for 12 hours. The extracts were filtered using Whatman filter paper No. 42.

2.3 Preliminary phytochemical screening

The phytochemical includes alkaloids, Carbohydrates, saponins, phenolic compounds, tannins, flavonoids, phytosterols, Fixed oils and fats.

2.4 Qualitative screening test:

Alkaloids (H. Wagner's test 1993):

0.5 g of powder was stirred with few ml of diluted HCl and filtrated. To this, 2 ml of Hager's reagent was added. A prominent yellow precipitated indicated the presence of Alkaloids.

Glycosides (Borntrager test):

A few amount of extract was hydrolyzed with Con. HCl for 2 hours in boiling water bath and filtrated. Drop of filtrate was treated with chloroform and shaken well. The chloroform layer was separated and 10% ammonia solution was added to it. Pink color is presence of glycosides.

Saponins (Frothing test):

The plant extract (0.5g) was dissolved with distilled water made up to 20ml. The suspension was shaken in a graduated cylinder for 15 min. A 2cm layer of foam indicated the presence of saponins.

Phenolic (Ferric chloride test):

A few drops of filtrate and a drop of neutral 5% ferric chloride solution were added. A dark green colour was indicated the presence of phenolic.

Tannin (Potassium hydroxide test):

About 1 g of extract was dissolved into 10ml of 10% potassium hydroxide in a beaker and shaken to dissolve. A dirty precipitate indicated the presence of tannins.

Flavonoids (Alkaline reagent test):

A drop of aqueous filtrate was treated with 10% ammonium hydroxide solution. A bulky white is presence of flavonoids.

Proteins and Amino acid

Xanthoproteic Test: The extracts were treated with few drops of conc. Nitric acid. Formation of yellow colour indicates the absence of proteins.

Ninhydrin Test: To the extract, 0.25% w/v ninhydrin reagent was added and boiled for few minutes. Formation of blue colour indicates the absence of amino acid.

3. Results and Discussion

The Phytochemical analysis of methanol extract from leaves explant. The medicinal plant are tribal's for the treatment of Brain disorders, liver disorders, diarrhoeal diseases and cancer disorders Injury with classical signs of warmth, reddening pain, swelling and loss of function. The present investigation, quantitative phytochemical screening test were analysed in leaves extract. The result are shown in **table -1** which indicated the presents or absences in compounds of *Solanum pubescens* the results showed was present in high intensity followed by *Alkaloids, Saponins, Phenolic compounds, Tannins, Flavonoids, phytosterols, fixed oils and fats.* These compounds also can be correlated with the medicinal potential of the plant. Other group of Proteins and amino acid were not present in the leaves plant extract. Reported the phenolic compound are present in most widely distributed in the plant kingdom. Mainly, the phenolic and flavonoids compounds extracted from the leaves samples antibiotics activity of the plant leaf extracts (Hossain *et al*., 2013). Secondary metabolites are considered products of primary metabolism but not involved in metabolic activity (alkaloids, phenolics, essential oils and terpenes, sterols, flavonoids, lignins, tannins, *etc*.) (Pal, 2007). (Subhadra Devi, 2012). Further, the phenyl propanoidal derivatives such as phenol, flavone, flavonoids, lignin and lignan etc. have been experimental proved in many pharmacological studies that act as antimicrobial agents in wide spectrum of bacterial and fungal strains (Nitiema *et al.,* 2012; Alves *et al.,* 2014). These compounds also have been reported as a good source of

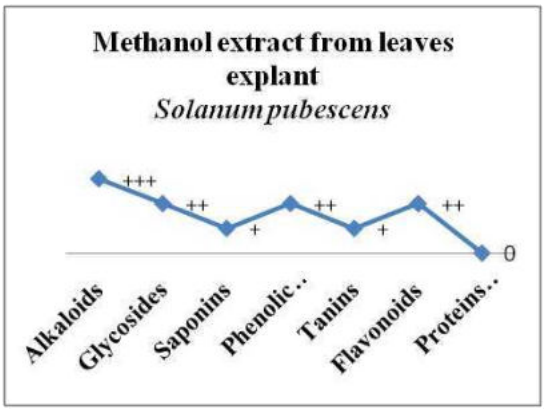
antioxidant agents (Gengaihi *et al*., 2014). The presence of tannin in plant to protected from animal does not graze (Ulhe and Narkhede, 2013). Standardization of herbal drugs is a matter of great concern. Standardization is very much essential for assessment of purity and identification of any sample. The preliminary Phytochemical analysis of *Solanum pubescens* reveals the presence of *Alkaloids, Saponins, Phenolic compounds, Tannins, Flavonoids, phytosterols, fixed oils and fats* which could attribute to the medicinal efficacy. Heavy metal and inorganic elements are present within the permissible limits. Furthermore studies are required to isolate and characterize the active principles of *Solanum pubescens.*

Table No: 1 Preliminary Phytochemical screening of *Solanum pubescens* Leaves Explant

S. No.	Chemical constituent	Methanol extract from leaf explants
1	Alkaloids	+++
2	Glycosides	++
3	Saponins	+
4	Phenolic compounds	++
5	Tanins	+
6	Flavonoids	++
7	Proteins and amino acid	-

***The given results are statistically significant**

Graph: 1 Methanol extract from leaves explant *Solanum pubescens* Willd.



4. Conclusion

We concluded that the extract of *Solanum pubescens,* the preliminary Phytochemical studies have clearly demonstrated that the plant of *Solanum pubescens* has a rich source of essential oils, alkaloids, flavonoids, saponins, steroids, tannins and coumarins. The extract of methanol is found to have more phytoconstituents. It is presumed that the presence of these constituents together could be attributed to the presence of curative abilities. The exploitation of involves these pharmacological properties further investigation of these action ingredients by implementation of these techniques like anti-epileptic activity.

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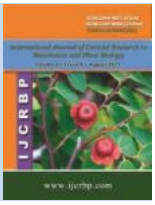

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Antifungal Activity and Quantitative Phytochemical Analysis of *Phyllodium pulchellum* L. Desv.- An Important Medicinal Plant

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Abstract

Phyllodium pulchellum L. Desv. is an subshrub, belongs to the fabaceae family. The present study has been attempted to antifungal activity and quantitative phytochemical analysis of the leaf of *P. pulchellum.* The plant extracted with different organic solvents *viz.,* aqueous, chloroform and ethanol. Antifungal activity of the leaf extract against some pathogenic fungus like *Aspergillus nigar, Pencillium notatum, Rhizhotonia solani* and *Colletotrichum falcatum.* The inhibitory effect of leaf distillates was compared with the standard fluconazole. Quantitative phytochemical analyses were performed using standard procedures. The ethanol leaf extracts of *P. pulchellum* showed maximum activity against *Aspergillus niger,* followed by *Colletotrichum falcatum, Penicillium notatum* and *Rhizoctonia solani.* The ethanolic extract showed higher level of phenol (88.68±2.081 mg/g), flavonoid (71.33±4.172 mg/g) tannin (30.23±3.025 mg/g) and than the other extracts which having secondary metabolites. These findings provide scientific evidence to support the traditional use of *Phyllodium pulchellum* and also indicate that the leaf of this species are a promising potential for the development of quantitative phytochemical and antifungal agent.

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Keywords

Antifungal activity
Fabaceae
Phyllodium pulchellum
Phytochemicals

Introduction

Medicinal herb as a potential source of therapeutic aid has a significant role in health system all over the world for both humans and animals not only in the diseased condition but also as a potential material for maintaining proper health (Pathak and Das, 2013). Plants are a rich source of diverse type of medicines in different countries and produce a diverse array of bioactive molecules, the source of potential and powerful drugs (Vashist and Jindal, 2012). Thus, natural products with pharmacological or biological activities still play a very important role in medicine (Bhore et al., 2012). Plant extract has a potential application as natural medicine and to treat diseases as well as the microbiological safety of the human health (Subashkumar et al., 2013). Medicinal plants and their parts represent a rich source of antibacterial agents. Plants are used medicinally in different countries and are a source of many potent and powerful drugs. Different extracts from traditional medicinal plants have been tested. Many reports have show the effectiveness of traditional herbs against microorganisms, as a result, plants are one of the bedrocks for modern medicine to attain new principles (Dey et al., 2010). They have been widely used as traditional treatments for numerous human diseases. In

less developed countries low income people such as farmers, people of small isolate villages and native communities use herbal medicine for the treatment of common infections. *Phyllodium pulchellum* is commonly known as *Vellalothi* which belongs to the family Fabaceae. *P. pulchellum* is an important medicinal plant and its leaf has been used in various ailments and as health tonic. Previously, no work has been carried out on the antifungal and quantitative phytochemical of leaf extracts of *P. pulchellum*, the present study dealing with the evaluation of phytochemicals and antimicrobial activities of leaf of *P. pulchellum* was undertaken.

Materials and methods

Plant material

Dried material of leaf parts was ground into fine powder in an electric blender and it was kept in airtight bottles at room temperature for further use.

Preparation of crude extraction

Solvent of extraction

For solvent extraction, 10 g of air-dried powder was taken in 100 ml of organic solvent (ethanol and chloroform) in a conical flask, plugged with cotton wool and then kept on a rotary shaker at 190-220 rpm for 24 hrs. After 24 hrs the supernatant was collected and the solvent was evaporated to make the final volume one-fourth of the original volume (Parekh et al., 2005) and stored at 4ºC in airtight bottles.

For aqueous extraction, 10 g of air-dried powder was added to distilled water and boiled on slow heat for 2 hrs. It was then filtered through 8 layers of muslin cloth and centrifuged at 5000rpm for 10 min. The supernatant was collected. This procedure was repeated twice. After 6 hrs, the supernatant collected at an interval of every 2 hrs, was pooled together and concentrated to make the final volume one-fourth of the original volume. It was then autoclaved at 121°C temperature and at 15 lbs pressure and stored at 4ºC.

Fungal isolates and their maintenance

The fungi employed in the study were *Penicillium notatum* (MTCC 4634), *Aspergillus niger* (MTCC 4325), *Rhizoctonia solani* (MTCC 4634) and *Colletotrichum falcatum* (lab strain). The isolates were procured from the MTCC, Chandigarh. The isolates were maintained on Potato Dextrose Agar slants by sub culturing at monthly intervals.

Screening of fungi for sensitivity towards plant extracts

PDA plates with crude plant extracts were used for testing the antifungal activity of plant extracts (Sharma et al., 2012). The discs were prepared by incorporating plant extracts in various concentrations.

Experimental procedure

The PDA plates were inoculated with fungal cultures and plant extract loaded sterile disc was impregnated on the surface of the medium and the plates were incubated in a humid chamber at room temperature. The activity of the extract was assessed by measuring the zone of inhibition and recorded.

Determination of total phenolic, total flavonoid and total tannin contents

Total phenolic content (TPC)

The amount of total phenolics in extracts was determined with the Folin-Ciocalteu reagents method described by Demiray et al. (2009). Gallic acid was used as a standard and the total phenolics were expressed as mg/g gallic acid equivalents (GAE). Concentration of 20 to 100 µg/ml of working standard solution was taken into a series of test tubes. The leaf extract were also prepared in various solvents about 0.125 ml of each sample were introduced into test tubes. To all the test tubes, including the blank, add distilled water to make up to 3.5 ml and add 0.125 ml of Folin's phenol reagent. Incubate the test tubes at room temperature for 6 minutes and add 1.25 ml of 7% sodium carbonate in all the test tubes. The tubes were covered with parafilm and allowed to stand for 90 minutes at room temperature before the absorbance was read at 760 nm spectrometrically.

All determinations were performed in triplicate. The Folin-Ciocalteu reagent being sensitive to reducing compounds including polyphenols is producing a blue colour upon reaction which is measured spectrophotometrically.

GAE was calculated using the following equation:

$$C = \frac{(c \times V)}{m}$$

Where, C = total content of flavonoid compounds (mg/g) plant extract, in quercetin equivalent, c = the concentration of quercetin established from the calibration curve (mg/ml), V= the volume of extract (ml), and m = the weight of crude plant extract (g).

Total flavonoid content (TFC)

The total flavonoids content of plant extract was estimated by Aluminium chloride method. (Wang and Jiao, 2000). Pipette out 0.5, 1.0, 1.5, 2.0 and 2.5 ml (Concentration varying from 50 to 250 µg) of the standard solution into a series of test tubes. Add 0.1 ml of the plant sample into test tubes. To all test tubes, including the blank, add distilled water to make up to 2.5 ml. After that to all tubes add 75 µl of 5% $NaNO_2$ and incubate at room temperature for 5 minutes. Add 150 µl of 10 % $AlCl_3$ and incubate at room temperature for 6 minutes. Then add 0.5 ml of 1 M NaOH, mix well and the pink coloured substance formed is spectrophotometrically measured at 510 nm. All determinations were performed in triplicates. Calculate the unknown sample concentration from the standard curve of the graph. The total content of flavonoid compounds was calculated by the following equation.

$$C = \frac{(c \times V)}{m}$$

Where, C = Total content of flavonoid compounds (mg/g) plant extract, in quercetin equivalent, c = The concentration of quercetin established from the calibration curve (mg/ml), V = The volume of extract (ml), and m = The weight of crude plant extract (g).

Total tannin content (TTC)

The total tannin content of plant extract was estimated by modified Prussian blue method (Graham, 1992). Tannic acid was used as a standard and the total tannins were expressed as mg/g tannic acid equivalents (TAE). Pipette out 0.1, 0.2, 0.3, 0.4 and 0.5 ml (Concentration varying from 10 to 50 µg) of the working standard solution into a series of test tubes. Add 0.1 ml of sample and to all the test tube, including the blank, add distilled water to make up to 7 ml. To all the test tubes, add 1 ml of potassium ferricyanide and 1 ml of FeCl3 mix well. Measure the absorbance spectrophotometrically at 700 nm. From the standard curve of the graph, calculate the unknown sample concentration. All determinations were performed in triplicate. The total content of tannin compounds was calculated by the following equation:

$$C = \frac{(c \times V)}{m}$$

Where, C = total content of tannin compounds (mg/g) plant extract, in tannic acid equivalent, c = the concentration of tannic acid established from the calibration curve (mg/ml), V = the volume of extract (ml) and m = The weight of crude plant extract (g).

Results

Antifungal activity

The results of antifungal property of *P. pulchellum* were extracted with different organic solvents *viz.,* aqueous, chloroform and ethanol. The antifungal activity of the leaf extract against some pathogenic fungus like *Aspergillus niger, Penicillium notatum, Rhizoctonia solani* and *Colletotrichum falcatum* are given in Table 1 and Fig. 1. The antifungal activity was tested by disc diffusion method (Taylor et al., 1995).

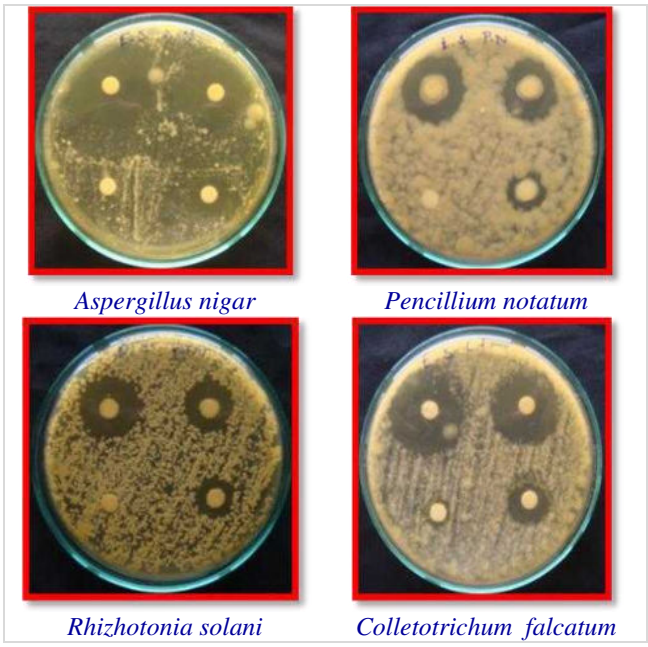

Fig. 1: Antifungal activity of *P. pulchellum* ethanol leaf extract.

The ethanol extracts of *P.pulchellum* showed maximum activity against *Aspergillus niger,* followed by *Colletotrichum falcatum, Penicillium notatum* and *Rhizoctonia solani*. The chloroform extract of this plant showed maximum activity against *Colletotrichum falcatum,* followed by *Aspergillus niger, Penicillium notatum* and *Rhizoctonia solani*. The antifungal activity of ethanol extracts showed more effective followed by chloroform extract against all the fungal strains. The water extract doesn't show comparative effectiveness on the pathogenic fungi with ethanol and chloroform extracts. As compared with fluconazole, the positive control ethanolic extract of *P. pulchellum* showed high activity against all the pathogenic fungi. It was evident that the inhibition of growth of fungus was more prominent with ethanol extract than chloroform extract.

Table 1. Antifungal activity of various extracts of *P.pulchellum.*

Test microorganisms	Concentration (mg)	Zone of Inhibition (mm)			Fluconazole 10 mcg / disc
		Aqueous extract	Chloroform extract	Ethanol extract	
Aspergillus nigar	25	-	1.0	0.8	2.6
	50	-	1.8	1.2	
	75	-	2.4	2.4	
	100	-	2.8	**3.6**	
Pencillium notatum	25	-	-	-	2.4
	50	-	1.6	1.2	
	75	-	2.2	1.8	
	100	-	2.4	**2.5**	
Rhizhotonia solani	25	-	0.8	-	2.0
	50	-	1.2	1.4	
	75	-	1.8	2.0	
	100	-	2.4	**2.5**	
Colletotrichum falcatum	25	-	1.0	0.8	2.6
	50	-	1.6	1.0	
	75	-	2.4	2.2	
	100	-	3.0	**3.0**	

Quantitative analysis

Quantitative phytochemical analysis was studied for total flavonoids, phenol and tannin contents, which were responsible for the major pharmacological activity of the plants. For the quantification of leaf extracts having strong presence of phenols, flavonoids and tannin contents were determined. Knowledge of the chemical constituents of plants is desirable because such information will be of value for synthesis of complex chemical substances. Hence, to characterize the formulation of total flavonoids, phenol and tannins contents were estimated and shown in (Table 2).

Table 2. Total Flavonoids, Phenolic and Tannin contents of *P. pulchellum* of leaf extracts.

Extracts leaf	Total flavonoids content (mg/g)	Total phenolic content (mg/g)	Total tannin content (mg/g)
Aqueous	26.66±4.163	80.12±3.055	30.23±3.025
Ethanol	**71.33±4.172**	**88.68±2.081**	**40.72±5.131**
Chloroform	27.61±3.511	35.36±1.814	14.33±7.023

Determination of total flavonoids content

The total flavonoid content of the extract was expressed in quercetin equivalents. Total flavonoid content in various solvent extracts such as aqueous, ethanol and chloroform were found to be 26.66 ± 4.163 mg/g, 71.33 ± 4.172 mg/g and 27.61 ± 3.511 mg/g quercetin equivalents/g dry weight. Ethanolic leaf extract of *Phyllodium pulchellum* was found to contain the highest amount of flavonoid. It has been recognized that flavonoids show antioxidant activity and their effects on human nutrition and health are considerable.

Determination of total phenolic content

The content of total phenol in the extracts of *Phyllodium*

pulchellum was determined by using the Folin–Ciocalteu assay and expressed as gallic acid equivalents (GAE). The total phenol content of the test fractions were calculated using the standard curve of gallic acid. In ethanol leaf extracts of higher amount of total phenol content was found to be 88.68 ± 2.081 mg/g. The descending orders of the total phenol content of extract in ethanol > aqueous > chloroform.

Determination of total tannins content

The total tannin contents of different leaf extracts of *Phyllodium pulchellum* were determined and found to be 30.23±3.025 mg/g, 40.72 ± 5.131 mg/g and 14.33 ± 7.023 mg/g with respect to various solvents, as follows aqueous, ethanol and chloroform. Total tannin content was calculated using the standard curve of tannic acid and was expressed as tannic acid equivalents (TAE) per gram of the plant extract. Ethanolic leaf extract of *Phyllodium pulchellum* was found to contain the maximum amount of tannin. Tannin contents of the extracts were found to decrease in the following order of Ethanol extract > Aqueous extract > Chloroform extract.

Discussion

The present study is the first report on the antifungal activity of various extracts of *Phyllodium pulchellum*. An ethanol extract of the leaf shows high activity against the fungal strains than other extracts. The study evidences that plant species are having antifungal activity of their own for survival in different environmental conditions. The finding in disc diffusion assay of leaf extracts of *Phyllodium pulchellum* correlate with the results of earlier works like *Desmodium gangeticium* (Vijayalakshmi et al., 2011), *Desmodium heterocarpon* (Al Hasan et al., 2011), *Desmodium elegans* (Khan et al., 2013), *Aloe vera* (Arunkumar and Muthuselvam, 2009), *Mimosa pudica* (Gandhiraja et al., 2009).

The quantitative estimation of primary metabolites reveals various chemical constituents present in the plant. Quantization of the phytocompounds such as phenol, flavonoids and tannins from various solvent extracts of *Phyllodium pulchellum* was studied in this work. Highest concentrations of the bioactive principles were detected in ethanolic extracts of the plants, except in the case of tannins where chloroform extract produced the bioactive compounds. The ethanolic extract showed higher level of phenols (88.68 mg/g of dried weight) than the other extracts which having secondary metabolites. The higher amount of phenol is important in regulation of plant growth, development and disease resistance. Triterpenoid saponins, tetrahydroiso-quinolones, phenylethylamines and indole-3-alkyl amines have been isolated from the leaves of *Desmodium adscendens* (Addy, 1989). Similar results were reported in *Indigofera tinctoria* (Singh et al., 2015).

Conclusion

In the present study conclude that the *Phyllodium pulchelllum* leaf have the potential to act as a source of useful drugs because of presence of various phytochemical constituents such as alkaloids, flavonoids and phenol. Thus, these plants have great potential as antimicrobial agents and can be used in the treatment of infectious diseases caused by resistant microorganisms. The finding of this study suggests that this plant leaf could be a potential source of natural phytochemical and antifungal activity that could have great importance as therapeutic agents. Further investigation on the isolation and characterization of the antioxidant constituents is however required.

Conflict of interest statement

Authors declare that they have no conflict of interest.

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In vitro Shoot Multiplication Studies on *Solanum pubescens* Willd an Important Antiepileptic Activity Plant

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ABSTRACT

Solanum pubescens Willd is an important medicinal plant which belongs to the family Solanaceae. It is widely used as folk medicine and treating for many diseases. Efficient in vitro regeneration of Solanum pubescens was achieved from node and Internode explants on MS medium with B5 vitamins and different concentrations and combinations of PGRs like BAP, GA_3 and KIN. The maximum numbers of multiple shoots were achieved from nodal and internodal explants on 3.0 mg/l BAP+1.0mg/l GA3+0.5mg/l KIN (80.5%). The regenerated shoots were transferred in to half strength MS medium fortified with IBA for root induction. Rooted plantlets were successfully acclimatized. The current study showed efficient in vitro shoot regeneration capabilities of Solanum pubescens.

Keywords: Multiple shoots, *Solanum pubescens*, MS medium, BAP, GA_3, KIN

INTRODUCTION

Solanum pubescens is a Willd. plant it is an annual erect, unarmed shrub growing up to 1.5 m tall abundantly growing as weed of forest and the hills of South-Eastern Ghats in Andhra Pradesh peninsular India and Sri Lanka. Commonly known as Ushtichettu, Kasivuste and pajarito in Telugu and Kaattu sundai kaai in Tamil, flowering and fruiting is in the month of July to February. *Solanum pubescens* is a traditional medicine plant for the treatment of headache, menstrual pain, rheumatoid arthritis, tuberculosis, ulcers, etc [1]. It exhibits gastro protective activity [2]. The use of herbal preparations in the management of various forms of epilepsies is very common in many parts of the world. Epilepsy affects more than 50 million persons worldwide [3]. Seizure is a characteristic feature in epilepsy and is associated with disordered and rhythmic high frequency discharge of impulses by a group of neurons in the brain and status epilepticus is characterized by repeated episodes of epilepsy without the patient having recovered from the previous attack [4]. There are many classes of anticonvulsants that are of clinical usefulness with good prognosis for controlling seizures in most patients [5]. These and the treatment cost have made traditional herbs and herbalists very useful and indispensable in the struggle for seizure management and future antiepileptic drug development. Despite this many patients have seizures that are not adequately managed by the established antiepileptic drugs [6] for this above medicinal purposes; this plant is highly focused in many countries and pharmaceutical industries. Tissue culture plays an important key role for medicinal plants in rapid propagation, conservation and enhanced the production of secondary metabolites. The secondary metabolites production can be possible through *in vitro* plant cell culture [7,8]. In this present investigation was undertaken with an objective to develop an efficient *in vitro* Shoot regeneration protocol for important medicinal plant *Solanum pubescens* through nodal and internodal explants.

MATERIALS AND METHODS

Plant material and surface sterilization

Healthy plant of *Solanum pubescens* were collected from Western Ghats, Sirumalai, Dindugal district, Tamilnadu. The node and Internode explants were taken from 4-5 months old plants. All the explants were washed thoroughly with running tap water for 20 mins. The sterilization of explants was done by dipping them in 70% ethanol for 10 seconds followed by continuous shaking. Then the explants were washed with detergent Tween-20 for 5 mins and after that explants were surface sterilized by 0.1% mercuric chloride ($HgCl_2$) for 1 min then finally rinsed for 3 times with sterilized distilled water the explants were aseptically transferred onto nutrient medium for shoot induction.

Shoot regeneration

In a laminar air flow cabinet, sterilized node and Internode explants (about 1.0 cm in length) were inoculated in culture tubes (22 × 150 mm) containing 25 ml of sterile Murashige and Skoog (MS) [9] with B5 vitamins [10] supplemented with 3% (w/v) sucrose, 8 g/l agar, and pH adjusted to 5.8. Explants were maintained in a growth room in the dark at a temperature of 25ºC. After 20 days, shoot induction. The basal medium was supplemented with different growth regulators in different concentrations and combinations. In the present study, two types of media were employed on the basis of growth regulator used. The shoot differentiating medium. The former medium was fortified with various concentrations of N6-benzylaminopurine BAP; 1.0–5.0 mg/l alone or in combination with α-naphthalene acetic acid KIN; 0.5 mg/l and GA_3 1.0 mg/l the shoot was periodically sub cultured on MS medium supplemented with 4.0 mg/l BAP for shoot regeneration from node and Internode were transferred to each culture tube. Data on percentage of shoot forming shoots and mean shoot number and length of differentiated shoots were recorded after 45 days of culture. MS medium lacking growth regulators served as the control.

Shoot elongation, rooting and field transfer

The shoots below 2.5 cm in length were excised and sub cultured on MS medium supplemented with 4.0 mg/l BAP for shoot elongation. The shoots having approximately 3.0 cm in length were harvested from the shoot elongation medium and cultured on half strength MS medium supplemented with various concentrations of indole-3-butyric acid (IBA; 0.5-2.5 mg/l) or NAA (0.2–1.0 mg/l) for root induction. Data were recorded for percent rooting, root number and length after 45 days of transfer on rooting medium. Plantlets with well developed roots were removed from culture tubes, washed well to remove the remnants of agar from roots and transplanted to plastic cups (6 cm diameter) containing garden soil and sand (1:1). The plantlets were placed in a glasshouse set at 24 ± 2ºC, 82–88% relative humidity and irradiance (60 mg/l m−2s−1) provided by cool white fluorescent tubes. Plants were irrigated with half-strength MS salt solution for 3 weeks and thereafter with water. After two months the plants were transferred to larger pots and kept under shade in a net house for another two weeks before transferring outside under full sun to develop into mature plants.

Culture conditions

The pH was adjusted to 5.8 with 1.0 N HCl or 1.0 N NaOH before autoclaving the medium at 1.06 kg cm^{-2} and 121ºC for 20 mins. The cultures were maintained in a culture room with a 16 hrs /8 hrs light/dark photoperiod at 23 ± 2ºC unless otherwise mentioned. Light was supplied at intensity of 80 _mol m−2s−1 supplied by two Philips TL 40W cool-white fluorescent lamps. Each treatment consisted of 20 tubes and all experiments repeated 3 times. The data were presented as mean and its standard deviation (mean ± SD) and comparisons of means were carried out with Duncan's multiple range tests [11] at 0.05% significance.

RESULT

Plant regeneration

The Node and Internode explants were inoculated on MS medium with B5 vitamins supplemented with various concentrations of BAP (0.5–5.0 mg/l) alone or in combination with KIN (0.5 mg/l) and GA_3 (1.0 mg/l) were used for culture initiation and multiplication of shoots. After 12 days of inoculation multiple shoot induction was observed from the explants. The mean number of multiple shoots was recorded on after 4 weeks of inoculation. In nodal and internodal explants were showed the maximum number of multiple shoots on BAP (3.0 mg/l)+GA_3 (1.0 mg/l) KIN (0.5 mg/l) and obtained the best response (Figures 1a-1f).

Shoot elongation, rooting and field transfer the length of some shoots (about 22%) were less than 1.0 cm and not suitable for root induction. Therefore, such shoots were excised from the shoot clumps and transferred to a fresh MS medium containing BAP (3.0 mg/l). The shoots elongated to a mean Number of shoots of 8.6 ± 0.32, Response 99% with minimum 5 nodes in 4 weeks. Although rooting was observed on half strength MS basal medium, the percent response and number of roots were low. Hence, further experiments were carried out with the half strength MS medium supplemented with NAA or IBA. The elongated shoots measuring a size of 8.6 ± 0.32 were transferred to half strength MS medium supplemented with NAA (0.2–1.0 mg/l) or IBA (0.5–2.5 mg/l). Comparatively, IBA was more effective for root induction than NAA, as the former resulted in optimum rooting frequency (98%) than the latter (68%). Half strength MS medium supplemented with 2.0 mg/l IBA was the best for percentage induction (98%) and average number of roots per culture the rooted shoots were successfully transplanted to thermocol cups containing sand: soil (1:1) and acclimatized two months after transplantation of the 98 plants transplanted to soil 83 survived they grew well with irrigation and showed new growth after 4 weeks (Graph 1).

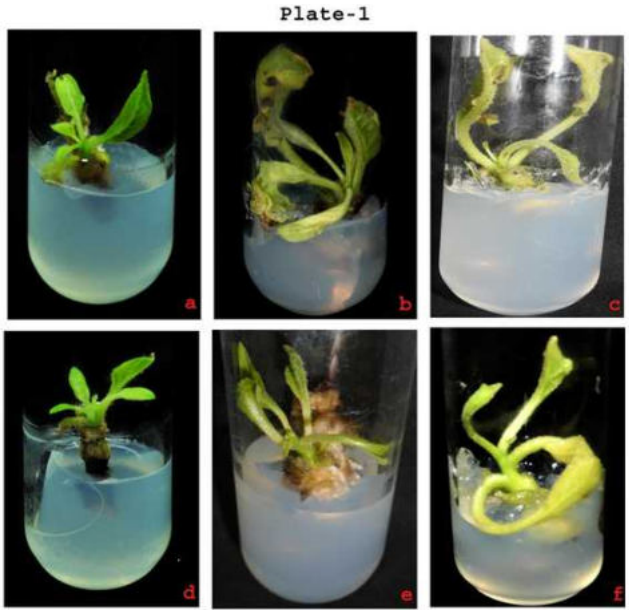
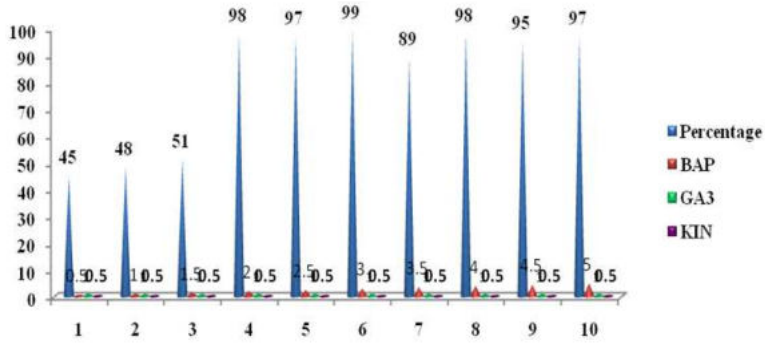


Figure 1: a-Shoot induction from intermodal explants, b-Multiple shoot induction, c- Shoot elongation, d-Shoot induction from nodal explants, e- Multiple shoot induction, f- Shoot elongation.



Graph: 1 Effect of various media compositions of plant growth regulators on multiple shoot induction from *Solanum pubescens* Willd.

DISCUSSION

The aim of the present investigation was to obtain high frequency shoot regeneration from nodal and internodal explants. There are some reports available on another species *Withania somnifera* [12] and [13]. We have used several explants for callus induction as a preliminary study. However, the satisfactory result was obtained with nodal and internodal explants only. Therefore, only the nodal and internodal explants were used for the present study. Similar results on superiority of intermodal explants on callus induction and shoot organogenesis have been reported in other systems like *Achillea millefolium* L [14]. The optimum plant growth regulator combination for callus induction was 4.0 mg/l 2, 4-D and 0.5 mg/l Kin. This study is in agreement with other systems where 2, 4-D and Kin induced callus has been reported in other systems like *Diplocyclous palmatus* L [15]. In this study, the light yellow, friable calli formed on all plant growth regulator combinations exhibited organic potential in the present study, MS medium supplemented with 4.0 mg/l BAP, GA3 1.0 mg/l and 0.5 mg/l NAA was optimum for shoot organogenesis from callus. The present report is in agreement with several previous reports where an auxin-cytokine combination provided maximum shoot induction response from callus. In *Physalis peruviana* highest shoot regeneration from callus was noted on MS medium supplemented with BAP 2.0 mg/l +NAA1.0 mg/l+GA_3 1.0 mg/l [16]. The two cytokinins used for shoot induction from callus, BAP was superior to Kin. It has been reported that BA being considered as one of the most potential cytokinin for shoot induction and used for micro propagation of several plants such as *Valeriana jatamansi Jones* [17], *Gentiana dinarica* [18], *Mentha piperita* [19], *Ajugabracteosa* [20] and *Stevia rebaudiana* [21]. Because of high frequency proliferation and regeneration potential, the present callus lines could be an ideal target material for Agro bacterium mediated or direct gene transfer (Table 1).

Table 1: Effect of various media compositions of plant growth regulators on multiple shoot induction from node and Internode Medium: MS; culture period: 20 days

Plant growth regulators (mg/l)			Number of shoots/explants (Mean ± SD)	% Response
BAP	**KIN**	**GA3**		
0.5	0.5	1.0	3.4 ± 0.89	45
1.0	0.5	1.0	5.3 ± 0.13	48
1.5	0.5	1.0	6.5 ± 0.56	51
2.0	0.5	1.0	7.5 ± 0.21	98
2.5	0.5	1.0	5.7 ± 0.26	97
3.0	0.5	1.0	8.6 ± 0.32	99
3.5	0.5	1.0	7.4 ± 0.47	89
4.0	0.5	1.0	7.5 ± 0.21	98
4.5	0.5	1.0	5.2 ± 0.57	95
5.0	0.5	1.0	4.8 ± 0.36	97

Mean values within a column followed by the same letter are not significantly different by Duncan's multiple range tests ($P \geq 0.05$). The values represent the means (± SE) of three independent experiments. At least 20 cultures were raised for each experiment.

Shoot elongation 3.0 mg/l BA was optimum for *Solanum pubescens*. According to [22] *Withania coagulans,* BAP is the key plant growth regulator for shoot elongation and low concentration of BAP is ideal for optimum result. In this study full strength MS medium produced callus at the basal cut end and was not suitable for root induction as reported in other systems *Withania somnifera* [23]. Therefore, half strength MS medium was employed for the present study. Our study is in line with other reports where half strength MS medium produced optimum rooting response *Silybum marianum* and *Silymarin accumulation* [24] and [25] during the present investigation, it has been clearly indicated that the highest root induction from shoot was obtained on IBA. These results are comparable with those described by other researchers for IBA induced rooting in other species *Pelargonium graveolens* [26]. *Azadirachta indica* [27]. *Jatropha curcas* L [28], *Withania somnifera* [29].

CONCLUSION

In the present investigation, we have reported very simple and efficient protocol for *in vitro* shoot regeneration of *Solanum pubescens* as compared to the methods described for other members of Solanaceae. This will be useful for conservation and sustainable utilization of this medicinal Shrub. These are the first protocol for *in vitro* shoot regeneration of *Solanum pubescens*. Further, this approach can be used for mass multiplication of targeted medicinal plants in short span of time to cater to the need of pharmaceutical industries. Our success with in-vitro establishment clearly indicates that micro propagation is an effective and useful technique for the reproduction of this species.

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PHYTOCHEMICAL ANALYSIS OF *PHYLLODIUM PULCHELLUM* L. DESV. LEAF BY UV-VISIBLE SPECTROSCOPY AND FTIR

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ABSTRACT

The present study investigates the characterization of the bioactive constituents showing antimicrobial activity present in the leaf extract of Phyllodium pulchellum using UV-VIS and FTIR spectroscopy. The ethanolic leaf extract of P. pulchellum prepared to analyze under ultraviolet and visible light. The scanning of the crude extract was done at the range from 380 to 900 nm through UV Visible spectrophotometer system and the characteristic peaks were detected. FTIR study was done on ranging 4000-400 cm-1which revealed the characteristic peak values showing the absorption and functional groups present in leaf extract. The UV-VIS profile showed the peaks at 382.70, 413.68, 536.18, 610.37 and 664.61 nm with the absorption 2.7930, 2.5932, 0.3114, 0.4185 and 1.5966. The result of FTIR spectra confirms the presence of alcohols, phenol, alkenes, aromatics, alkyl halides, primary and secondary amines compounds. The results of our study generated the UV-VIS and FT-IR spectrum profile of medicinally important plant P. pulchellum. In future, it can be used in the pharmaceutical industry for treating various diseases.

KEY WORDS

UV-VIS Spectroscopy; FTIR Spectroscopy; Phyllodium pulchellum; leaf extract

INTRODUCTION

Plants with medicinal properties are gaining a lot of importance due to their role in various health concerns of human population in different nations. There is an exponential growth in the need of the plant based drugs in the international market because of high effectiveness, easily available, economical, evidently negligible toxicity, as side effects and proving to be a good substitute for allopathic medicines.[1] Medicinal plants provide raw materials for indigenous health care systems such as Ayurveda, Unani and Siddha and also for modern medicines. Some estimates indicate that, over 25,000 effective plant based formulations are available in Indian medicine, 1.5 million practitioners use medicinal plants in preventive, promotional and curative applications.[2] Phytochemical characterization of plant material is important as it relates to the nature and extent of therapeutic action possible with its use. Among the thousands of naturally occurring constituents so far identified in plants and exhibiting a long history of safe use, there are none that pose- or reasonably might be expected to pose- a significant risk to human health at current low levels of intake when used as a flavoring substance.[3] The unknown organic compounds in a complex mixture can be determined by the interpretation and also by matching the spectra with reference spectra.[4] FT-IR Spectroscopy has demonstrated to be a reliable and sensitive method for finding out the functional groups, present in plant samples using IR region in the range of 400 to 4000 cm^{-1}. For most common plant compounds, the spectrum of an unknown compound can be identified by comparison to a library of known compounds.[5] UV-VIS spectroscopy uses light in the visible ranges or its adjacent ranges. The color of the chemicals involved directly affects the absorption in the visible ranges. Molecules undergo electronic transitions in these ranges of the electromagnetic spectrum.[6]

Phyllodium pulchellum L. Desv. is a perennial plant with slender, branching stems that become more or less woody. It can grow 50 - 250 cm tall. The plant is harvested from the wild for local use as a medicine. The plant is classified as 'Least Concern' in the IUCN Red List of Threatened Species. The roots and leaves are used for reducing fever and as an antiphlogistic and diuretic. The whole plant is used in a post-partum treatment; to treat rheumatic fevers; to cure toothache; to help dissolve internal blood clots; and is also considered a remedy for convulsions in infants. In recent years, in order to detect the quality of medicines plants, many studies have been carried out to understand the variation of chemical information caused by these factors.[7,8] The biological activities and phytochemical constituents of this expensive resource belonging to the plant kingdom have remained undocumented, so long and in order to correct the situation, the present research work has been taken up to produce the UV-VIS and FTIR spectrum profile of *Phyllodium pulchellum*.

MATERIALS AND METHODS

Plant Material

The fresh leaf of *Phyllodium pulchellum* (Threatened plant) was collected from Jambhuthu hamlet, Bodamalai, Namakkal district, Tamil Nadu. The leaf was washed with running water and then with distilled water. 10 g of air-dried powder was taken with 100 ml of organic solvent (ethanol) in a conical flask, plugged with cotton wool and then kept on a rotary shaker at 190-220 rpm for 24 h. After 24 hours the supernatant was collected, and the solvent was evaporated to make the final volume one-fourth of the original volume and stored at 4°C in airtight bottles.[9]

RESULTS AND DISCUSSION

Spectral studies

UV-VIS and FTIR analysis

The qualitative UV-Vis spectrum profile of *P.pulchellum*, ethanolic leaf extract was selected at wavelengths from 380 to 900 nm, due to sharpness of peaks and proper baseline. The profile showed the peaks 382.70, 413.68, 536.18, 610.37 and 664.61 with absorption 2.7930, 2.5932, 0.3114, 0.4185, 1.5966 respectively (Table 1 & Fig 1).

The characteristic absorption bands exhibited at 3432.65 cm^{-1} for O–H stretch, H–bonded, 1642.61 cm^{-1} for –C=C– stretch, 1445.74 cm^{-1} for C–C stretch (in–ring), 1296.18 cm^{-1} for C–H wag (–CH2X), 666.90 cm^{-1} for N–H wag. The absorption bands at 3415 cm^{-1} (OH) and 1064 cm^{-1} (O-H bending) are due to the hydroxyl group. The functional groups were present in plants extract of alcohols, phenol, alkenes, aromatics, alkyl halides, primary and secondary amines (Table 2 & Fig 2). Lakshmi *et al.,* reported the presence of alcohols, phenols, alkanes, primary, secondary, aromatic, aliphatic amines, carboxylic acids, nitro compounds, alpha, beta-unsaturated esters and alkyl halides as functional groups during Fourier Transform Infrared (FT-IR) Spectroscopic study of *Clitoria ternatea* and it's different leaf extracts.[10] Lakshmi *et al.,* during FT-IR analysis of *Acacia catechu* seed was revealed that powder showed lipids, carboxylic acids, aliphatic, aromatic nitro compounds, alkanes, alkyl halides, aliphatic amines and esters.[11] Analysis of the leaf extract of sample under FTIR and UV-VIS spectroscopic technique showed that the presence of phenolic compound and flavonoid which can be isolated and further screened for different kind of biological activities depending their therapeutic uses.

Table 1: UV Visible Spectroscopic studies on the ethanolic leaf extract of *Phyllodium pulchellum*

Nanometers	Absorption
382.70	2.7930
413.68	2.5932
536.18	0.3114
610.37	0.4185
664.61	1.5966

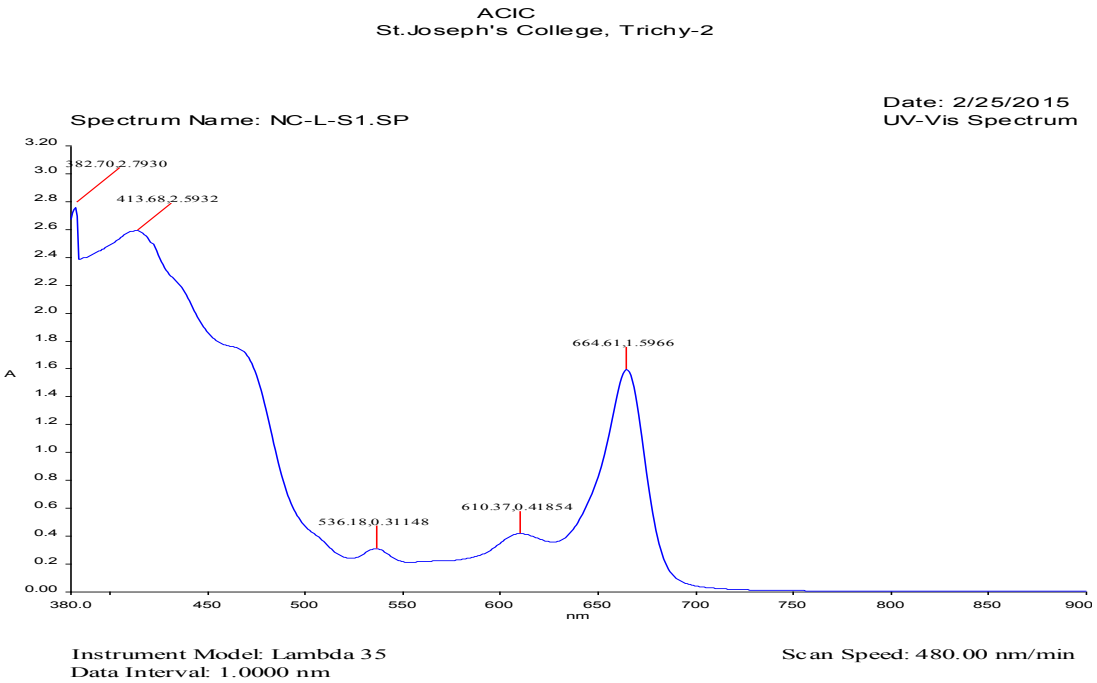

Figure 1: UV Visible Spectroscopic studies on the ethanolic leaf extract of *Phyllodium pulchellum*

Table 2: FTIR peak values and functional groups of ethanol leaf extracts of *P.Pulchellum*

Peak values	Bonds	Functional groups
3432.65	O–H stretch, H–bonded	Alcohols, phenols
2072.97	-	Unknown
1642.61	–C=C– stretch	Alkenes
1445.74	C–C stretch (in–ring)	Aromatics
1296.18	C–H wag (–CH_2X)	Alkylhalides
666.90	N–H wag	Primary, secondary amines

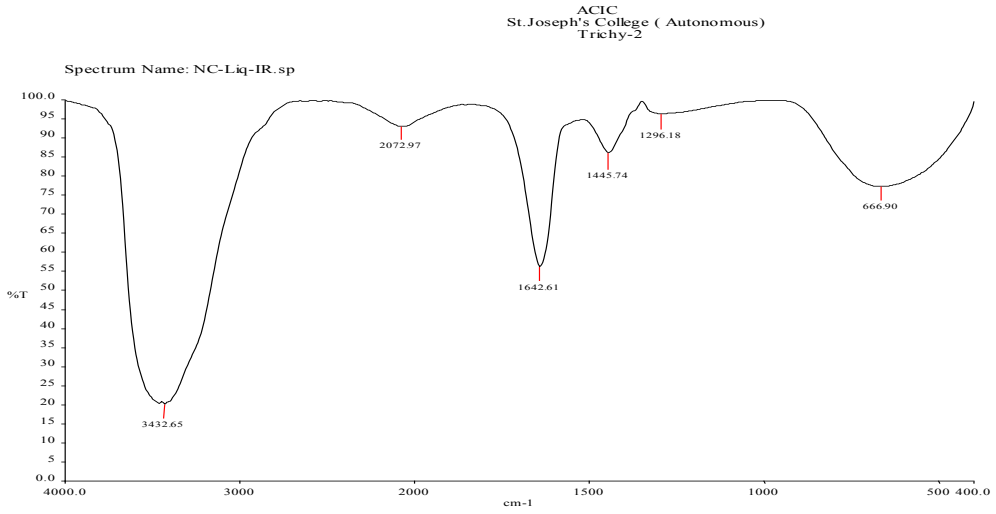

Figure 2: FT-IR Spectroscopic studies on the ethanolic leaf extract of *Phyllodium pulchellum*

Conclusion

The present study was carried to detect the spectroscopic characterization of the ethanolic leaf extract of *P.pulchellum*. The value of absorption obtained at these wavelengths indicates the presence of flavonoids and its derivatives. Furthermore, work is required to determine the structure of alkaloids and flavonoid compound by use of various more advanced analytical techniques such as Mass and NMR spectrophotometer.

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Research Article

IN VITRO ANTIOXIDANT ACTIVITY OF *PHYLLODIUM PULCHELLUM* L. DESV - AN THREATENED MEDICINAL PLANT

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ABSTRACT

Objectives: In this study, we determined the *in vitro* antioxidant capacity of *Phyllodium pulchellum* of aqueous, ethanol, and chloroform leaf extracts.

Methods: In this context, the *in vitro* antioxidant activity was demonstrated by 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,2′-azinobis(3-ethylbenzothiazolone-6-sulfonic acid) (ABTS+) radical scavenging assay, the total antioxidant activity of phosphomolybdenum assay and hydroxyl radical scavenging activity in different leaf extracts of *P. pulchellum*. The antioxidant activity of the extracts was compared to standard ascorbic acid.

Results: All the four methods of antioxidant showed good reducing power and reducing capacity with increasing concentration again taking the ethanol leaf extract to the top position. Remarkable of antioxidant activity was observed in ethanol leaf extract on the hydrogen peroxide scavenging activity with the lowest inhibitory concentration 50 values of (155.40 µg/ml) followed by DPPH (432.90 µg/ml) and ABTS+ (524.40 µg/ml).

Conclusion: These results suggest that the leaf of *P. pulchellum* could be a valuable source of new antioxidant properties, from the above results it seen that this plant exhibits pharmaceutical activity.

Keywords: *Phyllodium pulchellum,* Fabaceae, Leaf extracts, 2,2-diphenyl-1-picrylhydrazyl, 2,2′-azinobis(3-ethylbenzothiazolone-6-sulfonic acid), Inhibitory concentration 50.

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INTRODUCTION

Phyllodium pulchellum L. Desv. (Vellalothi in Tamil) is a flowering plant species and widely distributed in South India as a threatened medicinal plant belonging to the family of Fabaceae. It is a Subshrub 1(3) m; branchlets downy pubescent to tomentose. *P. pulchellum* (Syn. *Desmodium pulchellum* (L.) Benth) is used to treat various diseases such as anti-inflammatory, analgesic, antioxidant, hemorrhage, diarrhea, poisoning, and eye diseases [1]. The genus relative plants are reported to have anthelmintic [2], anti-hepatic fibrotic [3], antidiarrheal [4], anti-inflammatory [5], and antidiabetic [6]. The international union for conservation of natural and national resource has a long time ago listed *P. pulchellum* (L.) Desv. as a threatened species [7]. The genus Desmodium, of the Fabaceae family, includes about 350 species distributed in tropical and subtropical zones of the worldwide. However, no studies to date have been able to reveal the antioxidant effect of any *Desmodium* species other than *D. gangeticum* and *D. triflorum*. Hence, for there is no scientific report on the antioxidant activities in the particular species. Therefore, the present study was undertaken to evaluate and compare the antioxidative activities of different solvent leaf extracts of *P. pulchellum* in different methods.

MATERIALS AND METHODS

Plant material

P. pulchellum was collected from the *Jambhudu hamlet* of Bodamalai at Namakkal District, Tamil Nadu, India, and identified following the Botanical Survey of India and the voucher specimen (BSI/SRC/5/23/2012-13/Tech-1795 & Serial No. 2) was deposited in the herbarium of the Department of Botany, National College (Autonomous), Tiruchirappalli - 620 001, Tamil Nadu, India.

Preparation of plant extracts

Fresh plant material was washed under running tap water, air dried and powdered. About 30 g of coarsely powdered plant materials (30 g/300 ml) were extracted in a Soxhlet extractor for 8-10 hrs, sequentially with aqueous, ethanol, and chloroform. All the solvent extracts were evaporated to remove the final traces of the respective solvents. Dried extracts were kept at 20°C until further test was carried out.

In vitro antioxidant activity

Free radical scavenging activity of the various solvent of leaf extracts in *P. pulchellum* was determined using various *in vitro* assays such as 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity, 2,2′-azinobis(3-ethylbenzothiazolone-6-sulfonic acid) (ABTS) radical scavenging assay, total antioxidant activity of phosphomolybdenum assay, and hydroxyl radical scavenging activity.

DPPH radical scavenging activity

Free radical scavenging activity was measured using DPPH method [8]. Different concentrations (1000, 800, 600, 400, and 200 µg/ml) of crude extracts and taken in test tubes in triplicates. Then, 5 ml of a 0.1 mM ethanol solution of DPPH (1,1,diphenyl-2-picrylhydrazyl) was added to each of the test tubes and was shaken vigorously. They were then allowed to stand at 37°C for 20 minutes. The control was prepared without any extracts. Ethanol was used for baseline corrections in absorbance (optical density [OD]) of the sample measured at 517 NM. Ascorbic acid is used as reference antioxidant compound. A radical scavenging activity was expressed as 1% scavenging activity and was calculated by the following formula:

$$\text{Radical scavenging activity}\,(\%) = \frac{\text{OD control} - \text{OD sample}}{\text{OD control}} \times 100$$

ABTS radical scavenging assay

The efficacy of plant extracts to scavenge free radicals was determined using ABTS radical scavenging assay with minor modification [9]. Freshly prepare the ABTS radical solution by adding 5 ml of 4.9 mM

ammonium persulfate solution to 5 ml of a 14 mM ABTS solution and keep for 16 hrs under dark condition. The solution is diluted with distilled water to yield an absorbance of 0.70±0.02 at 734 nm, and the same is used for the assay. To 900 µl of the ABTS radical solution, add 100 µl of the extract (1000, 800, 600, 400, and 200 µg/ml) and the reaction mixture is vortexed for 10 seconds and the assay was done. 6 minutes after record the absorbance at 734 nm against distilled water using (Beckman DU-530) ultraviolet-visible spectrophotometer. Ascorbic acid was used as reference standard. The radical scavenging activity was calculated using the formula:

$$\text{ABT scavenging activity} = \frac{\text{Absorbance of test sample}}{\text{Absorbance of blank sample}} \times 100$$

Total antioxidant activity of phosphomolybdenum assay

Determination of total antioxidant capacity developed by method [10]. 0.2 ml of plant extract (1000, 800, 600, 400, and 200 µg/ml) is mixed with 1.8 ml of distilled water, 2 ml of phosphomolybdenum reagent solution. Incubate it at 95°C for 90 minutes. The mixture is cooled to room temperature, and the absorbance is measured at 695 nm against a reagent blank. The test was performed in triplicate. The antioxidant capacity is expressed as ascorbic acid equivalent (AAE) and was calculated by the following theoretical formula:

$$A = \frac{c \times V}{M}$$

Where, A=Total content of antioxidant compounds, (mg/g) leaf extract, in AAE, c=The concentration of ascorbic acid established from the calibration curve, (mg/ml), V=The volume of extract (ml), and m=The weight of crude leaf extract (g).

Hydroxyl radical scavenging activity

The scavenging activity of the leaf extract on hydroxyl radical was measured according to the method [11]. Various concentrations (200, 400, 600, 800, and1000 µg/ml) of extracts were added to 1.0 ml of iron-ethylenediaminetetraacetate (EDTA) solution (0.13% ferrous ammonium sulfate and 0.26% EDTA), 0.5 ml of EDTA solution (0.018%), and 1.0 ml of dimethyl sulfoxide (0.85% v/v in 0.1 M phosphate buffer, pH 7.4). The reaction was initiated by adding 0.5 ml of ascorbic acid (0.22%) and incubated at 80-90°C for 15 minutes in a water bath. After incubation, the reaction was terminated by the addition of 1.0 ml of ice-cold trichloroacetic acid (17.5% w/v). 3 ml of Nash reagent (75.0 g of ammonium acetate, 3.0 ml of glacial acetic acid, and 2 ml of acetyl acetone were mixed and raised to 1 L with distilled water) were added and left at room temperature for 15 minutes, and the test was done 3 times. The reaction mixture without sample was used as a control. The intensity of the color formed was measured spectroscopically at 412 nm against the reagent blank. The percent hydroxyl radical scavenging activity is calculated by the following formula:

$$\text{Hydroxyl radical scavenging activity} = \frac{\text{Test sample absorbance}}{\text{Blank sample absorbance}} \times 100$$

RESULTS AND DISCUSSION

DPPH radical scavenging activity

The scavenging activity of all the extracts was found to be less when compared to that the standard ascorbic acid. Among the different extracts, the ethanol leaf extracts of showed high DPPH scavenging activity at 1000 µg/ml (81.5±0.02) followed by aqueous and chloroform (Table 1). From the results, it is known that the species, *P. pulchellum* possess hydrogen donating capabilities for ethanolic leaf extracts and execute scavenging free radicals.

ABTS radical scavenging assay

ABTS radical scavenging activity of different extracts of *P. pulchellum* is shown in Table 2. Ethanolic leaf extracts of *P. pulchellum* showed maximum free radical scavenging for ABTS assay at 1000 µg/ml concentration (75.13%) with a respective standard value of (82.13%) followed by aqueous and chloroform extracts. Among the all tested plant samples, ethanolic extracts of *P. pulchellum* exhibited the majority effective radical scavenging activity. All the extracts showed an increase in antioxidant capacity with an increase in the amount.

Total antioxidant activity of phosphomolybdenum assay

Phosphomolybdate method is also a quantitative assay, while the total antioxidant capacity is expressed as AAE. The total antioxidant activity of different concentrations in (200-1000 µg/ml) this method. The ethanolic leaf extract is higher than (2.069±0.002) with in respective standard value is 2.201±0.029. Although the antioxidant capacity of the extracts was found to the decrease arrange as followed by ethanol>aqueous>chloroform (Table 3).

Hydroxyl radical scavenging activity

The concentrations range from 200 to 1000 µg/ml of different extracts was assessed for their hydroxyl radical scavenging activity. From

Table 1: DPPH radical scavenging activity of leaf extract from *P. pulchellum*

Concentration (µg/ml)	Absorbance at 517 nm			
	Aqueous extract	Ethanol extract	Chloroform extract	Ascorbic acid (SD)
200	34.7±0.03	37.7±0.05	23.4±0.02	39.1±0.01
400	45.5±0.04	48.2±0.02	36.3±0.57	48.4±0.05
600	56.1±0.02	58.6±0.04	47.6±0.05	63.4±0.01
800	68.6±0.01	69.3±0.03	50.6±0.06	86.1±0.07
1000	76.8±0.03	81.5±0.02	67.2±0.10	91.1±0.08

Values were performed in triplicates and represented as mean±SD, DPPH: 2,2-diphenyl-1-picrylhydrazyl, *P. pulchellum: Phyllodium pulchellum*

Table 2: Activity of *P. pulchellum* leaf extracts in the ABTS cation radical assay

Concentration (µg/ml)	% inhibition of ABTS radical			
	Aqueous extract	Ethanol extract	Chloroform extract	Ascorbic acid (SD)
200	20.15	27.19	19.11	15.18
400	33.70	44.13	28.10	29.55
600	47.62	58.82	41.01	42.87
800	59.31	67.31	53.05	68.64
1000	72.41	75.13	68.82	82.13

ABTS: 2,2′-azinobis (3-ethylbenzothiazolone-6-sulfonic acid), *P. pulchellum: Phyllodium pulchellum*

Table 3: Total antioxidant activity of phosphomolybdenum assay

Concentration (µg/ml)	Absorbance at 695 nm			
	Aqueous extract	Ethanol extract	Chloroform extract	Ascorbic acid (SD)
200	1.258±0.008	1.311±0.021	1.125±0.012	1.121±0.018
400	1.422±0.005	1.572±0.011	1.322±0.010	1.346±0.024
600	1.629±0.006	1.692±0.013	1.492±0.023	1.657±0.072
800	1.811±0.007	1.881±0.005	1.662±0.043	1.824±0.043
1000	1.926±0.015	2.069±0.002	1.726±0.018	2.201±0.029

Values were performed in triplicates and represented as mean±SD

Table 4: Hydroxyl radical scavenging activity

Concentration (µg/ml)	% Inhibition of hydroxyl radical scavenging			
	Aqueous extract	Ethanol extract	Chloroform extract	Ascorbic acid (SD)
200	42.21	51.25	41.01	53.01
400	54.11	63.32	53.43	66.13
600	67.01	75.13	61.79	78.37
800	78.13	84.27	73.11	86.18
1000	84.51	93.70	81.15	96.67

Table 5: IC_{50} values of *P. pulchellum* in radical scavenging assay

Leaf extract	DPPH radical scavenging activity (µg/ml)	ABTS radical inhibition activity (µg/ml)	Hydroxyl radical scavenging activity (µg/ml)
Aqueous extract	481.37	651.32	320.29
Ethanol extract	432.90	524.40	155.40
Chloroform extract	698.42	728.18	357.80
Ascorbic acid (SD)	417.60	529.21	114.32

DPPH: 2,2-diphenyl-1-picrylhydrazyl, ABTS: 2,2′-azinobis (3-ethylbenzothiazolone-6-sulfonic acid), IC_{50}: Inhibitory concentration 50

Table 4, it is clear that the ethanolic leaf extracts of *P. pulchellum* showed greatest scavenging activity (93.70%) at 1000 µg/ml concentration followed by aqueous and chloroform with the standard values of 96.67%, respectively. The results showed the scavenging potential of *P. pulchellum* against hydroxyl radicals (Table 4).

The dosage of the extract is expressed in µg of the dry weight of the extract (compound)/mL of the assay mixture. Inhibitory concentration 50 (IC_{50}) value represents the concentration of test extract or compound where the inhibition of test activity reached 50%. Among the plant extracts, ethanolic extract showed the highest activity, with an IC_{50} value of 524.40 µg/ml. Moreover, the ABTs radical inhibition activity was in the order ethanol>chloroform>aqueous. The IC_{50} value of aqueous and chloroform extracts and ascorbic acid was 651.32 µg/ml, 728.18 µg/ml, and 529.21 µg/ml, respectively. The DPPH radical scavenging capacity in the order: Ethanol>chloroform>aqueous and then scavenging ability on hydroxyl radicals was in the order: Ethanol>chloroform>aqueous (Table 5).

Rising concern in the investigate for natural alternatives in favor of synthetic antioxidant has led to the evaluation of plant sources. In this study, leaf extract of *P. pulchellum* exhibited outstanding scavenging effects on DPPH radical scavenging activity, ABTS radical scavenging assay, total antioxidant activity of phosphomolybdenum assay, and hydroxyl radical scavenging activity. Along with the good number widely used procedures for measurement of antioxidant activity capacity, the DPPH radical scavenging analysis is one of the top known, correct, and regularly employed to measure the electron donating ability of the plant [12,13]. Dechayont *et al.,* reported that the moderate antioxidant activity from *Pogostemon cablin* and inhibited bacteria commonly responsible for community and hospital acquired infections [14]. Usmangani *et al.* reported that leaf and fruit extracts of *D. palmatus* were determined to have a certain level of radical scavenging effect, proportional to their level of phytochemicals [15]. Similar reported on antioxidant activity was Phyllodium genus relative synonymous species, *Desmodium gangeticum* (L.) DC., *Desmodium heterocarpon* (L.) DC., *Desmodium intortum* (DC.) Urb., *Desmodium microphyllum* (Thunb *ex* Murray) DC., *Desmodium renifolium* (L.) Schindl., *Desmodium scorpiurus* (Sw.) Desv., *Desmodium sequax* Wall. (DSE), *Desmodium tortuosum* (Sw.) DC., *D. triflorum* (L.) DC., and *D. uncinatum* DC.[16]. A similar observation was made in *Toddalia asiatica* [17], *Thevetia peruviana* [18], and *Leucas aspera* [19] reported that the amount of sensitivity increased with the regular increase in the concentration of extracts. There is no report that antioxidant activity of *P. pulchellum* leaf extracts. Hence, far we identify this is the first report that envisages the antioxidant activities of *P. pulchellum* leaf extracts. The extracts of *P. pulchellum* could be potential as a source of valuable phytochemical compounds used for the pharmaceutical industry and antioxidant mechanisms.

CONCLUSION

Based on the resulted find in this study, it is concluded that the ethanolic leaf extract of *P. pulchellum* exhibits considerable antioxidant radical scavenging activity on all tested assays. Therefore, further research is needed for the isolation and identification of the active components in the extracts.

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Antimicrobial activity, nutritional profile and phytochemical screening of wild edible fruit of *Catunaregam spinosa* (Thunb.) Tirveng

SP Anand, S Deborah and G Velmurugan

Abstract
The aim of the present study is to evaluate the nutritional profile, phytochemical screening and antimicrobial activity of wild edible fruits of *Catunaregam spinosa*. The fruits have been found to rich in nutrients such as crude fiber (12.6%), ash content (11.3%), moisture content (25%), protein (12.5%), lipids (0.018%) and carbohydrates (60.28%) with the energy value of 292±0.7 kcal/100g respectively. The phytochemical screening for the presence of flavonoids, saponin, phenol, tannins, alkaloids, anthraquinones, cardiac glycosides, phlobatannins, terpenoids and steroid in ethanol extract. Ethanol and chloroform extracts of *C. spinosa* showed maximum zone of inhibition against *Bacillus subtilis* followed by *Klebseila pneumonia, Pseudomonas aeruginosa, Escherichia coli* and *Salmonella typhi*. Aqueous extracts of the *C.spinosa* showed maximum zone of inhibition against *Klebseila pneumonia and Bacillus subtilis*. The results showed that the fruits contained higher value of energy level required per day by a person. Consumption of fruits may promote good health and well-being as well as reduce the risk of chronic diseases. These findings confirm that the *C. spinosa* fruit has a potential source for the formulation of new therapeutic drugs.

Keywords: Edible fruits, Nutritional analysis, Energy value, phytochemical analysis and Antibacterial activity

1. Introduction
Wild edible fruits played a vital role in food supplementing to maintain the diet of human beings. The dependence on the wild edible fruits has gradually decline due to exotic fruits have been introduced. But many people in tribal areas still use them as a supplement of their basic need of food. Some of them are preserved for use in dry period or sold in rural market. But the popularity of these wild forms has recently decreased. Apart from their traditional use of food, potentially they have many advantages. They are edible and having nutritional food value, which provides the minerals like sodium, potassium, magnesium, iron, calcium, phosphorus etc. They are immune to many diseases and often used in different formulation of 'Ayurveda' in Indian Folk- medicine. They provide fibres which prevent constipation [1]. It is consider that special attention should be paid in order to maintain and improve this important source of food supply.

Catunaregam spinosa belongs to the family rubiaceae commonly known as maniphal or Emetic nut [2]. In recent years plants and plant secondary metabolites (phytochemicals), previously with unknown pharmacological activities, have been extensively investigated. The *Catunaregam spinosa* fruits are edible and considered to be tonic, alternative, demulcent, diuretic and restorative. The drug is claimed as medicines to cure for piles, anti-dysenteric agent, asthma, jaundice, diarrhea, emetic and gonorrhea [3]. The fruit, seeds and barks posses insecticidal, anti-dysenteric, nauseant, expectorant, anthelmintic, abortifacient properties [4]. The fresh fruits contain high amount of carbohydrates and saponins [5]. The nutritional value describes mainly the percentage of major nutritional bio-molecules such as proteins, carbohydrates, lipids and fibere along with the presence of major minerals and their food value [6]. The fruits are a good source of various bioactive compounds and its importance being much unaware among the society. Hence, the present study has been framed to estimate the nutritional profile, phytochemical screening and antimicrobial activity of wild edible fruits of *Catunaregam spinosa.*

2. Materials and Methods

2.1 Sources of Plant Materials

The fresh fruits of *Catunaregam spinosa* were collected from the Kolli hills, Namakkal district, Tamil Nadu, India. The plants was identified and authenticated in the Botanical survey of India, Southern Regional Centre, Coimbatore, Tamil Nadu. The voucher registration No. BSI/SRC/5/23/2016/Tech/1751/specimen-3.

2.2 Fruit extract preparation

The samples were thoroughly washed with tap water. The fresh and dried edible portion of each sample was cut into tiny piece and crushed by using clean Mortar and Pestle, the grounded samples were stored in a labelled air tight container and placed in the refrigerator at 4°C and used immediately for subsequent analysis.

2.3 Nutritional Analysis

Determination of protein content by Folin-lowry's Method [7], Determination of Total Lipid [8], Determination of Carbohydrate, crude fiber, ash content, Moisture content by A.O.A.C Methods [9].

2.4 Determination of energy value

The total energy value in kcal/100g was estimated by using the method described by Jain and Sharma as shown below [10]. Energy value = 4x percentage of protein + 9x percentage of fat + 4x percentage of carbohydrate.

2.5 Qualitative phytochemical screening

Ethanol, chloroform and aqueous Solvent are used for the extraction. Flask extraction procedure was adapted for extraction. 25 grams of the powdered fruits sample was soaked in the conical flask containing solvent, wrapped with aluminum foil and placed in shaker for 48 hours at 120-130 rpm. After 48 hours, the extracts were filtered using Whatman filter paper No.1 Concentrated all the solvent extracts by vacuum evaporator. Dried extracts were stored at 4°C for further analysis. Phytochemical analysis of each extract has been carried out according to standard protocols [11, 12].

2.6 Antibacterial activity by Disc diffusion method

The antimicrobial assays of Ethanol, Chloroform and Aqueous extracts were performed by each fruits extract was tested for various concentration such as 25, 50, 75 and 100 µl, if different concentrations to see their inhibitory effects against microbial pathogens. Sterile paper discs (6 mm in diameter) prepared from Whatman No. 1 filter paper was impregnated with drug, containing solution placed on the inoculated agar. The inoculated plates were incubated at 37°C for 24 h [13]. The antibacterial activity was evaluated by measuring the diameter of the inhibition zone for the test microorganisms. The pure cultures of *Klebseila pneumonia, Pseudomonas aeruginosa, Escherichia coli, Streptococcus pyogenes, Salmonella typhi* and *Bacillus subtilis* were sub-cultured in nutrient agar.

3. Results and Discussion

The edible portion of the fruits is taken for the finding. The wild Edible fruits of plants can provide healthy alternatives to highly processed foods and pharmaceuticals, bringing greater health into our lives. Apart from their traditional use of food, potentially they have many advantages like antimicrobial properties [14]. They are edible and having fortified nutritional food value, which provides the proteins, lipid and carbohydrates. These are richest source of secondary metabolites with highest antimicrobial properties. They are immune to many diseases and often used in different formulation of 'Ayurveda' in Indian Folk medicine and traditional medicines. Documentation of wild edible fruits plays significant role to enhance the natural food resources which had been used with the help of religious knowledge [15]. Wild edible fruits today needs to be recommended for cultivation due to the reason which, they can serve as food material for ever increasing population [16]. The wild edible fruit are not only food but also contributes the beneficial natural nutrition source as food, diet, nutrition and nutrients to ever increasing population and in food scarcity. The wild edible fruits play an important role in sustainable livelihood of tribal communities residing in forest areas. Increased use of these wild edible fruits may raise as promising solutions on problems of malnutrition [17]. In order to medicate, a wider and sustained acceptance of wild fruits as important dietary components must be encouraged.

3.1 Nutritional analysis

Table 1: Nutritional analysis of *Catunaregam spinosa* fruits

S. No	Proximate analysis	Percentage
1.	Crude Fiber	12.6±0.2
2.	Ash content	11.3±0.2
3.	Moisture content	25±1.15
4.	Lipid	0.18±0.01
5.	Carbohydrate	60.28±4.6
6.	Protein	12.5±0.9
7.	Energy value	292±0.7

The proximate analysis was done in order to find out the nutritional value of *Catunaregam spinosa* fruits. The analyses were performed in triplicate and the values are expressed as mean percentage ± SD. The percentage proximate content of the fruit Catunaregam *spinosa* is shown in Tables-1**.** Proximate analysis is used to estimate the relative amounts of crude fiber, ash content, moisture content, carbohydrates protein, energy value in the fruits of *C. spinosa*. The proximate compositions are: crude fiber (12.6±0.2), ash content (11.3±0.2), moisture content (25±1.15), carbohydrates (60.28±4.6), Protein (12.5±0.9), Lipid (0.18±0.01) Energy value (292±0.7 kcal/100g). There is evidence that dietary fiber has a number of beneficial effects related to its indigestibility in the small intestine [18]. Carbohydrates are one of the most important components in many fruits. The results obtained showed that *C. spinosa* has high Energy value and carbohydrates contents while crude fiber, ash content, moisture content, lipid and protein content were low.

3.2 Phytochemical Screening

The preliminary screening showed in Table-2. The increasing interest in the phytochemical compound which could be relevant to their nutritional incidence and their role in health and diseases. Phytochemical analyzed on the *Catunaregam spinosa* fruits extracts shows the presence of bioactive compound which are known to reveal medicinal properties as well as physiological activities [12]. Screening of the fruits extracts is to find out the presence of phytochemicals such as phenols, tannins, flavonoids, saponins, cardiac glycosides, steroids, terpenoids, phlobatannins and alkaloids. Ten

phytochemical tested to show the presence and absence of these active compounds in the fruits extracts**.** Ethanol extracts have the presence of secondary metabolites such as phenol, tannins, flavonoids, alkaloids, saponins, phlobatannins, steroids, terpenoids and cardiac glycosides.

Table 2: Phytochemical Screening of Fruit extract of *Catunaregam spinosa*

S. No	Secondary metabolites	Aqueous	Ethanol	Chloroform
1.	Alkaloid	-	+	-
2.	Flavonoids	+	+	+
3.	Saponin	+	+	+
4.	Phenol	+	+	+
5.	Tannins	+	+	+
6.	Anthraquinones	-	-	-
7.	Cardiac Glycosides	-	+	-
8.	Phlobatannins	+	+	+
9.	Terpenoids	+	+	+
10.	Steroid	-	+	-

3.3 Antibacterial activity

The antibacterial screening of the *Catunaregam spinosa* fruit extracts were performed against *Klebseila pneumonia, Pseudomonas aeruginosa, Escherichia coli, Streptococcus pyogenes, Salmonella typhi* and *Bacillus subtilis* by the disc diffusion method. The activities of the compounds were compared with standard Chloramphenicol for antibacterial activity. The results of the antibacterial activity of the aqueous, chloroform and ethanolic extracts of *Catunaregam spinosa* against the test organisms are shown in Tables 3. In the case of the ethanol extracts at 100 µg concentration showed more potent antibacterial activity than other extracts tested. Maximum zone of inhibition was observed against the *Bacillus subtilis* of 28.0 mm, followed by *Klebseila pneumonia* of 24.0 mm, and the least was recorded in *Streptococcus pyogenes*. From the chloroform extracts, *Bacillus subtilis* showed maximum antibacterial activity of 26.0 mm zone of inhibition followed by *Pseudomonas aeruginosa* of 16.0 mm and the least was recorded in *Escherichia coli, Klebseila pneumonia* and *Streptococcus pyogenes*. In aqueous extracts, *Klebseila pneumonia* showed highest antibacterial activity of 18.0 mm zone of inhibition, followed by *Bacillus subtilis* of 14.0 mm zone of inhibition, and the least was recorded in *Escherichia coli*, *Pseudomonas aeruginosa* and *Streptococcus pyogenes*. However reported in the present study compaces with the findings of the reported in medicinal plants like [19, 20]. Hence, this fruits of *Catunaregam spinosa* show the high nutritional value, phyto screening analysis of the better remedies against the pathogenic bacteria.

Table 3: Antibacterial activity of the *Catunaregam spinosa* fruit extracts

S. No.	Microorganisms	Std*	Zone of Inhibition (mm)											
			Aqueous				Chloroform				Ethanol			
			25	50	75	100	25	50	75	100	25	50	75	100
	Bacillus subtilis	30	8	10	12	14	18	20	22	26	14	18	24	28
	Escherichia coli	30	2	0	2	6	0	2	2	4	8	10	16	18
	Klebseila pneumonia	30	0	12	12	18	0	0	0	2	14	18	22	24
	Pseudomonas aeruginosa	28	4	0	2	4	6	10	12	16	14	16	20	21
	Salmonella typhi	28	0	0	2	0	2	2	2	0	10	14	16	18
	Streptococcus pyogenes	30	2	0	0	2	2	4	6	2	2	4	6	6

Std* Chloramphenicol

4. Conclusion

The nutritional, Phytochemical and antibacterial activity of *Catunaregam spinosa* fruits extract was studied. From these findings, the scientific evidence is to support traditional medicinal plant for its nutritive value and indicate a promising potential for the development of an antimicrobial drugs. The phytochemical analysis of these plants also helpful for elucidation of bioactive molecules which inhibit the pathogen activity. Hence these *in-vitro* studies concluded that the *Catunaregam spinosa* fruits shows the promising effective to develop the novel antimicrobial drugs.

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A Study on the Investment Analysis of Equity Shares with Special Reference (BSE) Stock Index

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ct: The investors and stake holders of the equity stock are analyses the share price and earnings per share value in the ears. Estimating the required return on investment to be made in the stock market is a challenging job before an ry investor. Different market models and techniques are being used for taking suitable investment decisions. The past ior of the price of a security and the share price index play a very important role in security analysis. The present study ttempt to know risk and return analysis for measuring share price growth in the past three years. As the main object of idy is to test the relation between risk and return on equity shares in India, the period covered is from 31st December o 29 December 2017and the sample shares were randomly selected from amongst 10 equity shares included in the BSE dex. It is recommended that a proper estimation and analysis of standard deviation can be reliably taken recourse to in nanding the risk involved and the return generated from equity shares.

rds: risk and return, optimum portfolio, rate of return and so on.

I. Introduction

e potential for financial portfolio to minimize risk through diversification is central to the study of finance. The main ve of investment management to know market risk and create good investment plan or investment portfolio for decides gain from the investment. The investment of any types of assets must have risk of uncertainty. Without risk there no return Risk is defined as the chance that an investment's actual return will be different than expected. This includes the lity of losing some or all of the original investment.

vestors always think about the future return for their investment. When investing in stocks, bonds or any other ent instrument, there is a lot more risk investors think. Stock investing requires careful analysis of financial data to find company's true worth Stock market research is important to good investment decision making. It leads to determine the price and trading volume for the stock, high and low price for the stock over different periods and the earnings for the ny To determine the right choice of a security or portfolio to an investor, it depends on the level of risk that the stock. An estimation of the risk return profile of a security or portfolio is an important aspect in investment management. The arket research will allow one to assess the possible risk of a stock against the possible rewards of the stock.

e Indian stock market has increased a new life in the post-liberalization era. It has experienced a structural modificatinn e setting up of SEBI, opening up to the foreign investors, establishment of the BSE, commencement of the screen based system, dematerialization of equity securities and introduction of derivative instruments. The functions of the share have increased in all respects. Market capitalization has improved spectacularly. Number of listed companies has gone

up But the most important and wonderful phenomena of all are the movement of secondary market share prices which are reflected in either the upward or downward trend in the major share price indices in the country.

The stock market impacted the performance of an economy. When the economy does well and the companies make beneficial profit, people get induced to invest in stocks because they expect higher return from their stockholding. In the present globalised business scenario, risk is attached with every dimension. Financial markets are not free from imperfections, which make results inconsistent with the expectations. The concept of risk management in case of investment decision assumes greater importance in the modern day financial management.

The objective of financial investing is to earn the largest possible profit or return on investment.

Investing always involves a certain amount of risk, ie, there is a chance that an investment will yield not only profit but also loss. Thus investing aims at profit maximization and risk minimization.

II. Review of Literature

Suchaya Siamwalla (2016)[1] examines the factors that will affect the probability that a fund will deliver an outstanding low-risk, high-return performance using unbalanced panel logistic regression on a binary dependent variable. The results showed that funds with high non-systematic risk, also called idiosyncratic risk, and/or older funds, were more likely to deliver a low-risk, high-return performance, and the funds that were managed by the company that managed a high number of funds were less likely to deliver such performance. This study proposes a new performance evaluation tool called the "risk-return matrix." This matrix suggested the funds with outstanding low-risk, high-return past performance. This study applied the results to three new investment strategies. All simulations demonstrated returns better than the industry's average returns.

Thirugnanasoundari ed. al (2016)[2] explaining the parity between risk and return in the Indian equity market. It will definitely help the stakeholders to take appropriate decision regarding the time of investment, horizon of investment, quantum of investment and even portfolio selection. The analysis of testing the relationship between risk and return in the Indian stock market reveals that of all the different risk variables considered in the study, the distributional risk variables, variance, skewness and kurtosis of the return distribution, confirm the working of risk-return trade-off in the Indian context. Also, a positive association was exhibited between the security market return correlation and the average rate of return during the period of study. It also exposes the relation between systematic risk and rate of return on equities in India. The presence of randomness of the return series of both monthly market and monthly security returns in India has proved that the Indian stock market is weakly efficient.

Shaini Naveen & T. Mallikarjunappa (2016)[3] analyzes the risk and return in banking sector taking Nifty Bank Index as the benchmark. The study compares the performance of the 12 listed banks in the NSE. Indian banking industry, the backbone of the country's economy has always played a positive key role in prevention the economic disaster from reaching horrible volume in the country. Risk is a concept that denotes a potential negative impact to an asset or some characteristic of value that may arise from some present process or future event. It has achieved enormous appreciation for its strength, particularly in the wake of some of the worldwide economic disasters. Banking sector funds have proved to be more volatile than the pure diversified equity funds which make some of them a high risk proposition. The study evaluates the performance of banking stocks mainly to identify the required rate of return and risk of a particular stock based upon different risk elements prevailing in the market and other economic factors.

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Dr. S Poornima and Swathing (2017)[1] analyzing in selected stocks from sectors such as automobile sector and IT sector. five stocks in each sector have been taken for the sample. Automobile industry is considered to be one of the fastest growing sectors in any developing and even in a developed country. As global economies are getting integrated, technology companies are finding it an over task to align to the changing realities. In such a scenario, analyzing stocks from the technology sector requires utmost caution and understanding. By analyzing the stocks from two different sectors, investors will find beneficial in which sectors to invest. The risk and return analysis linked with any industry reveals the intricacies involved with the particular industry. A study revealed that automobile sector showing positive return and low risk and IT sector showing negative return and high risk during the study period.

III. Statement of the Problem

One of the most important financial decisions for business is investment with the aim of making gains in the future. Investment decisions are concerned with the use of funds including buying, holding or selling of assets and stock decision could be vital to a firm. A careless decision may result in a long-term loss or even worse, bankruptcy. Therefore, an in-depth understanding and analysis is necessary for a high quality investment decision process. This is also even more critical to investors who invest in stock of company or shareholders. The aim of investors' is getting investment opportunities with minimum risk and maximum returns.

Risk and returns are important variables that determine the future financial benefit. Risk and return is based on market risk and also investors' decision for investment. Naturally rational investors would expect a high return but they did not mind for high risk. The investors and stake holders of the equity stock are analyses the share price and earnings per share value in the past years. Estimating the required return on investment to be made in the stock market is a challenging job before an ordinary investor. Different market models and techniques are being used for taking suitable investment decisions. The past behavior of the price of a security and the share price index play a very important role in security analysis. The present study is an attempt to know risk and return analysis for measuring share price growth in the past three years.

IV. Objectives

The following objectives are framed for the present study

1. To ascertain the return from the equity shares for the selected study period
2. To know the risk through standard deviation of selected company share prices
3. To offer suitable suggestions to make optimum portfolio for investors

V. Methodology

As the main object of the study is to test the relation between risk and return on equity shares in India, the period covered is from 31st December 2015 to 29 December 2017and the sample shares were randomly selected from amongst 10 equity shares included in the BSE 500 index. The variables under consideration for the risk-return study are limited to only the distributional and financial risk variables. The distributional risk variables under observation are the variance of the return.

[1] Dr. S Poornima and Swathiga (2017) "A study on relationship between risk and return analysis of selected stocks on NSE using capital asset pricing model" International Journal of Applied Research 2017; 3(7): 375-378.

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VI. Analyses and Interpretations

S. No	Companies	31-12-2015 Rs.	30-12-2016 Rs.	29-12-2017 Rs	Return In Rupees	Returns In Percentage
1.	MRF	39847.60	48781.15	72348.15	32500.6	81.56
2	Polson	6066.00	6955.00	16034.65	9968.65	164.34
3.	Rasoi	16915.00	24116.00	38428.00	21513	127.18
4.	Eicher Motors	16855.20	21812.10	30290.55	13435.4	79.71
5	Vardhman Hold	959.25	1845.00	5059.20	4099.95	427.41

The above table shows that the calculation of return from the investment for the selected companies. It is found that MRF Company gives maximum return in Rs. 32500.6 and in percentage wise it gives 81.56% of return. The second most high return is getting from the Rasoi company Rs. 21513 and percentage wise 127.18%.

S. No	Companies.	31-12-2015 Rs.	30-12-2016 Rs.	29-12-2017 Rs.	Standard Deviation	Skewness
1	MRF	39847.60	48781.15	72348.15	16790.36	1.196974
2	Polson	6066.00	6955.00	16034.65	5516.71	1.681587
3	Rasoi	16915.00	24116.00	38428.00	10950.62	0.928416
4	Eicher Motors	16855.20	21812.10	30290.55	6794.16	0.754272
5	Vardhman Hold	959.25	1845.00	5059.20	2157.36	1.409411

The above table shows that the calculation of risk through standard deviation. It is found that maximum risks were found in the highly gaining company MRF. It is also give maximum return and maximum risk. The second highest risks are found from the Rasoi company.

S. No	companies	31-12-2015 Rs.	30-12-2016 Rs.	29-12-2017 Rs.	Return In Rupees	Returns in Percentage
1.	Bosch	18671.85	20999.40	20103.05	1431.2	7.67
2.	Shree Cements	11472.60	14724.70	18038.70	6566.1	57.23
3.	Claris Life	212.50	320.05	356.30	143.8	67.67
4.	Tide Water Oil	6980.75	5567.25	7036.60	55.85	0.80
5.	Page Industries	13342.30	13722.55	25462.75	12120.5	90.84

The above table shows that the calculation of return from the investment for the selected companies. It is found that Page Industries Company gives maximum return in Rs. 12120. 5 and in percentage wise it gives 90.84% of return. The second highest return is getting from the shree cements Rs. 6566.1 and percentage wise 57.23%.

S No	companies	31-12-2015 Rs.	30-12-2016 Rs.	29-12-2017 Rs.	Standard Deviation	skewness
1.	Bosch	18671.85	20999.40	20103.05	1173.97	-0.66762
2.	Shree Cements	11472.60	14724.70	18038.70	3283.10	0.02828
3.	Claris Life	212.50	320.05	356.30	74.79	-1.28562
4	Tide Water Oil	6980.75	5567.25	7036.60	832.68	-1.72329
5	Page Industries	13342.30	13722.55	25462.75	6890.60	1.726119

The above table shows that the calculation of risk through standard deviation. It is found that maximum risks were found in the highly gaining company Page Industries. It is also give maximum return and maximum risk. The second highest risks are found from the shree cements company.

VII. Suggestions

- From the analysis the researcher suggest that investors must take decisions before investing share. MRF and Polson companies are having good return and high growth rate. So that they invest both companies.

- The regular income-seeker-investors can use the return values in fixing and formulating portfolios.
- It is recommended that a proper estimation and analysis of standard deviation can be reliably taken recourse to in understanding the risk involved and the return generated from equity shares
- The risk-return analysis can be used as a stable platform by the investors in establishing the tradeoff between portfolio risk and return.

VIII. Conclusion

The present study can be used to analyze the relationships between different elements of a firm in order to provide an overview as well as an in-depth view of company's equity stock condition. Moreover, by looking at the calculated financial information, in the connection with economic data, investor can make judgments about past and future financial performance and conditions. Besides, earnings analysis and risk and return analysis may provide even more detailed information about the firm, and also help investor to perceive potential risk. Therefore, it is safe to assume that financial analysis play an irreplaceable role in making investment decisions.

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Synthesis of Annulated Thiophenes Involving Benzo-DMTHFs/Triflic acid-Mediated Domino Reactions

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A facile protocol for synthesis of naphth-annulated thiophenes has been developed via benzo-DMTHFs/triflic acid-mediated annulation of thiophenes. Furthermore, this methodology was found to be successful with substituted benzo-DMTHFs as well as higher homologues of benzo-DMTHF.

Introduction

Owing to their privileged status and enormous importance, the π-conjugated organic heterocycles received prominent attention as advanced materials with unique electronic and photonic properties including organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), solar cells, semiconductor and other electro-optical devices.[1,2] In particular, polycyclic sulfur heterocycles constitute an important class of fused heterocycles. They have been explored in medicinal applications, for example thiophene and benzo[*b*]thiophene ring system and its derivatives are the core of numerous medicinal molecules such as clinically used plavix,[3a] clopidogrel,[3] raloxifene,[4] arzoxifene,[5] zileuton,[6] sertaconazole nitrate,[7a] and SB-271046.[7b] In particular, the thiophene-based π-conjugated materials possessing interesting electronic and optical properties have been investigated as advanced molecular electronic materials.[8]

Among the polycyclic aromatic hydrocarbons (PAHs), linearly annulated acenes such as tetracene, pentacene, hexacene and related derivatives are attractive molecules with respect to structure and electronics but also exciting in their applications for organic electronics including remarkable charge-carrier mobilities.[9] Eventhough, the carrier mobility of such acene-based OFETs is traditionally enhanced by increasing the number of fused aromatic rings, these higher acenes suffer from insolubility and high reactivity making their processing difficult. Stabilizing these acenes through bulky substituents that kinetically protect them from possible reactions, which makes their devices more stable under ambient conditions, enhancing the practical use of the larger polyacenes-based OFETs.[10] In order to avoid such instability, thiophenes are incorporated into simple hydrocarbon-based large acenes affording thienoacenes to produce good stability and also enables high carrier mobility simultaneously.[11] In the past few decades, benz-annulation is one of the powerful method to construct substituted benzene ring and various benz-annulation reactions have been developed for linearly substituted benzene and fused-benzene compounds.[12–14] Development of elegant strategies using annulation has allowed the synthesis of PAH-arenes and heteroarenes. Recently, Hashmi and co-workers have reported the gold-catalyzed benz-annulation of 2-substituted thiophenes.[13a] A new strategy for the construction of benzo[*b*]thiophenes involving domino annulation was achieved by Wang and co-workers.[13b]

Indeed, several strategies have been explored for the syntheses of naphth-annulated arenes and heteroarenes (Figure 1) through acid-catalyzed annulation of diacetates,[15] and

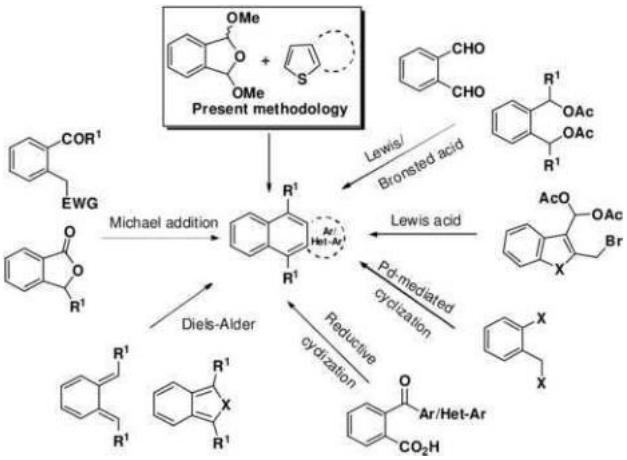

Figure 1. Synthesis of naphth-annulated arenes and heteroarenes.

tetraacetate,[16] $ZnBr_2/SiO_2$ catalyzed annulation of electron-rich arenes with acetyl bromide-phthalaldehydes,[17a] Lewis acid-induced cyclization of aldehydes,[17b] A Lewis acid-mediated annulation of 2/3-(bromomethyl)indoles with arenes/heteroarenes,[18] palladium-catalyzed annulation of an in situ generated aryne annulation by *o*-halostyrene,[19] HI/P-mediated reductive

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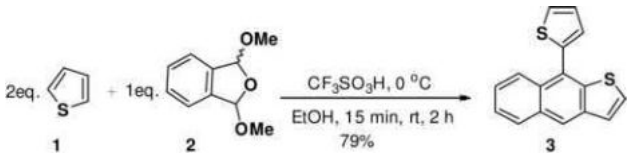
cyclization or successive reductions followed by oxidation and Bradsher cyclization of 2-aroylbenzoic acid,[20] Diels-Alder reactions of 1,3-disubstituted benzo[*c*]furans as well as 5,6-bis (bromomethylene)cyclohexa-1,3-diene,[21] and base mediated annulation of 3-phenylsulfonyl-substituted isobenzofuranone with Michael acceptors.[22] However, many of these protocols suffer from limitations such as harsh reaction conditions and low chemical yields coupled with restricted substrate scope. Hence, considering the prominent application potential of annulated heterocycles, the development of a straightforward approach for the same will be highly useful.

The dimethoxytetrahydrofuran (DMTHF) found extensive use as a four carbon synthon for the syntheses of nitrogen containing heterocycles.[23] We have recently reported[24] a new and efficient synthetic approach to the annulation of thiophenes and electron-rich arenes using DMTHF. In further continuation of this work, we report herein the full details on the domino-type naphth-annulation of thiophenes using benzo-DMTHFs and its derivatives.

Results and Discussion

Initially, the naphth-annulation of thiophene **1** (1 eq.) with 1,3-dimethoxy-1,3-dihydroisobenzofuran (benzo-DMTHF) **2**[25] (1 eq.) in the presence of triflic acid and ethanol at room temperature for 2 h followed by workup and column chromatographic purification failed to produce naphtho[*b*]thiophene, instead 9–2′-thiophenyl naphtho[*b*]thiophene **3** was isolated in 32% yield. After, considerable experimentations, annulation of 2 eq. of thiophene **1** with 1 eq. of benzo-DMTHF **2** furnished the product **3** in 79% yield (Scheme 1). The formation of



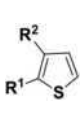
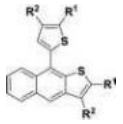
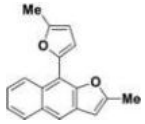
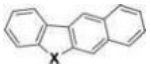
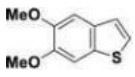
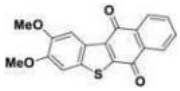
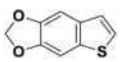
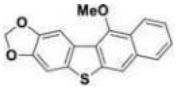
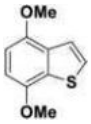
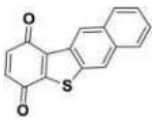
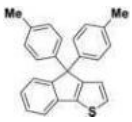
Scheme 1. Naphth-annulation of thiophene **1.**

heterocycle **3** can be visualized through bis-2-thiophenylation at geminal position followed by cyclization and aromatization.

Under identical condtions, the heterocycles **4a–d**, **6a–e** and **8a** upon reaction with benzo-DMTHF **2** and triflic acid in the presence of ethanol in dry DCM at room temperature followed by workup and column chromatographic purification furnished respective naphth-annulated heterocycles. The structures of annulated heterocycles obtained along with their yields are presented in Table 1.

The domino reaction of 2,3-disubstituted thiophenes **4a–c** with benzo-DMTHF **2** and triflic acid at room temperature afforded 9–2′-thiophenyl naphtho[*b*]thiophenes **5a–c** in 69–84% yields (Table 1, entry 1). To our delight, the structures of the naphtho[*b*]thiophenes **5a–c** could be easily assigned based on our earlier work.[16] A similar type of naphth-annulation could also be performed with 2-methylfuran **4d** to furnish naphthofuran **5d** (Table 1, entry 2). However, the naphth-annulation of benzo[*b*]heterocycle **6a**/**6b** (2 eq.) with 1 eq. of benzo-DMTHF **2** furnished only the respective benzo[*d*] naphtho[2,3-*b*]heterocyle **7a**/**7b** (Table 1, entry 3). The naphth-annulation of electron rich 5,6-dimethoxy benzo[*b*]thiophene **6c** with benzo-DMTHF **2** followed by usual workup led to the isolation of quinone **7c** as an exclusive product in 82% yield (Table 1, entry 4). The similiar naphth-annulation of 5,6-methylenedioxybenzo[*b*]thiophene **6d** gave heterocycle **7d** in 86% yield (Table 1, entry 5). Under identical conditions, the naphth-annulation of 4,7-dimethoxybenzo[*b*]thiophene **6e** followed by workup furnished respective quinone **7e** as a yellow solid in 77% yield (Table 1, entry 6). Finally, the indeno[1,2-*b*]thiophene **8a**[26] upon reaction with benzo-DMTHF **2** led to the formation

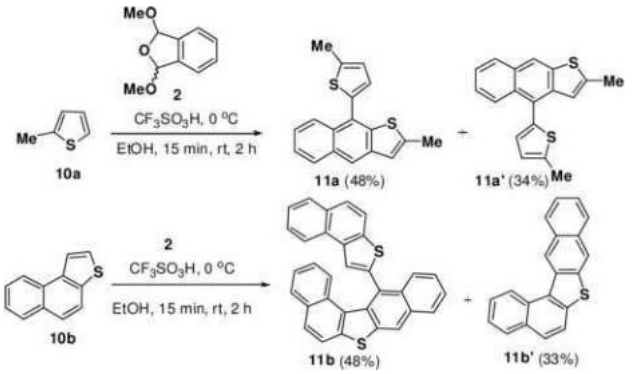
Table 1. Naphth-annulation of heteroarenes using benzo-DMTHF **2**

Entry	Heterocycle	Product	Condition	Yield[c]
1				
	4a R^1 = Br, R^2 = Me	**5a** R^1 = Br; R^2 = Me	2 h[a]	84
	4b R^1 = H, R^2 = Me	**5b** R^1 = H, R^2 = Me	2 h[a]	79
	4c R^1 = Br, R^2 = H	**5c** R^1 = Br, R^2 = H	2 h[a]	69
2				
	4d	**5d**	3 h[a]	79
3				
	6a X = S	**7a** X = S	2 h[b]	84
	6b X = O	**7a** X = O	2 h[b]	78
4				
	6c	**7c**	2 h[b]	82
5				
	6d	**7d**	2 h[b]	86
6				
	6e	**7e**	2 h[b]	77
7				
	8a	**9a**	6 h[a]	83

Reaction conditions: [a] Substrate (1 mmol), benzo-DMTHF **2** (0.5 mmol) and CF_3SO_3H (0.5 mmol) in dry DCM. [b] Substrate (0.5 mmol), benzo-DMTHF **2** (0.5 mmol), CF_3SO_3H (0.5 mmol) and ethanol (5 drops) in dry DCM. [c] Isolated yield after column chromatography.

of 9–2′-indeno[1,2-*b*]thiophenyl naphtho[*b*]thiophene **9a** in 83% yield (Table 1, entry 7).

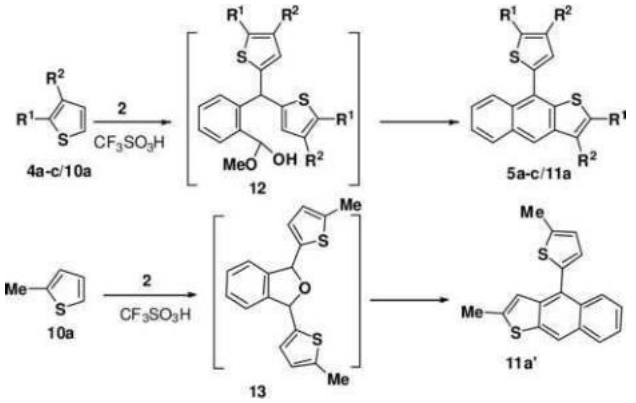
Under identical conditions, naphth-annulation of 2-methyl thiophene **10a** afforded isomeric naphtho[*b*]thiophenes **11a** and **11a′.**[16] Next, the domino reaction of naphtho[2,3-*b*] thiophene **10b**[27] with benzo-DMTHF **2** led to the isolation of annulated thiophenes **11b** and **11b′** (Scheme 2). The structures



Scheme 2. Synthesis of isomeric naphtho[*b*]thiophenes.

of these heterocycles **11b** and **11b′** are assigned based on the literature reports.[28]

The formation of isomeric naptho[*b*]thiophenes **5a–c/11a** and **11a′** can be visualized through the intramolecular cyclization of 1,1-di-(2′-thienyl)compound **12** as well as 1,2-di-(2′-thienyl)isobenzofuran intermediates **13** (Scheme 3). Obvi-

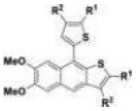
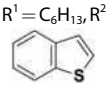
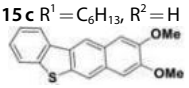
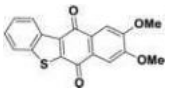
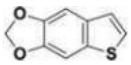
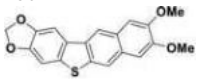
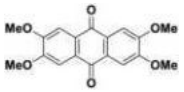


Scheme 3. Mechanistic hypothesis for isomeric naphtho[*b*]thiophenes.

ously, the presence of electron releasing groups at 2/3-positions of thiophene **4a–c/10a** facilitated gem-di-2-thienylation to give 1,1-di-(2-thienyl) compound **5a–c/11a.** Similarly, the formation of **11b/11b′** can be visualized through 1,1-di-(naphtho[2,3-*b*]thiophenyl)isobenzofuran and 1-(2-naphtho[2,3-*b*] thiophenyl)isobenzofuran intermediates, respectively.

Towards generalization of this protocol, triflic acid-mediated naphth-annulation could be successfully performed with 5,6-dimethoxybenzo-DMTHF **14**[29] to afford corresponding heterocycles (Table 2). The naphth-annulation of thiophenes **4a/10a/**

Table 2. Naphth-annulation using 5,6-dimethoxybenzo-DMTHF **14**

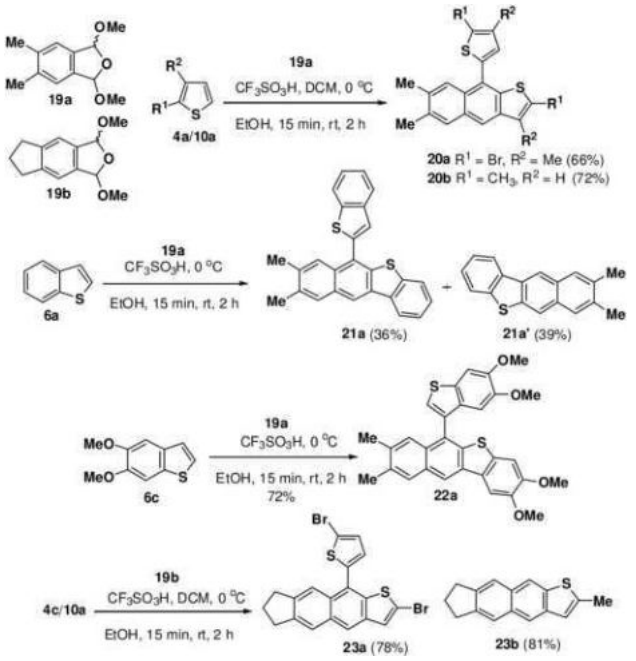
Entry	Heterocycle	Product	Condition	Yield[c]
1				
	4a R^1 = Br, R^2 = Me	**15a** R^1 = Br, R^2 = Me	3 h[a]	86
	10a R^1 = Me, R^2 = H	**15b** R^1 = Me, R^2 = H	2 h[a]	76
	10c $R^1 = C_6H_{13}$, R^2 = H	**15c** $R^1 = C_6H_{13}$, R^2 = H	2 h[a]	72
2				
	6a	**16a**	2 h[b]	42
				
		16a′		36
3				
	6d	**16b**	2 h[b]	81
4				
	17a	**18a**	3 h[b]	77

Reaction conditions: [a] Substrate (1 mmol), 5,6-dimethoxybenzo DMTHF **14** (0.5 mmol) and CF_3SO_3H (0.5 mmol) in dry DCM. [b] Substrate (0.5 mmol), benzo-DMTHF **14** (0.5 mmol), CF_3SO_3H (0.5 mmol) and ethanol (5 drops) in dry DCM. [c] Isolated yield after column chromatography.

10c with 5,6-dimethoxybenzo-DMTHF **14** in the presence of triflic acid furnished naphtho[*b*]thiophenes **15a–c** in 72–86% yields (Table 2, entry 1). The benzo[*b*]thiophene **6a** upon reaction with **14** furnished respective benzo[*d*]naphtho[2,3-*b*] thiophene **16a** as well as quinone **16a′** (Table 2, entry 2). The similar naphth-annulation of 5,6-methylenedioxybenzo[*b*] thiophene **6d** led to the isolation naphth-annulated compound **16b** as an exclusive product (Table 2, entry 3). The veratrole **17a** also underwent naphth-annulation with 5,6-dimethoxy-benzo-DMTHF **14** to afford respective quinone **18a** as a yellow solid (Table 2, entry 4).

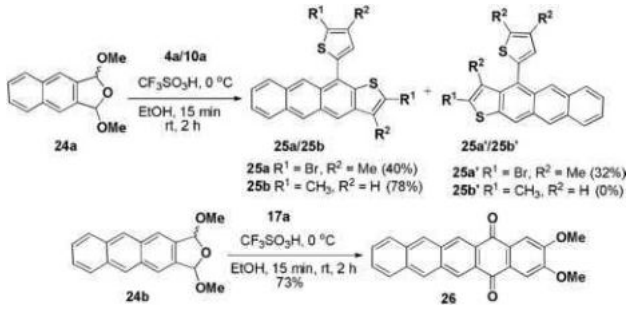
Next, *o*-xylene as well as indane fused DMTHF **19a** and **19b** were prepared from the respective aldehydes.[30] The annulation of substituted thiophene **4a/10a** with *o*-xylenyl-DMTHF **19a** using triflic acid led to the formation of respective naphth-annulated products **20a** and **20b.** Using similar condtions, the naphth-annulation of benzo[*b*]thiophene **6a** with *o*-xylenyl-DMTHF **19a** afforded annulated products **21a** and **21a′** in 36 and 39% yields, respectively. The structures of these heterocycles **21a** and **21a′** are established based on their ^{1}H NMR spectral data. To our delight, the naphth-annulation of electron rich 5,6-dimethoxybenzo[*b*]thiophene **6c** furnished annulated heterocycle **22a** as an exclusive product. The annulation of 2-

bromothiophene **4c**/2-methylthiophene **10a** with indanyl-DMTHF**19b** furnished annulated products **23a** and **23b** in 78 and 81% yields, respectively (Scheme 4).



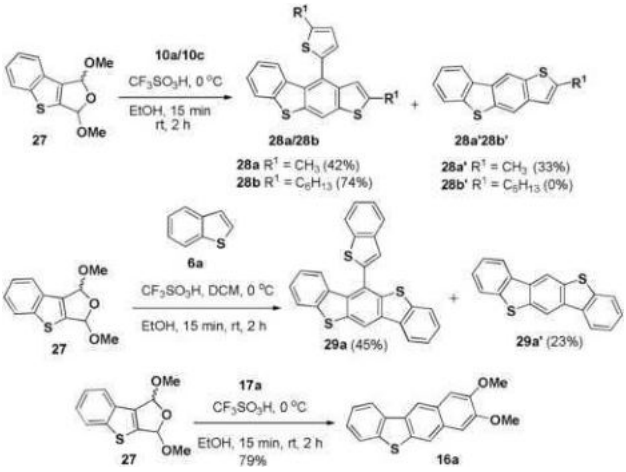
Scheme 4. Annulation using *o*-xylenyl/indanyl-DMTHF **19a**/**19b**.

To our delight, triflic acid-mediated annulation could be performed with higher homologues of benzo-DMTHFs namely naphtho-DMTHF **24a** and anthro-DMTHF **24b.**[31] As a representative case, the anthra-annulation of substituted thiophene **4a/10a** with naphtho-DMTHF **24a** led to the isolation of anthra[*b*]thiophenes **25a/25b** and **25a′.** Based on our rearlier reports,[16] the structures of these isomeric anthra[*b*]thiophenes could be easily assigned. Due to the solubility issues, domino reaction of anthro-DMTHF **24b** could be performed only with the veratrole **17a** to give quinone **26** as a yellow solid (Scheme 5).



Scheme 5. Annulation using naphtho/anthro-DMTHF **24a**/**24b**.

Finally, the annulation of 2-methylthiophene **10a** with benzo[*b*]thio-DMTHF **27**[32] in the presence of triflic acid and ethanol at room temperature for 2 h followed by workup and column chromatographic purification led to the isolation of heterocycles **28a** and **28a′.** Under identical conditions, the annulation of 2-hexylthiophene **10c** with **27** furnished annulated heterocycle **28b** as an exclusive product. The similiar reaction of benzo[*b*]thiophene **6a** with benzo[*b*]thio-DMTHF **27** led to the isolation of annulated heterocycles **29a** and **29a′** in 45 and 23% yields, respectively. Fortunately, the structures of the annulated heterocycles **29a** and **29a′** could be easily confirmed based on literature reports.[33] Finally, the annulation of veratrole **17a** with benzo[*b*]thio-DMTHF **27** afforded **16a** as an exclusive product in 79% yield (Scheme 6).



Scheme 6. Annulation using benzo[*b*]thio-DMTHF **27.**

Conclusions

In summary, we have accomplished a facile synthesis of naphth-annulated thiophene analogues involving triflic acid-mediated annulation of thiophenes with benzo-DMTHFs. The domino type annulation methodology was also found to be applicable with substituted benzo-DMTHFs as well as higher homologues of benzo-DMTHF. Our present study clearly demonstrated that triflic acid-mediated annulation can be used as an effective catalyst for annulation of a wide variety of thiophenes and other heterocycles. The attractive feature of this methodology is that a large number of π-conjugated thiophenes are easily accessible under mild conditions. The annulated thiophene derivatives reported herein may find application in OLEDs.[34]

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Annulation · naphtho[*b*]thiophenes · synthetic methods · thiophenes · triflic acid

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Kinetics and Mechanism of oxidation of Maltose By N-Bromonicotin amide (NBN)

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ABSTRACT

Kinetics study of oxidation of maltose, by aqueous alkaline solution of N-Bromonicotinamide (NBN) has been carried out in the temperature range 308-323K.The reaction exhibits first order in [KOH] and [Maltose] and zero order about oxidant. Addition of nicotinamide (NA) has no effect. Increase in ionic strength of the medium does not change the rate. Effect of temperature on the rate of oxidation has been followed to show the validity of Arrehenius equation and various activation parameters have been computed. The stoichiometry of the reaction was found to be 1:1. 1,2-enediol is found to be the reactive intermediate. Maltobionic acid is the product of oxidation.

Keywords: Maltose, N-Bromonicotinamide, oxidation, mechanism.

Introduction

Carbohydrates are biologically important substrates. The oxidation of sugars, especially the mono and disaccharides has been the subject of extensive research. Their oxidation can provide new compounds and materials with interesting physicochemical properties. Sugar oxidation occurs under different conditions of pH, temperature and ionic strength giving products that depend on the oxidants used. The kinetics and mechanism of oxidation of monosaccharides and disaccharides have been studied in both acidic and alkaline media, employing different transition metal ions, inorganic acids, complex ions and hydrogen peroxide as oxidants. The results showed that the mechanism may depend on the nature of the substrates, in some cases it involves the formation of

intermediate complex, free radical or transition states. Sheila Srivastava[1] followed the oxidation of dextrose and maltose by acidic solution of sodium periodate catalysed by rhodium(III).Ashok Kumar Singh[2] investigated the kinetics and mechanism of oxidation of xylose and maltose by potassium iodate in aqueous alkaline medium. Fahim Uddin[3] reported the kinetics of maltose and lactose by alkaline iodine solution. Ashok Kumar Singh[4] investigated the kinetics and mechanism of oxidation of maltose by aqueous alkaline solution of periodate.H. K. Okoro[5] and E. O. Odebunmi reported the kinetics and mechanism of oxidation of sugar and sugar alcohols by potassium permanganate. E.O. Odebunmi and S.O. Owalude[6] investigated the kinetics and mechanism of oxidation of some simple reducing sugars by permanganate ion in alkaline medium. Ashok Kumar Singh[7] followed mechanistic studies of oxidation of maltose and lactose by $[H_2OBr]^+$ in presence of chloro-complex of Rh(III) as homogeneous catalyst. E.O. Odebunmi[8] followed the kinetics of oxidation of fructose, sucrose and maltose by potassium permanganate in $NaHCO_3$/NaOH buffer and iridium(IV) complex in sodium acetate/acetic acid buffer. Kinetics and mechanism of the oxidation of disaccharides by Cr(VI) was reported by Viviana Roldán.[9] N-halo reagents like N-halo derivatives of amines, amides, imides, urea, saccharins, sulfonamides, sulfonimides are widely used in organic synthesis for their potential to promote important reactions such as halogenation, oxidation, and protection as well as formation of C-X, C-O, and C=O bonds. They play a key role in the chemistry of natural compounds[10].Scant reports are available for oxidation of sugars by haloamides. NBN is chosen for the reasons, its easy method of synthesis, handling, rate of oxidation, shelf life and versatility. Our earlier study on the oxidation of amino acids had focused attention on the kinetic aspects of oxidation by NBN[11] in aqueous acetic acid medium.In our continuing efforts to exploit NBN as oxidant, the present study investigates the kinetics of oxidation of maltose in aqueous alkaline medium.

Materials and methods

N-Bromonicotinamide (NBN) was prepared by the reported method[12]. Standard solution of NBN(m.p.210•C) was prepared afresh in water and its purity was checked iodometrically. The standard solution of maltose (Aldrich) was always prepared afresh in

double distilled water. The other chemicals used were potassium hydroxide, sodium perchlorate, mercuric acetate etc. All chemicals used were of A.R. grade. Mercuric acetate was added to suppress the formation of free bromine which otherwise would have vitiated the results. Mercuric acetate did not interfere with the results[13]. Ionic strength of the medium was kept at 0.1 mol dm^{-3} by employing concentrated aqueous solution of sodium perchlorate (Merck).

Kinetic measurements

The solution of maltose and oxidant were kept in black coated bottles separately. These solutions were kept in the thermostat to attain the thermostatic temperature. The appropriate quantity of oxidant was added to the substrate containing other reagents and the reaction bottle was shaken well. The reaction was followed potentiometrically by setting up a cell made up of the reaction mixture into which the platinum electrode and reference electrode(SCE) were dipped. The e.m.f of the cell was measured periodically using a Equip-Tronics (EQ-DGD) potentiometer. Different studies such as variation of maltose, oxidant (NBN), potassium hydroxide, sodium perchlorate, nicotinamide and temperature were carried out. The reaction was carried out under pseudo-first order condition ([maltose] >>[NBN]). The pseudo-first order rate constants computed from the linear ($r^2 > 0.9990$) plots of log (E_t–E_∞) against time. Duplicate kinetic runs showed that the rate constants were reproducible within ±3%. The course of the reaction was studied for more than two half-lives.

Stoichiometry

N-Bromonicotinamide was taken in large excess as compared to maltose in different ratios. Reaction mixture containing maltose, potassium hydroxide and N-bromonicotinamide (in excess) were equilibrated for 42 hours at room temperature(~ 30°C). After the reaction was complete, the excess of NBN was determined iodometrically and indicated 1:1 stoichiometry. The overall stoichiometry of the oxidation reaction may be represented as

$C_{12}H_{22}O_{11}$+NBN+H_2O ⟶ $C_{11}H_{21}O_{10}$(COOH) + Br^-+NA

Maltose Maltobionic acid

Product Analysis

In a typical experiment, a mixture of freshly prepared maltose (1 mol dm^{-3}) and NBN(1.5g, 0.2 mol dm^{-3}) was made up to 50 ml with water. The mixture was allowed to stand for 12hours in the dark to ensure completion of the reaction. The product of oxidation was maltbionic acid. Nicotinamide was the by-product. The product was identified by spot test analysis[14]. The product was also identified by the following method. A little of the product was added to 1ml of 5% sodium bicarbonate solution. Evolution of carbon dioxide with effervescence indicated the presence of acidic group in the compound. Evidence for the formation of an enediol is furnished by observed ability of alkaline solution of carbohydrates to decolorize solution of 2,6-dichlorophenolindophenol.

Results

The kinetic results for the oxidation of maltose by N-Bromonicotinamide (NBN) can be summarized as follows. The kinetic studies were carried out under pseudo-first order conditions with [maltose] >> [NBN].

Effect of varying [oxidant]

The constancy of pseudo-first order rate constant at different [NBN] at constant [maltose] indicates the reaction exhibits zero order about the oxidant (Table 1).

Table 1- Effect of variation of [NBN] on reaction rate

[substrate]=0.02 mol dm^{-3} [KOH]=0.06 mol dm^{-3},
[$NaClO_4$]=0.1mol dm^{-3}, $Hg(CH_3COO)_2$=0.005 mol dm^{-3}, Temp. =308 K

[NBN] 10^3 moldm^{-3}	**k_{obs} 10^7 sec^{-1}**
0.5	7.83
1.0	7.85
1.5	7.86
2.0	7.87
2.5	7.86

Effect of varying [maltose]

At constant [OH^-], [NBN], the plot of log(E_t– E∞) (where E_t is the e.m.f. of the cell at time t and E∞, the corresponding value at the completion of the reaction) Vs time is linear, indicating a first order dependence of rate on [maltose]. The rate constant increases in direct proportionality with the increase in the concentration of maltose, proving the reaction is of first order in [maltose]. (Table 2).

Table 2- Effect of variation of [Substrate] on reaction rate

[NBN]=0.001 mol dm^{-3} [NaOH]=0.06 mol dm^{-3},
[$NaClO_4$]=0.1mol dm^{-3}, $Hg(CH_3COO)_2$=0.005 mol dm^{-3}, Temp. =308K

[Sub] 10^2 moldm^{-3}	**k_{obs} 10^7 sec^{-1}**
2.0	7.86
2.5	8.32
3.0	8.68
3.5	9.04
4.0	9.41

Effect of varying [OH^-]

A scrutiny of table 3 shows that the rate increases proportionally with the increase in [KOH]. The plot of log k_{obs} versus log [OH^-] was linear with a unit slope indicating first order dependence on [potassium hydroxide] (Table 3).

Table 3- Effect of variation of [OH^-] on reaction rate

[NBN]=0.001 mol dm^{-3} [substrate]=0.02mol dm^{-3},
[$NaClO_4$]=0.1mol dm^{-3}, $Hg(CH_3COO)_2$=0.005 mol dm^{-3}, Temp. =308 K

[NaOH] 10^2 moldm^{-3}	**k_{obs} 10^7 sec^{-1}**
6	7.86
8	8.53
10	9.13
12	9.65
15	10.29

Effect of addition of nicotinamide

The effect of one of the product of the reaction has been studied by adding various concentrations of nicotinamide, keeping concentration of maltose, NBN constant. There is no significant change in the rate of reaction.

Effect of ionic strength

The effect of ionic strength was studied by carrying out investigations in the presence of different amounts of sodium perchlorate. No appreciable salt effect was detected.

Effect of added salts

Added salts like $BaCl_2$, KCl, Na_2SO_4 and K_2SO_4 do not have any effect on the rate.

Test for free radicals

The possibility of free radical intervention in the NBN oxidation reaction was tested by the following procedure. The reaction mixture containing acrylonitrile scavenger was kept for 24hours in an inert atmosphere and then diluted. On dilution, formation of precipitate was not observed indicating the absence of free radical intervention in the reaction.

Effect of temperature

Increase in temperature increases the rate of oxidation and plot of log k_{obs} Vs reciprocal of temperature is linear. The oxidation of maltose by NBN was studied at different temperatures (308to 323K) (Table 4) and the activation parameters were evaluated (Table 5) .

Table 4-Effect of Temperature on reaction rate

[substrate]=0.02 mol dm^{-3} [KOH]=0.06 mol dm^{-3},
[NBN]=0.001 mol dm^{-3} [$NaClO_4$]=0.1mol dm^{-3},
$Hg(CH_3COO)_2$=0.005 mol dm^{-3}

Temperature K	k_{obs} 10^7 sec^{-1}
308	7.84
313	10.30
318	13.24
323	16.95

Discussion

The possible oxidizing species in alkaline medium are NBNBr, Br_2 and HOBr. The observed zero order dependence of the reaction rate on NBN rules out NBNBr and molecular bromine as the reactive oxidizing species. Addition of nicotinamide having no effect on the rate indicates that HOBr may not be the oxidizing species. H_2OBr may be discarded because of negligible effect of addition of nicotinamide on reaction rate. A careful study of the kinetics of oxidation of maltose shows that the rate expression is of the form

Substrate	**E_a kJmol^{-1}**	**$\Delta H^{\#}$ kJmol^{-1}**	**$\Delta S^{\#}$ J K^{-1}mol^{-1}**	**$\Delta G^{\#}$kJmol^{-1}**
Maltose	20.96	18.40	– 174.4	72.12

$$-\frac{d[NBN]}{dT} = k\,[\text{maltose}]\,[OH^-]$$

which implies that the rate of reaction is independent of the concentration of [NBN], while the reaction is of first order both with respect to maltose as well as alkali. In cases where the concentration of maltose as well as alkali is large as compared to the concentration of [NBN], the rate expression becomes

$$\frac{d[NBN]}{dT} = k_s = \Delta\chi/\Delta t$$

where

$k_s = k[\text{maltose}][OH^-]$

Mechanism

On the basis of the above experimental results, it appears that the first slow step involves a reaction between hydroxide ion and maltose, leading to the formation of an intermediate reactive form:

$$S+HO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H\text{-}C(OH)=CR(OH)+H_2O \quad \text{(I step)}$$

1,2 Enediol (E)

(slow)

where S represents the sugar. The fact that this step is slow explains how the order of the reaction is unity with respect to reducing sugar. Further, this intermediate reactive form, which is called, 1,2 enediol, is subsequently oxidized by NBN to form nicotinamide and maltobionic acid.

$$\text{en (E)} + \text{NBN} \xrightarrow[\text{fast}]{k_2} \text{product+NA} \quad \text{(II step)}$$

{Product- maltobionic acid}

where " en " represents 1,2 enediol. The fact that the second step is fast explains the zero order of the reaction with respect to [NBN].

It may be pointed out that in the present study, oxidation by bromine was completely suppressed as the oxidative studies were carried out in presence of mercuric acetate which combines with bromide ions formed in the reaction[13]. Thus kinetics of only NBN oxidation was followed.The involvement of substrate molecule in the rate-determining step leads to different values of k_{obs} for different initial concentrations of maltose.

Conclusions

At the end of this research work, it is inferred that the reaction rates are enhanced by increase in [substrate], [alkali] and temperature. Added nicotinamide has no effect on the rate. 1,2-Enediol form of sugar is the reactive intermediate leading to products. Maltobionic acid is the product of oxidation. Suitable mechanism in compliance with experimental observations was proposed and the rate law was derived. NBN can be used as a better oxidant for the facile oxidation in the grounds of its easy method of synthesis, handling, rate of oxidation, shelf life and versatility.

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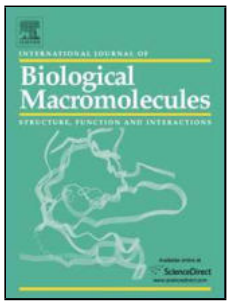

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Removal of Cd(II) and Hg(II) from effluents by ionic solid impregnated chitosan

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Abstract

Ethylhexadecyldimethyl ammonium bromide impregnated chitosan (EHDAIC) was prepared to remove cadmium and mercury from synthetic effluent. The adsorbent was characterized by FTIR, XRD, SEM, EDX and TGA-DTA. Adsorption studies were carried out under different conditions of pH, adsorbent dose, temperature, and contact time. The results showed that the adsorption capacity of EHDAIC is a function of the solution pH and the optimum pH for these metal ions was found to be 3.0. The equilibrium data has been described using Langmuir and Freundlich isotherm models. The maximum adsorption capacity of 341.3 mg/g was observed for Cd(II) and 43.43 mg/g for Hg(II) in accordance with Langmuir adsorption isotherm in the form of their chloro complexes. The kinetic data fitted well with pseudo-second-order model, and equilibrium data was found to follow Freundlich isotherm model. The calculated thermodynamic parameters showed that the adsorption process was feasible, exothermic and spontaneous. Effect of common excipient ions was studied. Also the material was tested for large sample volumes using column extraction process. The adsorbent material could be regenerated for repetitive applications.

Keywords: Ionic solid impregnated chitosan; cadmium; mercury

1. Introduction

Among the toxic metal pollutants in the atmosphere, cadmium and mercury are of prime concern. Common sources of cadmium and mercury pollution include refuse incineration, nonferrous metal production, iron and steel production, fossil fuel combustion, etc. Long-term exposure to cadmium and mercury can cause damage to the kidneys, liver, bone, and blood [1]. Symptoms of mercury poisoning are observed mainly in the form of neuronal disorders [2]. Therefore it is important to control the concentrations of these heavy metals in waste before it is discharged into the water bodies.

Techniques used for removal of cadmium and mercury include precipitation, ion-exchange, flocculation and adsorption [3]. Adsorption process makes use of various materials of natural origin, artificially prepared materials as well as the composites of the two. Activated carbon, rice husk, date pits, surfactant-modified zeolites etc, have been reported for the metal ion removal [4-7].

Biopolymers are attracting a lot of interest as adsorbents due to various properties like biodegradability, biocompatibility and non-toxicity. Among them, chitosan is a versatile and promising biomaterial which is a deacetylated chitin derivative. It has wide applications in medicinal and environmental fields [8-10]. Chitosan has the ability to form complexes with a large number of metal ions. However, the use of native chitosan in acidic medium is limited due to its solubility in acid leading to formation of gel. It becomes difficult to separate the material from the gel form [11]. Native chitosan has been reported for the removal of cadmium and mercury from water bodies [12,13]. In order to overcome the limitation of solubility in acidic medium and also to enhance the adsorption capacity, various modifications have been made. The reactive amino and hydroxyl groups in chitosan offer possibilities of structural modifications leading to formation of a large variety of beneficial derivatives. By dispersing chitosan on physical supports or by modifying it chemically via cross-linking, the difficulty of gel formation in acidic medium can be overcome. But, this leads to decrease in adsorption capacity. In order to enhance the adsorption capacity, impregnation with various organic or inorganic moieties can be carried out. We have reported the synergistic behavior of ionic liquid impregnated sulphate crosslinked chitosan for the removal of Cr(VI) [14].

Reported literature using impregnated chitosan is mostly based on the chelation of metal ions in the form of cations. However, the metal ions like Cd(II) and Hg(II) form very stable chloro complexes in the presence of high chloride concentrations. [15] They exist in anionic forms leading to strong interaction with protonated amine groups of chitosan. If the chitosan is impregnated with quaternary ammonium compounds including ionic solids or ionic liquids, there is further enhancement in the adsorption capacity towards chloro complexes. Such material can be used for multielemental removal.

Chitosan has also been modified for removal of various metal ions including cadmium and mercury by Kawamura et al [16]. The proposed modification is based on synthesis of porous polyaminated chitosan chelating resin by introducing poly(ethylene amine) cross-linked onto the chitosan beads. The resultant beads showed more adsorption capacity towards various metal ions including cadmium and mercury. Becker et al studied the adsorption characteristics of cadmium, along with other metals, on dialdehyde or tetracarboxylic acid cross-linked chitosan [17]. Chitosan can also be modified by impregnation quantum dots for the heavy metal removal including cadmium [18].

In present work, we report the use of ionic solid (EHDAIC) impregnation on chitosan and adsorption of Cd(II) and Hg(II) in the form of their chloro complexes. These two aspects have simultaneously enhanced not only the adsorption capacity but also the material can be used in water treatment where a single source leads to both metal ions simultaneously.

2. Materials and methods

2.1 Materials

Ethylhexadecyldimethyl ammonium bromide (EHDAB), cadmium chloride, mercuric chloride and sodium hydroxide, were procured from Merck, India. Aqueous solutions were prepared using double distilled water. Uniloid Bio-Chemicals India Limited, Hyderabad supplied chitosan having 85% of degree of deacetylation. All the reagents were of analytical grade and used without further purification.

2.2 Preparation of adsorbent

2.0 g of chitosan was added to 10 mL of 0.2 M ethylhexadecyldimethyl ammonium bromide solution in dichloromethane and subjected to microwave irradiation for 2 min with an intermittent time interval of 30 s. The microwave irradiation was carried out in domestic microwave oven (LG, India model MS2049) at 2450 MHz. The resulting residue (EHDAIC) was

washed with double distilled water and dried at room temperature, sieved through a 500μ mesh and used for further adsorption studies. The schematic method of preparation has been shown in Fig. 1.

Fig. 1 Interaction between chitosan and ethylhexadecyldimethyl ammonium bromide (EHDAB)

2.3 Physico-chemical characterization

Structural specifics of adsorbents could be explained on the basis of FT-IR spectra recorded using BrukerAlpha spectrometer in the range 500-4000 cm^{-1}. The XRD pattern was recorded by X-ray diffractometer system Righaku-Miniflex 300. Surface morphology of adsorbents prior and consequent to adsorption of heavy metals was studied using Scanning Electron Microscope (SEM) model TESCAN VEGA 3 SBH. Energy dispersive spectral (EDX) analysis performed for elemental quantitation using X- ray analyzer Oxford INCA Energy 250 EDS System during SEM observations. The concentration of cadmium was determined using ICP-AES. For analysis of cadmium, the solutions were diluted with 5% HNO_3. The solution phase concentration of Hg(II) was estimated by the standard Cold Vapour-Atomic Absorption Spectrophotometric (CV-AAS) technique. The mercury vapours were analyzed by CV-AAS technique using a Mercury Analyzer Model MA-5840(Electronics Corporation of India Ltd. Hyderabad, India) pH adjustments were done with dilute sulphuric acid and sodium hydroxide solutions using Equiptronics pH meter EQ-615.

2.4 Adsorption procedure

Absorption studies were performed by using varying concentrations of Cd(II) from 100 mg L^{-1} to 800 mg L^{-1} and Hg(II) from 20 mg L^{-1} to 500 mg L^{-1}. The required pH was maintained and the solutions were stirred with optimized adsorbent dose in a stoppered conical flask for 60 min at 298 K.

The amount of metal ions adsorbed (mg g^{-1}) on EHDAIC at equilibrium (q_e) can be given by

$$q_e = \frac{C_0 - C_e}{W} \times V \qquad (1)$$

where C_0 and C_e specify the initial and equilibrium liquid phase concentrations in mg L^{-1} of metal ions , V is the volume of metal ions solution in liters and W is the weight of adsorbent in

gram used for adsorption process. All the batch adsorption experiments were performed with three simulates.

3. Results and discussion

3.1 Characterization of ionic solid impregnated chitosan

The FT-IR spectra of native chitosan showed distinct characteristic broad peaks corresponding to O-H and N-H stretching vibrations in the region 3808 cm^{-1} and 3276 cm^{-1}, the N-H bending vibration around 1556 cm^{-1}, C-N bending vibration at 1379 cm^{-1} and the C-H and C-O stretching bands around 2868 $cm^{-1}$and 1012 (Fig 2 a). After impregnation with ethylhexadecyldimethyl ammonium bromide, two additional peaks appeared at 2806 and 2717 cm^{-1} corresponding to -CH_2 groups of aliphatic chains confirming the impregnation [19] (Fig 2 b).

Fig. 2 FTIR spectra of a. chitosan, b. EHDAIC

The X ray diffraction patterns of chitosan, EHDAIC and EHDAIC with adsorbed Cd(II) and Hg(II) ions were recorded (Fig. 3). XRD spectra of chitosan showed characteristic peaks at $2\theta = 10.5^0$ and 20.3^0. In case of EHDAIC, these peaks were found to get shifted to $2\theta = 10.2^0$ and 19.2^0 respectively. These changes in the 2θ angle are mainly due to the decrease in crystallinity of the adsorbent which accounts for interaction of ionic solid with chitosan [20]. After adsorption of Cd(II) ions on EHDAIC, additional peaks were observed at $2\theta = 22.50^0$ and 36.30^0 which belong to Cd(II) [21] and after adsorption of Hg(II) , an additional peak was observed at $2\theta = 37.67^0$ which matches with the reported value for Hg(II).

Fig. 3 XRD pattern of a. chitosan, b. EHDAIC, c. EHDAIC with adsorbed Cd(II), d. EHDAIC with adsorbed Hg

TGA/DTA curves of chitosan and EHDAIC were recorded to understand thermal characteristics (Fig.4). The TGA curve of chitosan shows two stages of thermal decomposition. The initial degradation observed at around 50 to 200 ^{0}C with 4.6% weight loss which corresponds to a loss of moisture in the chitosan. The second degradation of chitosan was started at 283 ^{0}C and continued up to 377 ^{0}C. During second stage of degradation, 52.4% weight loss was occurred

due to degradation of chitosan biopolymer at 334.6 ^{0}C. [22] At the end of 900 ^{0}C, the total weight loss of chitosan was found to be 71%. EHDAIC also shows two stages thermal decomposition. The first stage corresponds to loss of moisture with weight loss of 8% in between 100 to 200 ^{0}C. The second stage decomposition starts at 293 ^{0}C and continued till 336 ^{0}C with weight loss of 56 %. At the end of 900 ^{0}C, the total weight loss for EHDAIC is 73%. Hence, weight loss in EHDAIC is greater than that of chitosan which is quite obvious due to presence of impregnated EHDA moiety.

Fig. 4a. TGA curves for chitosan and EHDAIC, b. DTA curves for chitosan and EHDAIC.

SEM micrographs (Fig.5) define the physiology of the adsorbent material. Chitosan has irregular and loose surfaces. After impregnation of ionic solid, surface morphology was uniformly dense and porous. SEM micrographs of the EHDAIC with adsorbed metal ions shows glossy and bright spots on uniform dense surface ascribe persuasive interaction of metal ions with the adsorbent.

Fig. 5 SEM micrographs of a. chitosan, b. EHDAIC, c. EHDAIC with adsorbed Cd(II), d. EHDAIC with adsorbed Hg(II).

EDX spectra (Fig.6) of EHDAIC before and after adsorption of the metal ions clearly show the presence of metal ions on the surface of adsorbent. After adsorption, characteristic peaks K_α and K_β of metal ions could be distinctly observed.

Fig. 6 EDX spectra for a. chitosan, b. EHDAIC, c. EHDAIC with adsorbed Cd(II), d. EHDAIC with adsorbed Hg(II).

3.2 Effect of pH

Speciation of adsorbate and surface charge of adsorbent depends upon pH of the solution. Hence, it is customary to study pH effect on adsorption efficiency. In the present study, 50 mL of 100 mg $L^{-1}$of Cd(II) and 20 mgL^{-1} Hg(II) solutionswere equilibrated with 200 mg of EHDAIC. pH of the solutions was varied from 2.0 to 8.0. From Fig.7 it is clear that, at pH 3.0 adsorption of Cd(II) and Hg(II) is maximum. This is because of stability of chloro complexes of Cd(II) and

Hg(II) at pH 3.0 and also the positive surface charge of EHDAIC. The pH_{zpc} of EHDAIC was found to be 3.5 indicating that the material surface is positively charged below this pH and negatively charged above it. Among the various possible chloro complexes of mercury, the tetrachloro complex has a high stability constant value [23]. At pH greater than 6.0, Cd(II) and Hg(II) undergo hydrolysis to form corresponding hydroxides and hence adsorption efficiency decreases substantially.

Fig.7 a.pH_{zpc} of EHDAIC, b. effect of pH (adsorbent dose = 200mg, contact time = 45min. [Cd(II)] =100 mgL^{-1}, [Hg(II)] = 20 mgL^{-1})

3.3 Adsorption isotherms

Langmuir and Freundlich adsorption isotherm models were studied quantitatively. Absorption studies were performed by using varying concentrations of Cd(II) from 100 mg/L to 2000 mg/L and for Hg(II) from 20 mg/L to 500 mg/L maintaining all the optimized parameters like pH, adsorbent dose, contact time and temperature constant.

3.3.1 Langmuir isotherm

The purpose of Langmuir isotherm model study is to understand the monolayer adsorption on homogeneous surface and to calculate the maximum adsorption capacity of adsorbent [24]. It relates the maximum adsorption capacity (q_0) and the Langmuir constant related adsorption energy (b) in linearized Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \qquad (2)$$

The maximum adsorption capacity q_0 and the constant b were obtained from the slope and intercept of the plot of C_e/q_e against C_e(Fig. 8). High adsorption capacities (Table 1) refer to excellent adsorption behavior of EHDAIC towards metal ions. A separation factor R_L that relates to the favourable nature of adsorption is given by the equation:

$$R_L = \frac{1}{1 + bC_o} \qquad (3)$$

R_L value less than unity (Table 1) indicates effective interaction between the EHDAIC and metal ions at the optimized experimental conditions [25].

3.3.2 Freundlich isotherm

Inequivalent adsorbent sites leading to surface heterogeneity during adsorption has been explained by Freundlich isotherm model[26]. k_F refers to adsorption capacity and n indicate the adsorption intensity with the linearized expression given as

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \qquad (4)$$

The logarithmic plot of q_e against C_e (Figure.8) gives the constants $k_F$andn(Table 1).The smaller value of 1/n (0.1 <1/n< 1.0) signifies an active interaction between EHDAIC and metal ions[27].

Table 1 Isotherm parameters

Fig. 8 Isotherm studies (adsorbent dose = 200mg, contact time = 45min, pH = 3.0, [Cd(II)] =100 mgL^{-1}, [Hg(II)] = 20 mgL^{-1}) a. Langmuir isotherm -1.Cd (II) adsorption 2. Hg(II) adsorption, b. Freundlich isotherm- 1.Cd(II) adsorption 2. Hg(II) adsorption, c. Comparison of experimental q_e with other isotherms-1.Cd(II) adsorption 2. Hg(II) adsorption.

3.4 Kinetics of adsorption

The amount of metal ion adsorbed by the adsorbent depends on the contact time and thus, kinetics of adsorption of metal ions on to the EHDAIC was explained through pseudo-first-order and pseudo-second-order kinetic models. The studies were carried out using 50 mLof100 mg $L^{-1}$of Cd(II) and 20 mgL^{-1} Hg(II) solutions at pH 3.0. It was equilibrated with 200 mg of EHDAIC at 298 K for different time intervals (5-90min). The pseudo-first-order kinetics [28] is given by the equation

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (8)$$

where q_e and q_t refer to the amounts of metal ions adsorbed at equilibrium and at time t with the first- order rate constant k_1.The plot of log (q_e - q_t) against t gives pseudo-first-order rate constant with regression coefficient (Fig. 9).

The pseudo-second-order equation [29] is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad (9)$$

where k_2 is the pseudo-second- order rate constant in g mg^{-1} min^{-1}. The plot of log t/ q_t against t (Fig.9) gives pseudo-second-order rate constant. Regression coefficient of 0.99 for pseudo-second-order rate kinetics offers a best fit model to describe the adsorption of metal ions on to EHDAIC (Table 2).During adsorption whether intraparticle diffusion is the rate determining step can be confirmed by Weber –Morris model [30] .According to this model, $q_t$and $t^{1/2}$ of adsorption process are related as

$$q_t = k_{int}.t^{1/2} + C \quad (10)$$

If the plot of q_t verses $t^{1/2}$ (Fig.9) passes through origin and is linear, then intraparticle diffusion is the only rate-limiting step. The slope gives the intraparticle rate constant k_{int}(mg^{-1} $g^{-1}min^{1/2}$) and non-zero intercept showed that diffusion is not the only rate-limiting step(Table 2). Rate of adsorption of metal ions may be influenced by external mass transfer of metal ions from solution phase to solid phase, pore diffusion and at interior sites of the adsorbent.[31] Thus the adsorption of metal ions byEHDAIC was controlled by boundary layer as well as diffusion process.

Fig. 9 Kinetic studies (adsorbent dose = 200mg, pH = 3.0, [Cd(II)] =100 mgL^{-1}, [Hg(II)] = 20 mgL^{-1}) a. Pseudo-first-order kinetics 1.Cd (II) adsorption 2. Hg (II) adsorption b. Pseudo-second-order kinetics1.Cd (II) adsorption 2. Hg (II) adsorption c. Intraparticle diffusion 1.Cd (II) adsorption 2. Hg (II) adsorption

Table 2 Kinetic parameters

3.5 Thermodynamics of adsorption

Effect of temperature on adsorption of metal ions by EHDAIC was studied in order to obtain relevant thermodynamic parameters at 298 K, 303 K, 308 K, 318 K and 328 K. These parameters describe the spontaneous nature of adsorption . The free energy change of adsorption (ΔG^0) is given by

$$\Delta G^0 = -RT\ln K \quad (11)$$

van't Hoff equation[32]which relates entropy (ΔS^0) and enthalpy (ΔH^0) changes is given by

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

where R is the gas constant (8.314 J $mol^{-1}K^{-1}$). The value of equilibrium constant K has been evaluated from the ratio of concentration of metal ions adsorbed to that in the solution phase. The values of ΔH and ΔS were obtained from slope and intercept of the plot of ln K against 1/T (Fig10) respectively. The negative free energy change indicates the spontaneous nature, negative enthalpy change indicates the exothermic nature of adsorption process while negative entropy change indicates the decrease in randomness of metal ions as it passes from solution to adsorbed state. (Table 3)

Table 3 Thermodynamic parameters

Fig. 10 Van't Hoff plot (adsorbent dose = 200mg, contact time = 45min, pH = 3.0, [Cd(II)] =100 mgL^{-1}, [Hg(II)] = 20 mgL^{-1}) a. cadmium adsorption b. mercury adsorption

3.6 Column studies

Column adsorption studies were performed using glass column of 30.0 cm length and 1.0 cm inner diameter to understand the applicability of adsorbent for larger sample volumes. Column was packed with 1.0 g of adsorbent to the height of 6.0 cm. Metal ion solutions were passed through the column at the flow rate of 6mL min^{-1}.Concentrations of metal ions in solution phase were analyzed to quantify the column efficiency. Adsorption of metal ions was found to be quantitative up to 1100ml for 200mgL^{-1} of cadmium solution and 900ml for 50 mgL^{-1} of mercury solution (Fig. 11and Table 4). The identical results were obtained in three replicates. These results clearly indicate that larger sample volumes containing these metal ions can be effectively treated using column method compared to batch extraction.

Fig.11 Effect of sample volume on column efficiency a. cadmium adsorption b. mercury adsorption

Table 4 Column parameters

3.7 Effect of co-anions

The real effluent synthetic effluent contains diverse anions and cations which compete for the available active adsorption sites on the adsorbent surface. Hence, it is important to understand

the effect of individual ions on adsorption efficiency. Cations such as Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, $Fe^{2+}$and anions such as SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-} were individually tested for their effect on adsorption of Cd(II) and Hg(II) by EHDAIC. For interference in cadmium adsorption, 50 mL solution containing 100 mg/L Cd(II) and 200 mg/L interfering ion has been equilibrated with 200 mg EHDAICmaintaining all other optimized parameters constant. For interference in Hg(II) adsorption 50 mL of 20 mg/ L Hg(II) was mixed individually with 50 mL 100 mg/L concentrations of these ions and stirred with 200 mg of EHDAIC. From Fig.12,it is apparent that the NO_3^- anion and Fe^{2+}cation affect the % removal of Cd(II) and Hg(II) to the maximum extent. However, the percentage removal is more than 90% in all the cases.

Fig.12 Effect of Co-anions

3.8 Application to synthetic effluents

In order to confirm the applicability of EHDAIC for removal of cadmium and mercury, two different synthetic effluents containing Cd(II) in first while Hg(II) in second were prepared having similar composition to that of the real effluents and adsorption efficiency was determined for these metal ions. The results have been depicted in Table 5.The decrease in the removal efficiency can be attributed to presence of iron and nitrate ions.

Table 5 Application of EHDAIC to synthetic effluents

3.9 Regeneration and reusability of EHDAIC

The regeneration of adsorbent material is very important from a greener point of view. Various reagents such as sodium hydroxide, ammonium hydroxide, sodium carbonate, hydrochloric acid and sulphuric acid were examined for desorption. The best results were obtained with 5% (v/v) ammonium hydroxide solution (Fig. 13a). 2 g of EHDAIC loaded with Cd(II) and Hg(II) was taken in conical flask. To it, 25 mL of 5% (v/v) ammonium hydroxide solution was added and stirred for 30 min. The reaction mixture was filtered and washed with distilled water to give back EHDAIC. The regenerated EHDAIC was tested for ten adsorption-desorption cycles. The adsorption efficiency was found to decrease with number of cycles (Fig. 13b).

Fig. 13a. Effect of various reagents on desorption of Cd(II) and Hg(II) loaded EHDAIC b. Efficiency of regenerated EHDAIC in succeeding adsorption cycle.

3.10 Mechanism of Adsorption of Metal ions byEHDAIC

In EHDAIC, protonated amino groups of chitosan and EHDA moiety undergoes feasible interaction with tetrachlorometalate(II) complex. The resulting binding energies were due to the electrostatic and van der Waals interactions. In present work, Cd(II) and Hg(II) shows ion pair interactions with quaternary nitrogen of EHDA. Also amino groups of chitosan get protonated in acidic medium and this further enhances the electrostatic interaction between tetrachlorometalate (II) anion and the EHDAIC (Fig. 14).

Fig. 14 Mechanism of adsorption.

3.11 Comparison with other related adsorbents

The adsorption capacity is a yardstick to assess an adsorbent. The adsorption capacity of EHDAIC is compared with some of the other reported biopolymer adsorbents.

Table 6 Comparison of adsorption capacity with other adsorbents.

Conclusion

Chitosan could be easily modified with EHDAB in microwave irradiation within 2 minutes. The method of synthesis was simple and did not require any special conditions. The interaction between the chitosan and ionic solid exquisite the potential application of adsorbent for the effective adsorption of potentially toxic metal ions like Cd^{2+} and Hg^{2+}. Experimental data showed adsorption process follows pseudo- second order kinetics. The EHDAIC adsorbent has shown admirable adsorption capacities of 341.3mg g^{-1} for cadmium and 43.4 mg g^{-1} for mercury. Adsorption process was found to be spontaneous, exothermic and leads to decrease in randomness. The regeneration and reusability of EHDAIC makes it a greener material for metal ion removal from industrial effluents.

Acknowledgements

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Table 1 Isotherm parameters

Elements	Langmuir isotherm				Freundlich isotherm		
	q_0 (mg/g)	b (L/mg)	R_L	r^2	k_F (mg/g/L)	n	r^2
Cd^{2+}	341.30	0.004	0.70	0.736	12.15	2.20	0.968
Hg^{2+}	43.43	0.03	0.40	0.773	3.84	2.29	0.952

Table 2 Kinetic parameters

Elements	Pseudo-first-order kinetics		Pseudo-second-order kinetics		Intraparticle diffusion	
	k_1 (1/min)	r^2	k_2 (g/mg/min)	r^2	k_{int} (mg/g/min$^{1/2}$)	r^2
Cd^{2+}	0.101	0.755	0.287	0.999	0.072	0.673
Hg^{2+}	0.0018	0.714	0.052	0.999	0.021	0.855

Table 3 Thermodynamic parameters

Temperature	ΔG (kJ/mol)		ΔH (kJ/mol)		ΔS (kJ/mol/K)	
	Cd^{2+}	Hg^{2+}	Cd^{2+}	Hg^{2+}	Cd^{2+}	Hg^{2+}
298K	-7.96	-9.52				
303K	-7.93	-9.12				
313K	-7.83	-6.85	- 12.31	- 55.40	- 0.014	- 0.153
323K	-7.70	-5.67				
333K	-7.53	-4.55				

Table 4 Column parameters

Parameter	Result	
	Cd^{2+}	Hg^{2+}
Inlet metal ion concentration	200 mg/L	50 mg/L
Breakthrough volume	1100 mL	900 mL
Exhaustion volume	1900 mL	1300 mL
Breakthrough Capacity	220 mg/g	45 mg/g
Exhaustion Capacity	380 mg/g	65 mg/g
Degree of column utilization	57.89%	69.23%

Table 5 Application of EHDAIC to synthetic effluents

Synthetic Effluent	Concentration of Ions (mg/L)	% Removal efficiency
1	Cl^-(626), SO_4^{2-}(1155), NO_3^-(200), Mn^{2+}(200), Fe^{2+} (200), Zn^{2+}(200), Cd^{2+}(200)	86.4 ± 0.2
2	Cl^-(235), SO_4^{2-}(577), NO_3^-(100), Mn^{2+}(100), Fe^{2+}, Zn^{2+}(100), Hg^{2+}(100)	73.8 ± 0.2

Table 6 Comparison of adsorption capacity with other adsorbents.

Adsorbents	Adsorption capacity (mg/g)		References
	Cd^{2+}	Hg^{2+}	
Chitosan flakes	9.9	-	[12]
Chitosan/activated carbon composite	52.6	-	[33]
Thiourea-modified magnetic ion-imprinted chitosan/TiO_2	256.4	-	[34]
Polyaniline grafted cross-linked chitosan beads	145.0	-	[35]
Dihydroxyazacrown ether crosslinked chitosan	-	22.1	[36]
Thiocarbamoyl chitosan	-	27.2	[37]
Magnetic chitosan beads	-	152.0	[38]
EHDAIC	341.3	43.4	Present study

Figure captions

Fig. 1 Interaction between chitosan and ethylhexadecyldimethyl ammonium bromide (EHDAB)

Fig. 2 FTIR spectra of a. chitosan, b. EHDAIC

Fig. 3 XRD pattern of a. chitosan, b. EHDAIC, c. EHDAIC with adsorbed Cd(II), d. EHDAIC with adsorbed Hg

Fig. 4a. TGA curves for chitosan and EHDAIC , b. DTA curves for chitosan and EHDAIC.

Fig. 5 SEM micrographs of a. chitosan, b. EHDAIC, c. EHDAIC with adsorbed Cd(II), d. EHDAIC with adsorbed Hg(II).

Fig. 6 EDX spectra for a. chitosan, b. EHDAIC, c. EHDAIC with adsorbed Cd(II), d. EHDAIC with adsorbed Hg(II).

Fig. 7a pH_{zpc} of EHDAIC, b. effect of pH (adsorbent dose = 200mg, contact time = 45min. [Cd(II)] =100 mgL^{-1}, [Hg(II)] = 20 mgL^{-1})

Fig. 8 Isotherm studies (adsorbent dose = 200mg, contact time = 45min, pH = 3.0, [Cd(II)] =100 mgL^{-1}, [Hg(II)] = 20 mgL^{-1}) a. Langmuir isotherm -1.Cd (II) adsorption 2. Hg(II) adsorption, b. Freundlich isotherm- 1.Cd(II) adsorption 2. Hg(II) adsorption, c. Comparison of experimental $q_e$with other isotherms-1.Cd(II) adsorption 2. Hg(II) adsorption.

Fig. 9 Kinetic studies (adsorbent dose = 200mg, pH = 3.0, [Cd(II)] =100 mgL^{-1}, [Hg(II)] = 20 mgL^{-1}) a. Pseudo-first-order kinetics 1.Cd (II) adsorption 2. Hg (II) adsorption b. Pseudo-second-order kinetics1.Cd (II) adsorption 2. Hg (II) adsorption c. Intraparticle diffusion 1.Cd (II) adsorption 2. Hg (II) adsorption

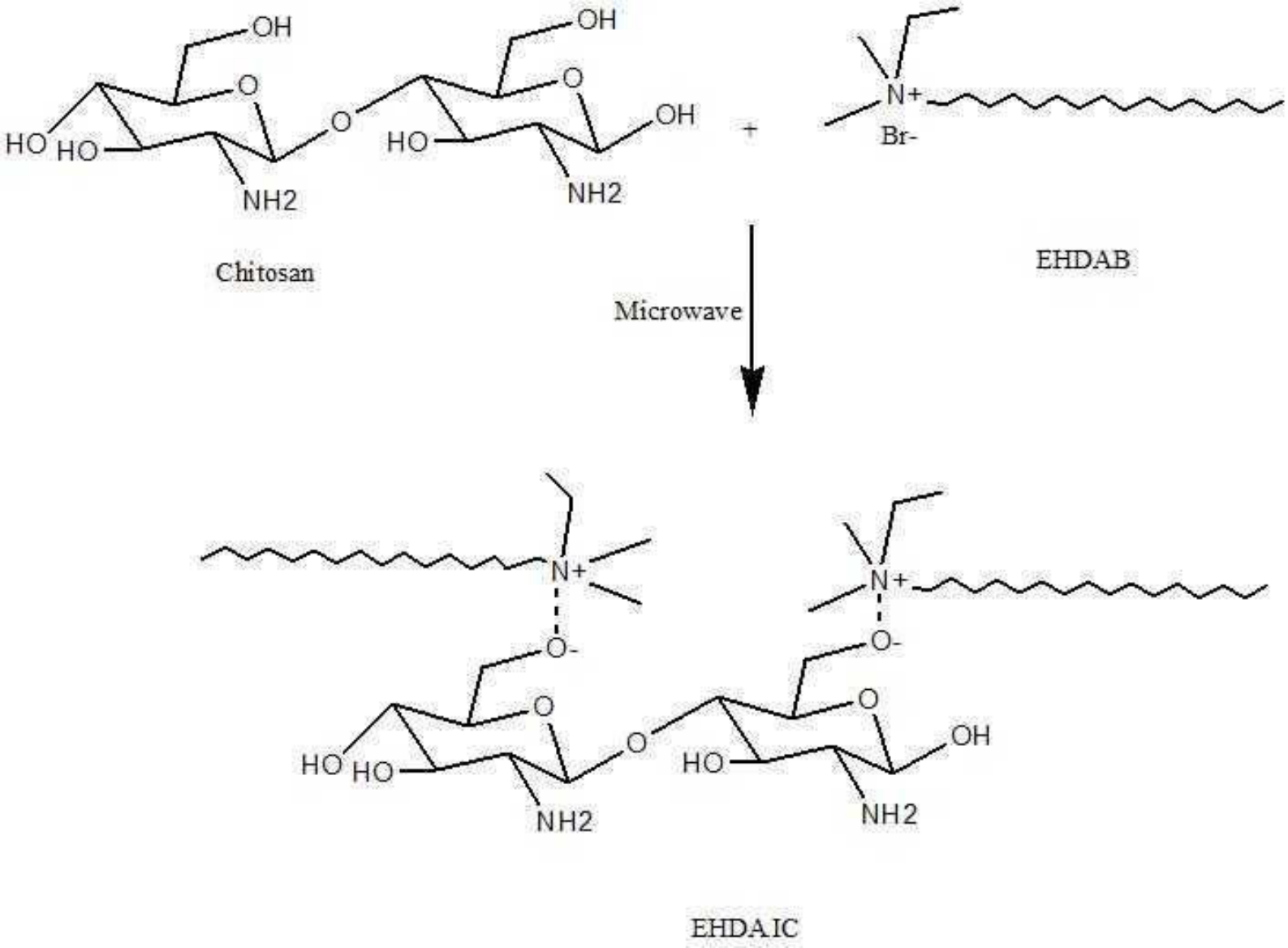
Fig. 10 van't Hoff plot (adsorbent dose = 200mg, contact time = 45min, pH = 3.0, [Cd(II)] =100 mgL^{-1}, [Hg(II)] = 20 mgL^{-1}) a. cadmium adsorption b. mercury adsorption

Fig. 11 Effect of sample volume on column efficiency a. cadmium adsorption b. mercury adsorption

Fig. 12 Effect of Co-anions

Fig. 13a Effect of various reagents on desorption of Cd(II) and Hg(II) loaded EHDAIC b. Efficiency of regenerated EHDAIC in succeeding adsorption cycle.

Fig. 14 Mechanism of adsorption.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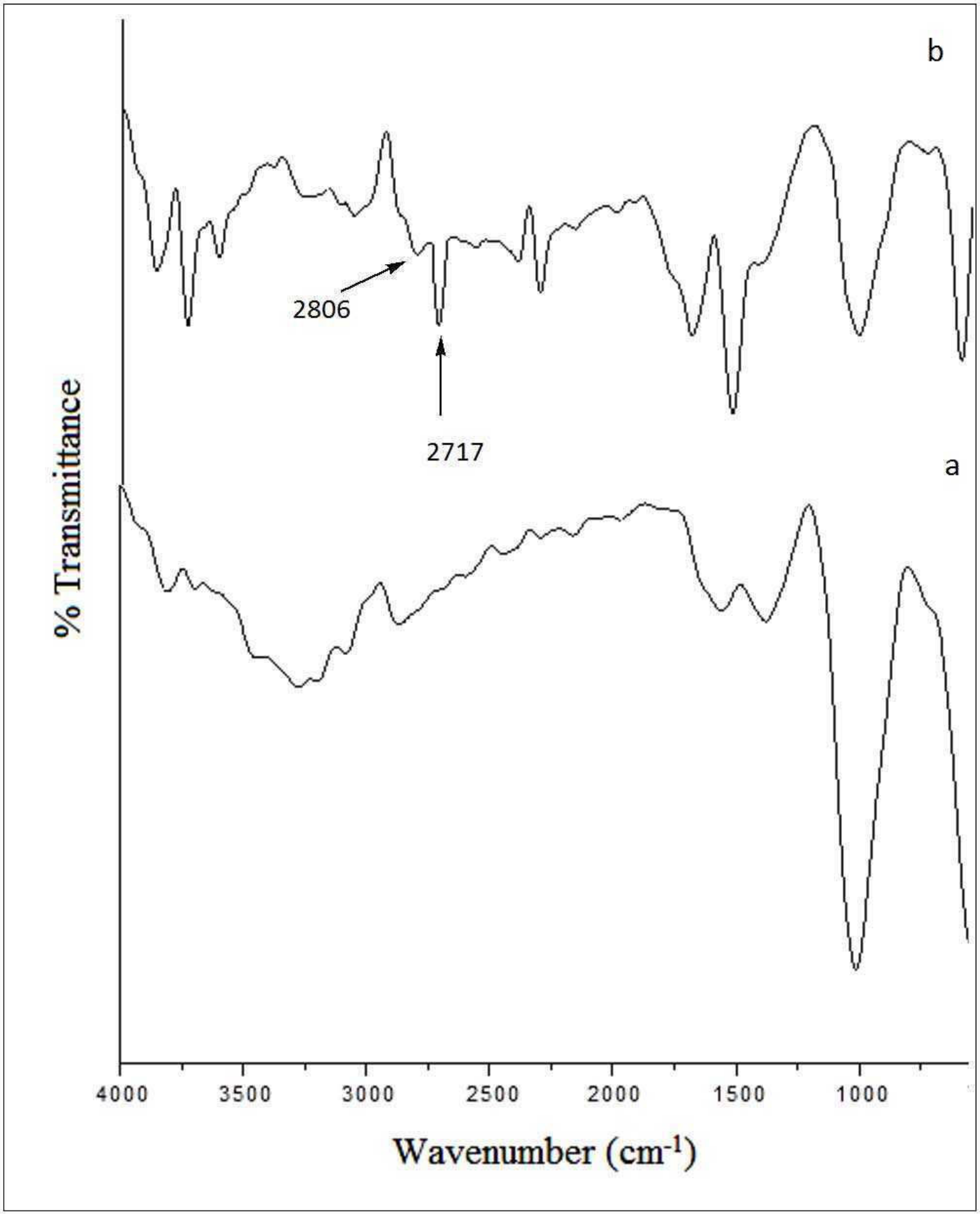
EHDAIC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% Transmittance
4000
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3000
2500
2000
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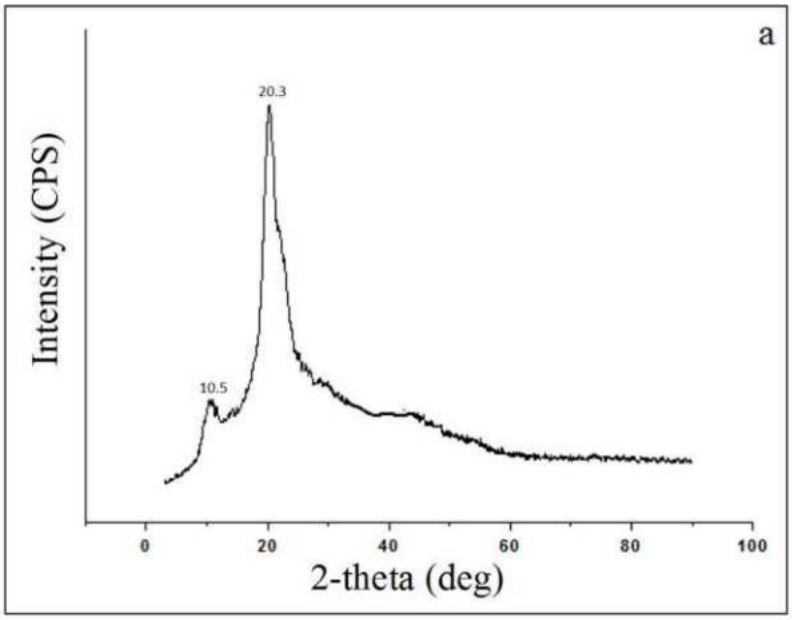
1000
Wavenumber (cm-1)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20
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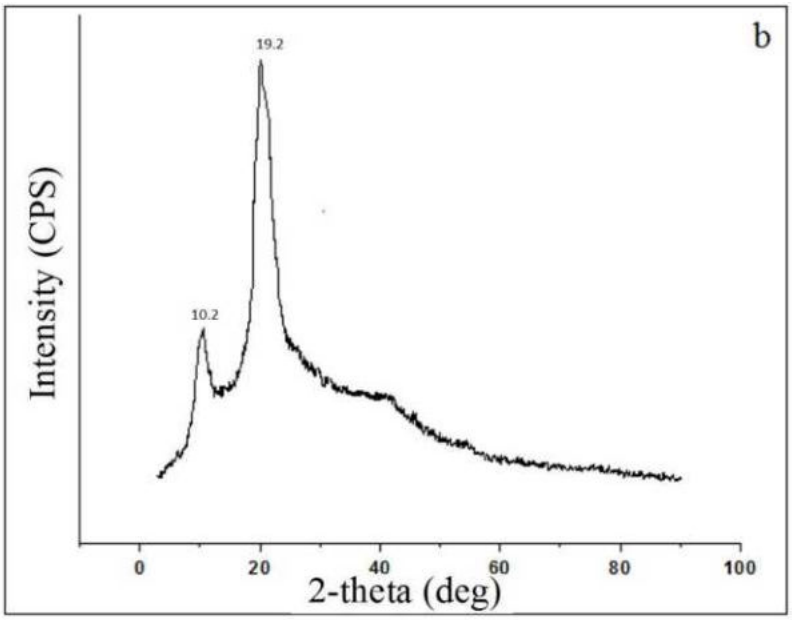
60
80
100
2-theta (deg)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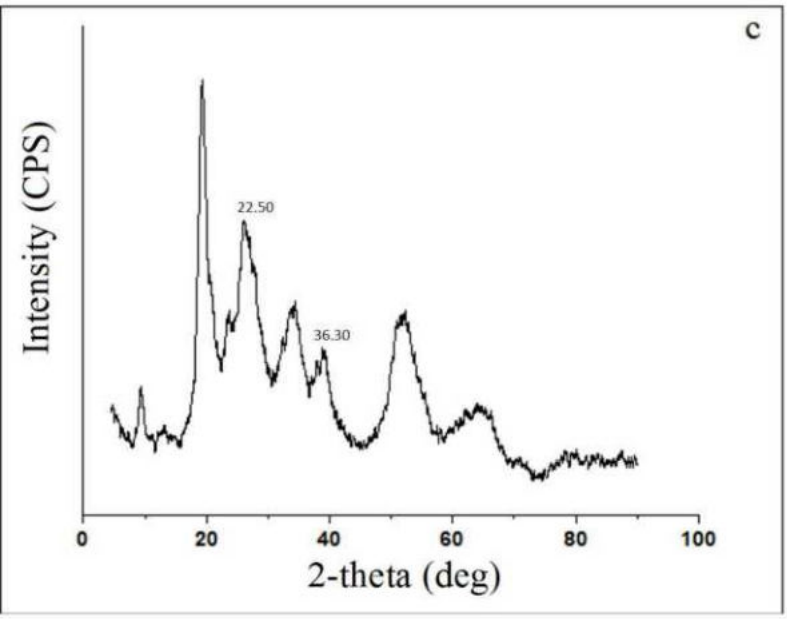
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20
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100
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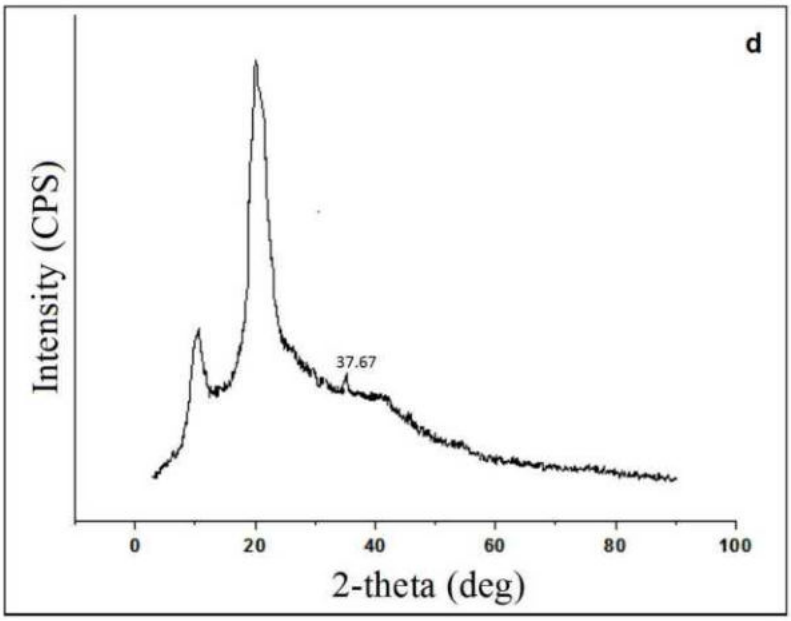
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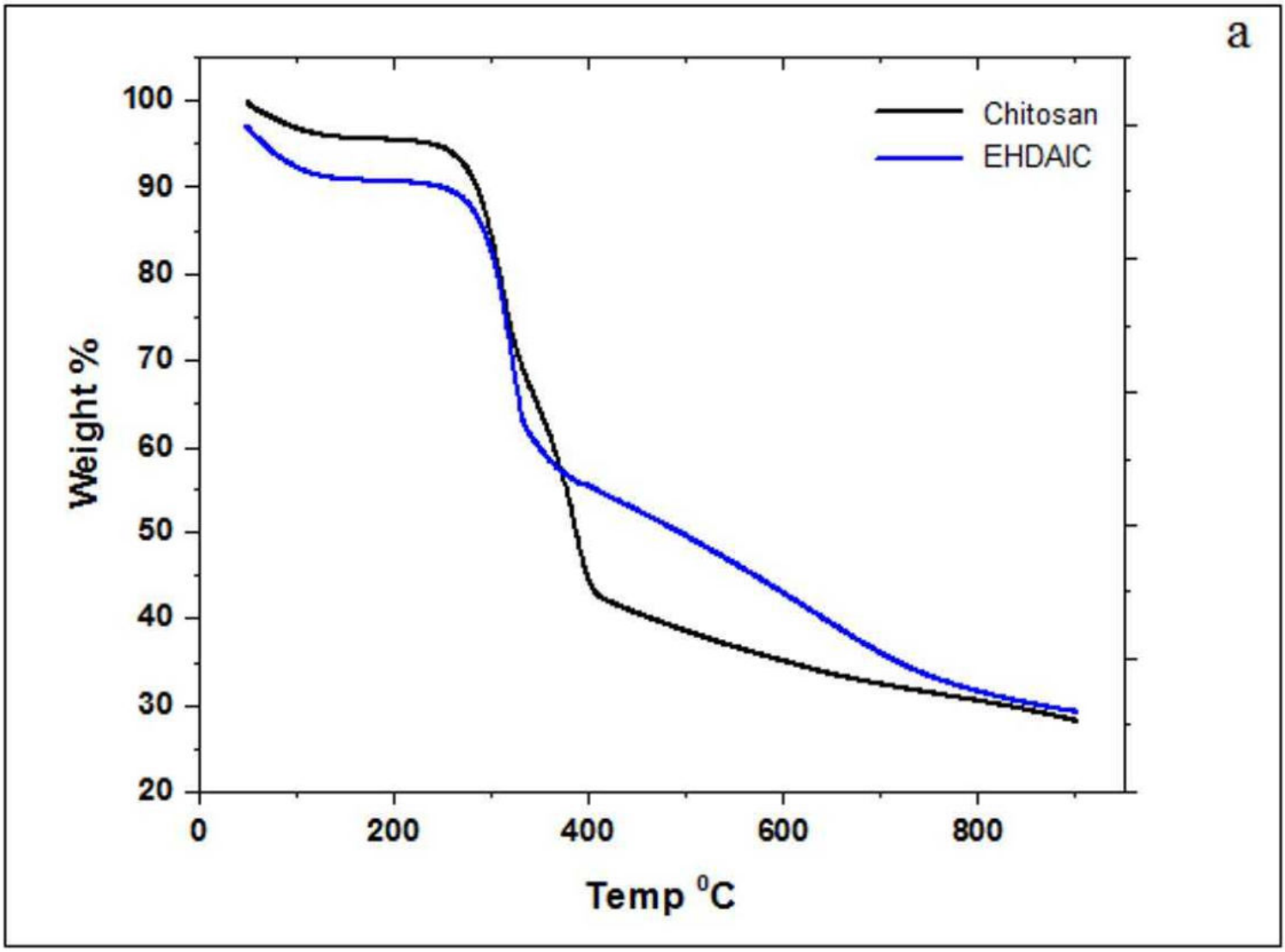
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200
400
600
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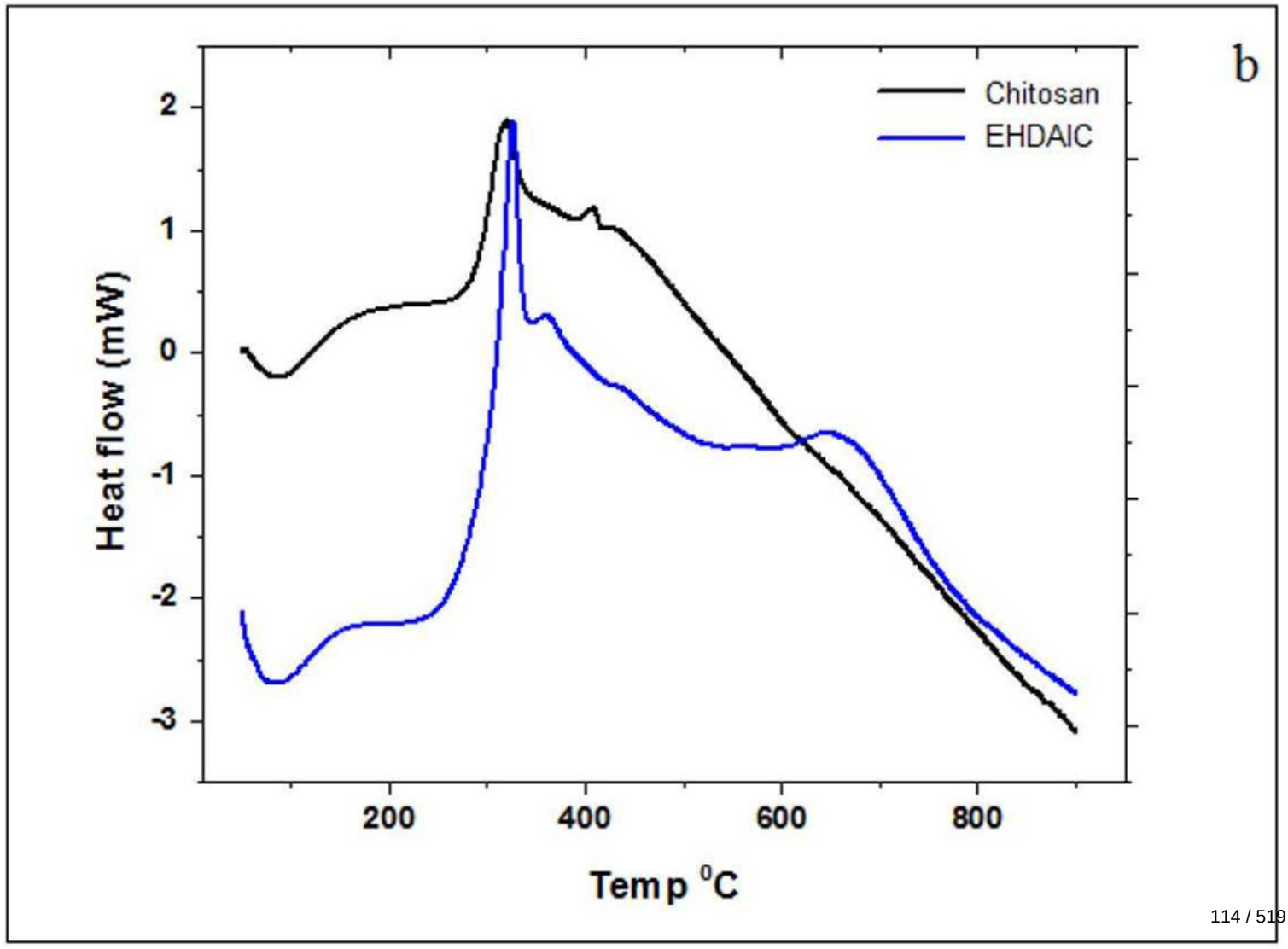
Temp °C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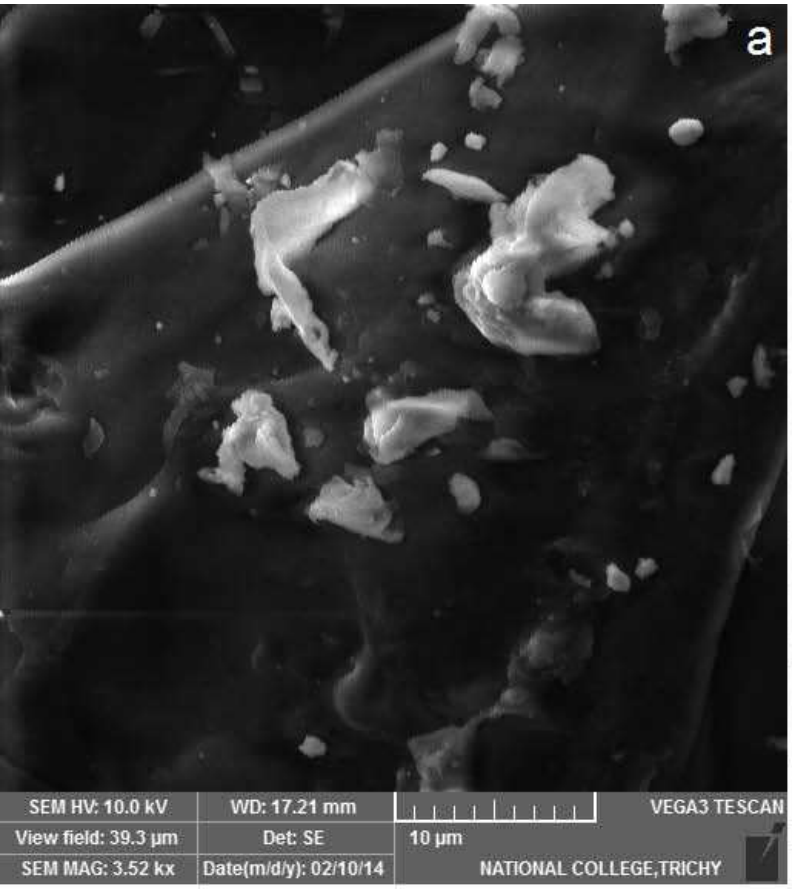
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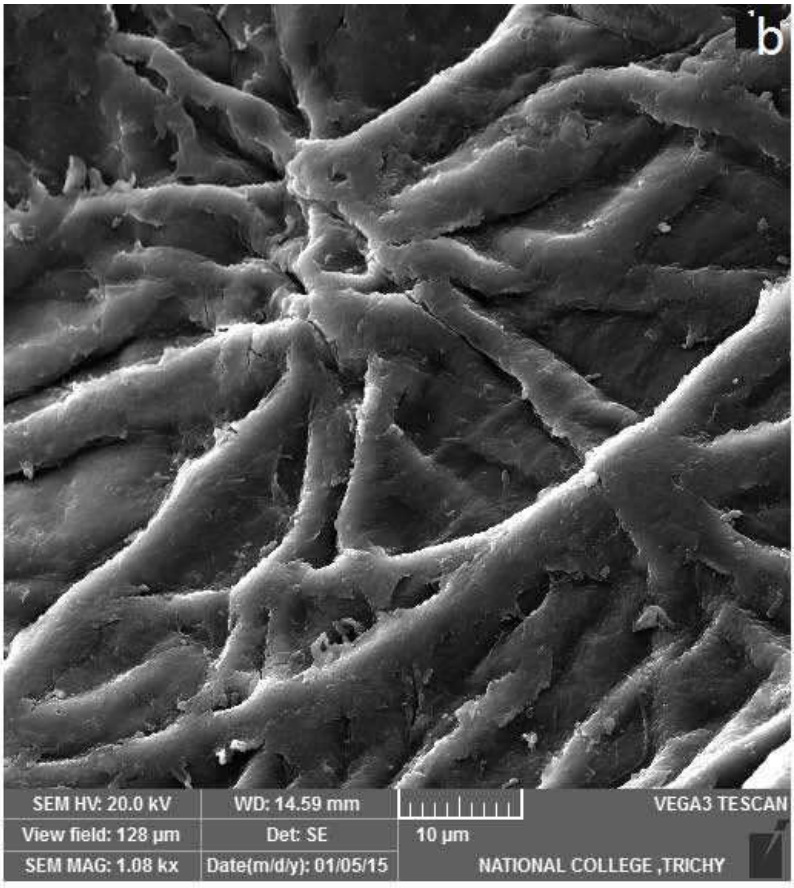
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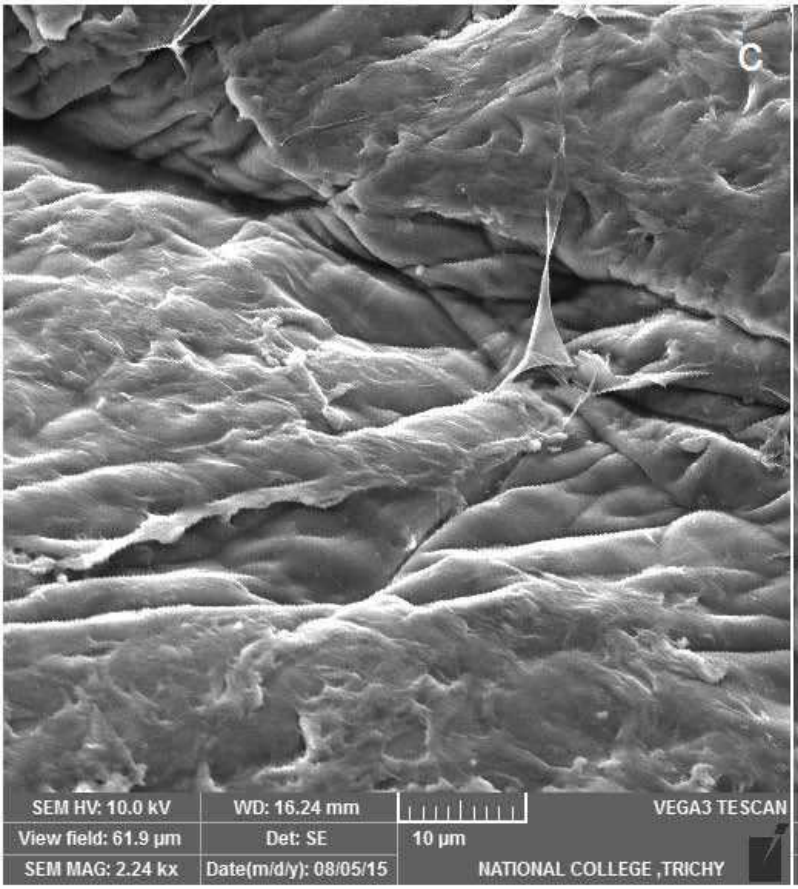
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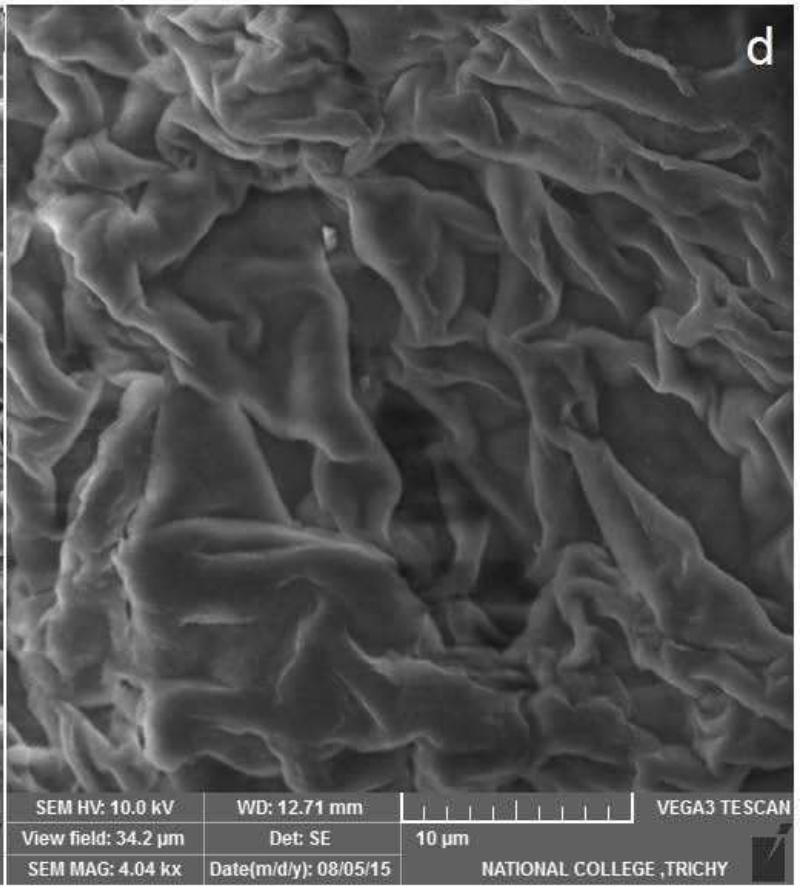
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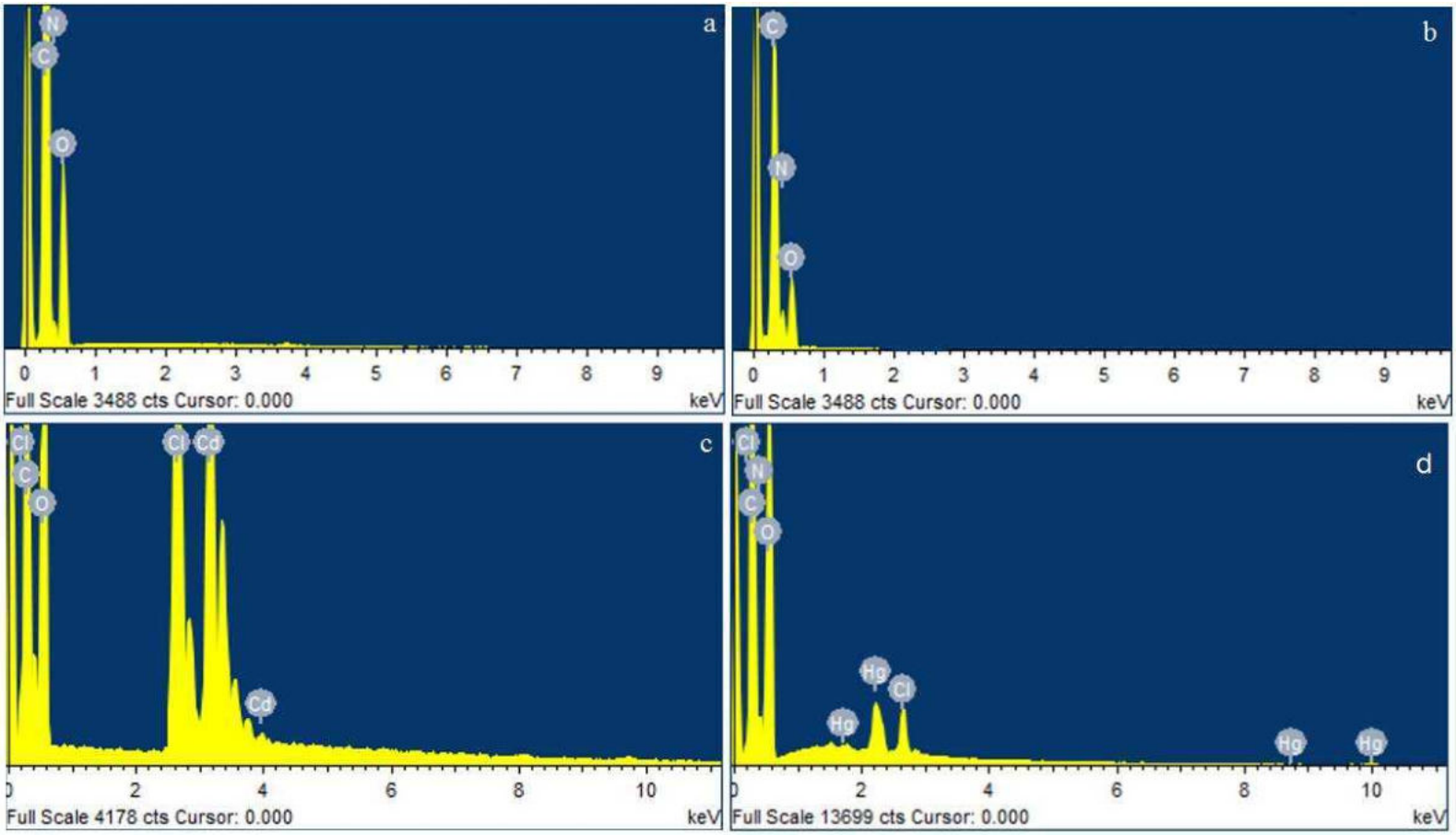
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Cl
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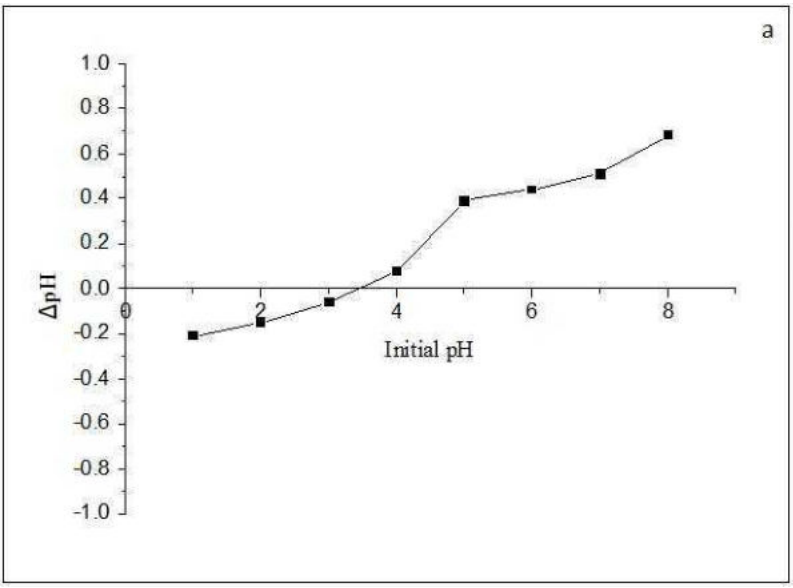
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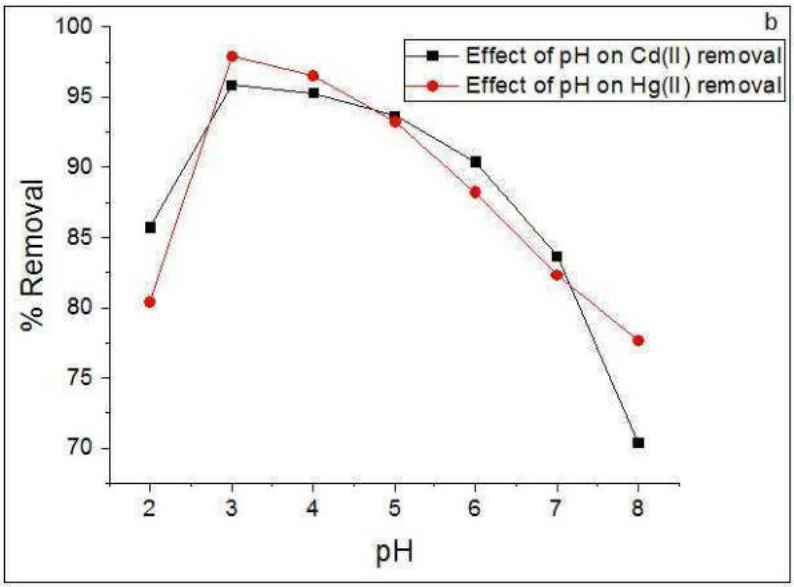
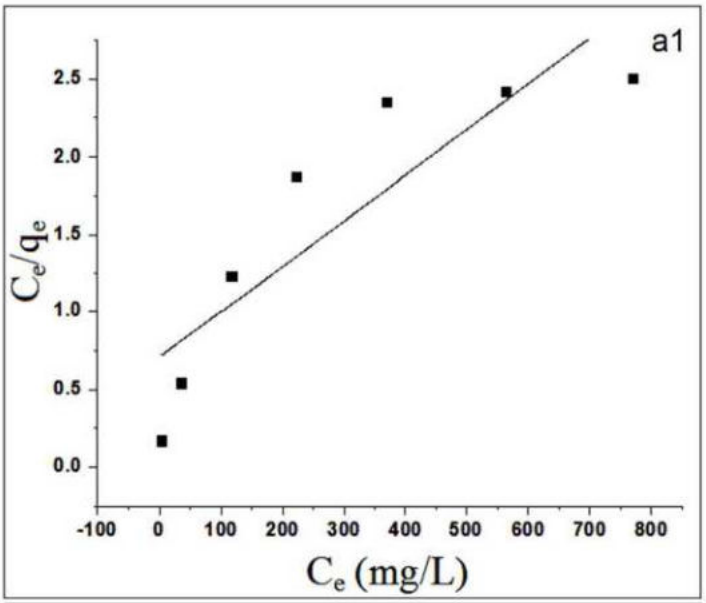
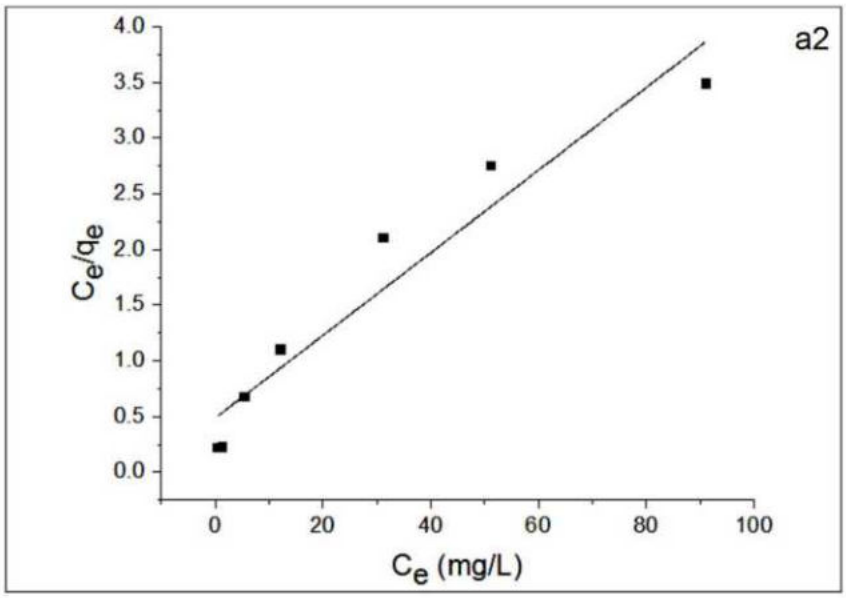
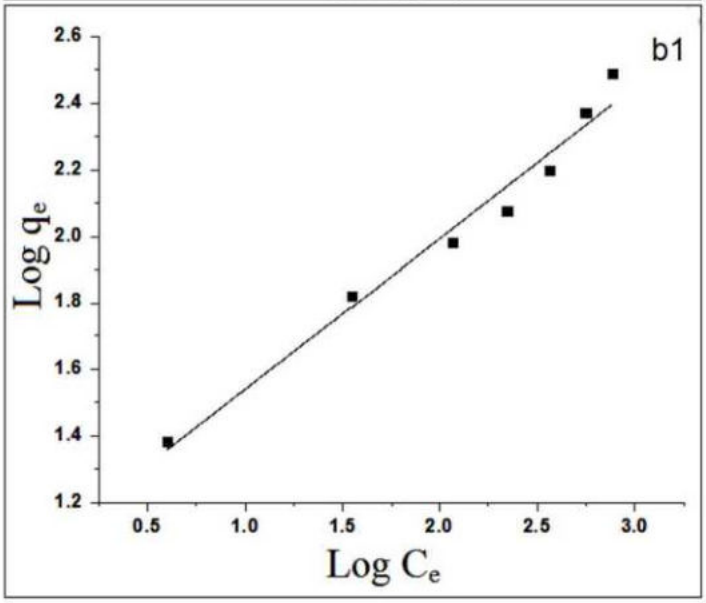
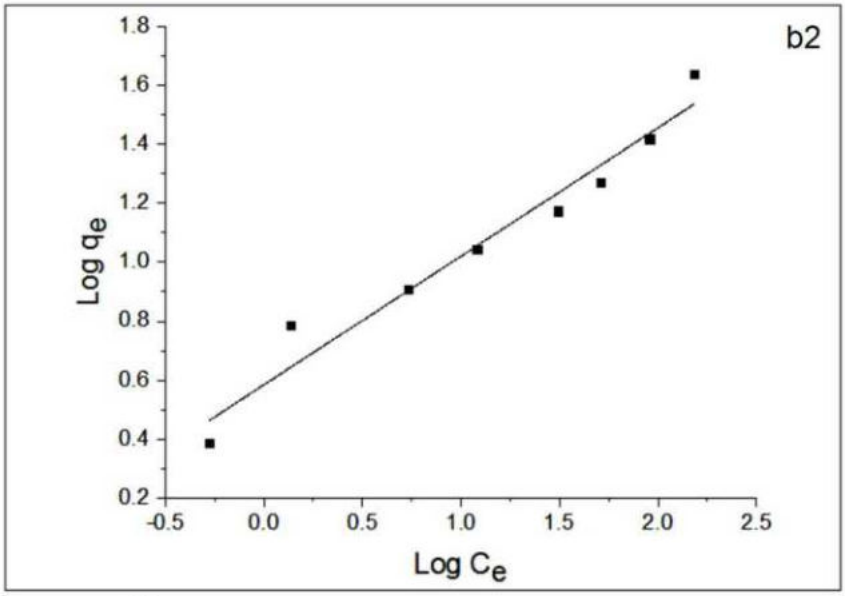
-1.0
0
2
4
6
8

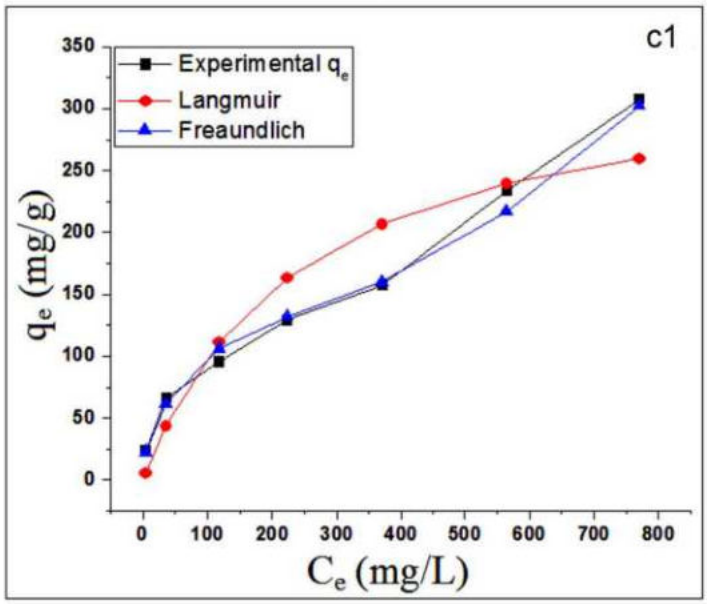

b
% Removal
pH
Effect of pH on Cd(II) removal
Effect of pH on Hg(II) removal
100
95
90
85
80
75
70
2
3
4
5
6
7
8

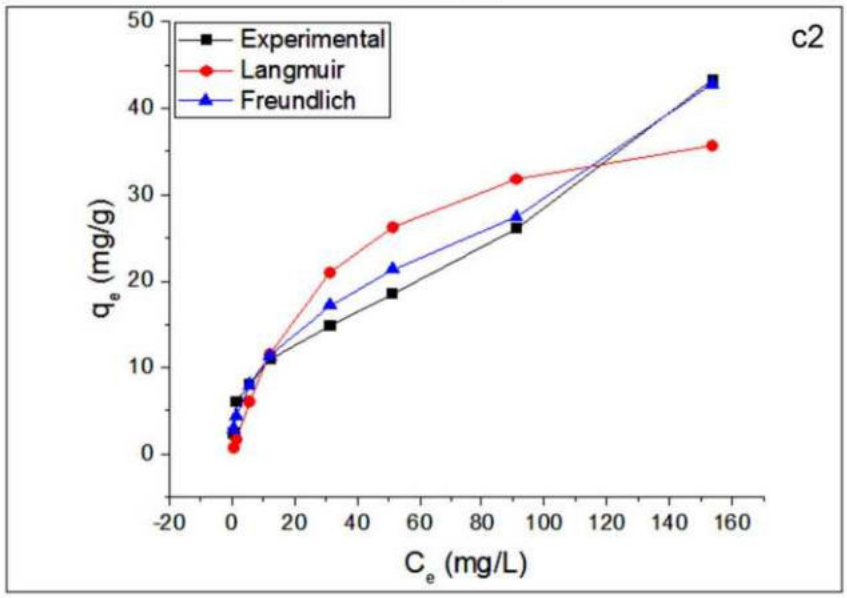

a1
C_e/q_e
C_e (mg/L)

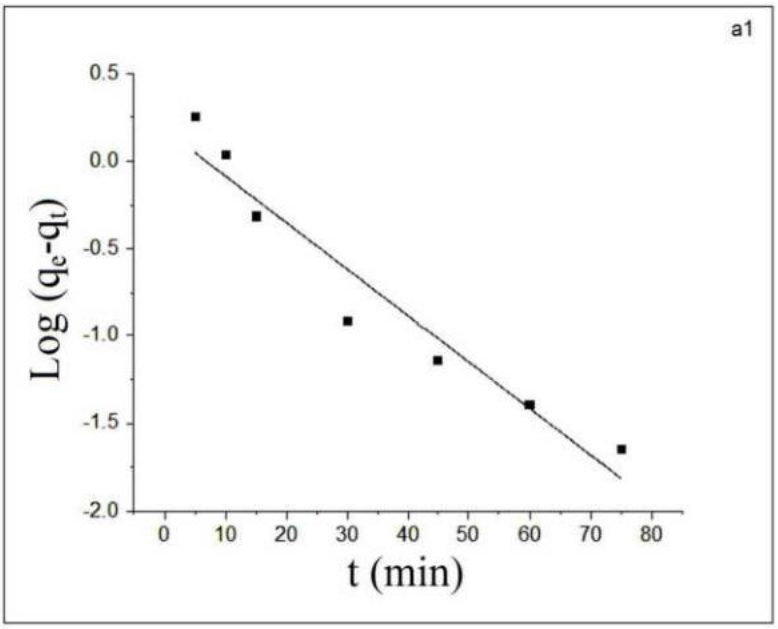

a2
C_e/q_e
C_e (mg/L)

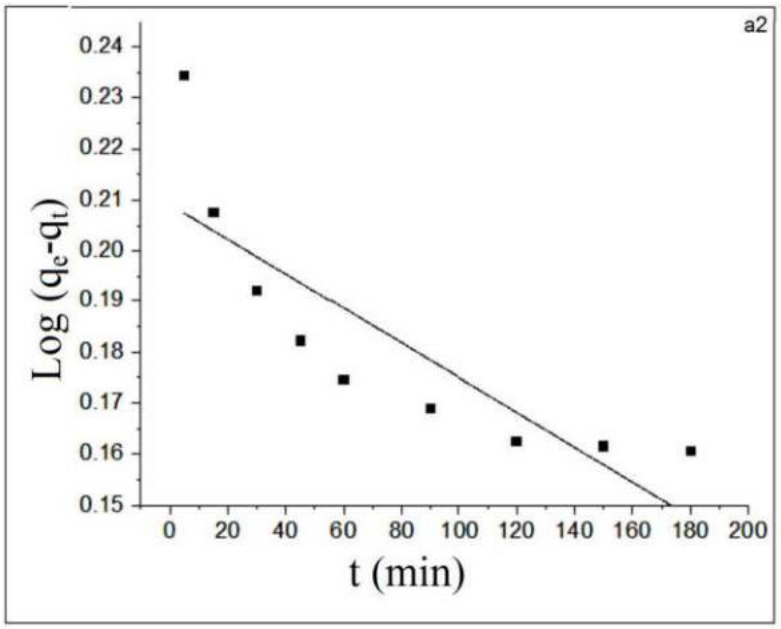

b1
Log q_e
Log C_e

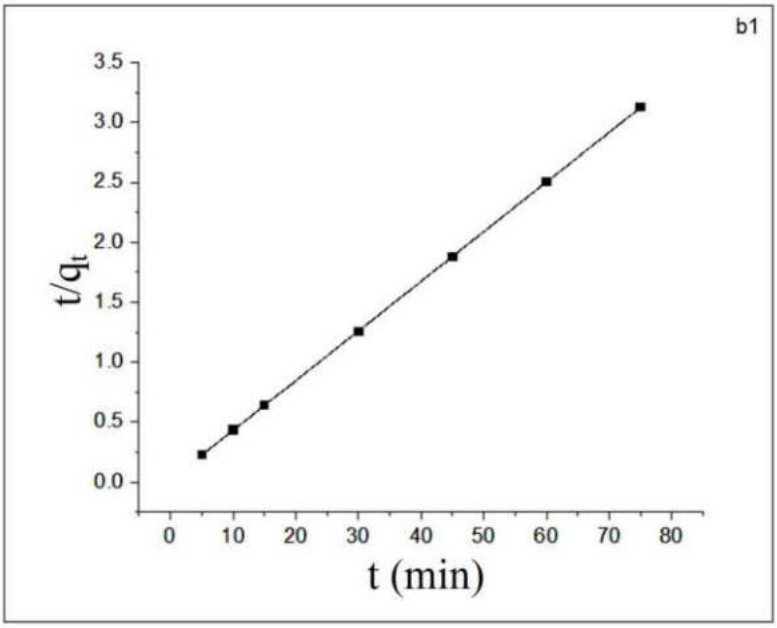

b2
Log q_e
Log C_e

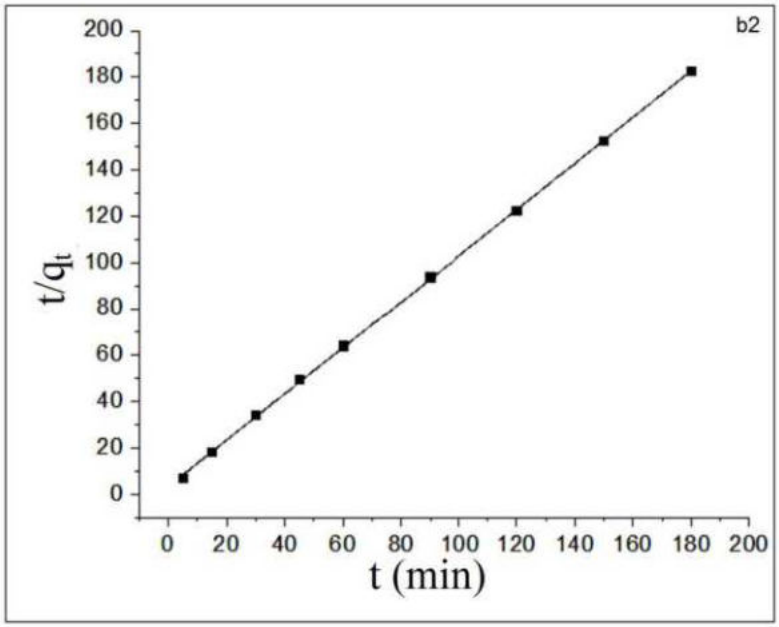

c1
Experimental q_e
Langmuir
Freaundlich
q_e (mg/g)
C_e (mg/L)

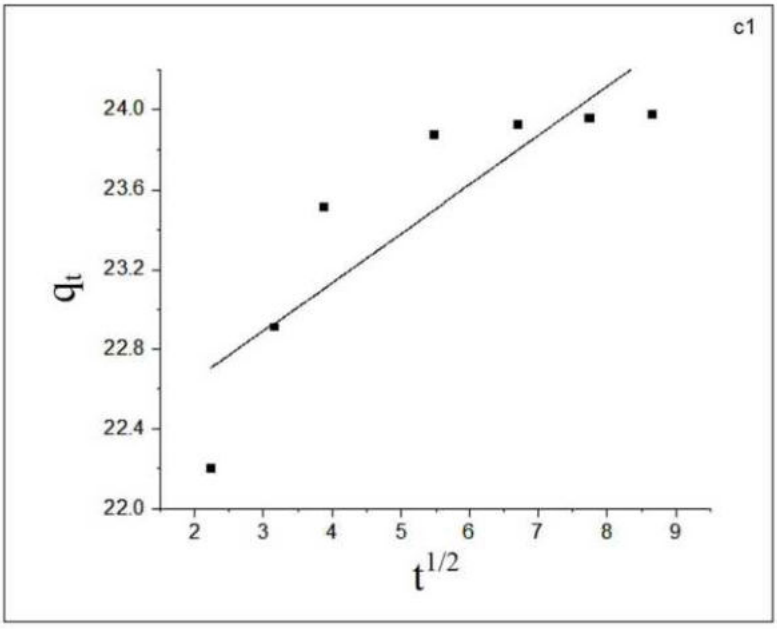

c2
Experimental
Langmuir
Freundlich
q_e (mg/g)
C_e (mg/L)

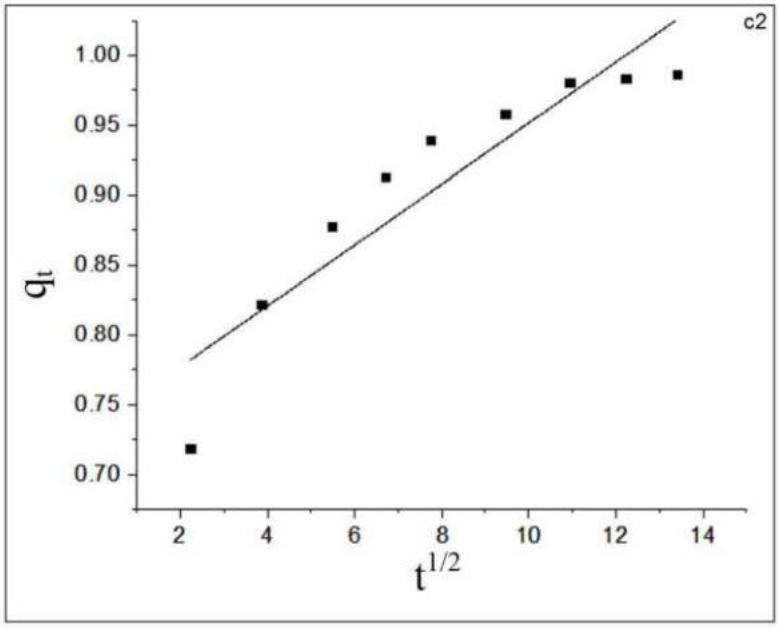

a1
Log (qe-qt)
t (min)

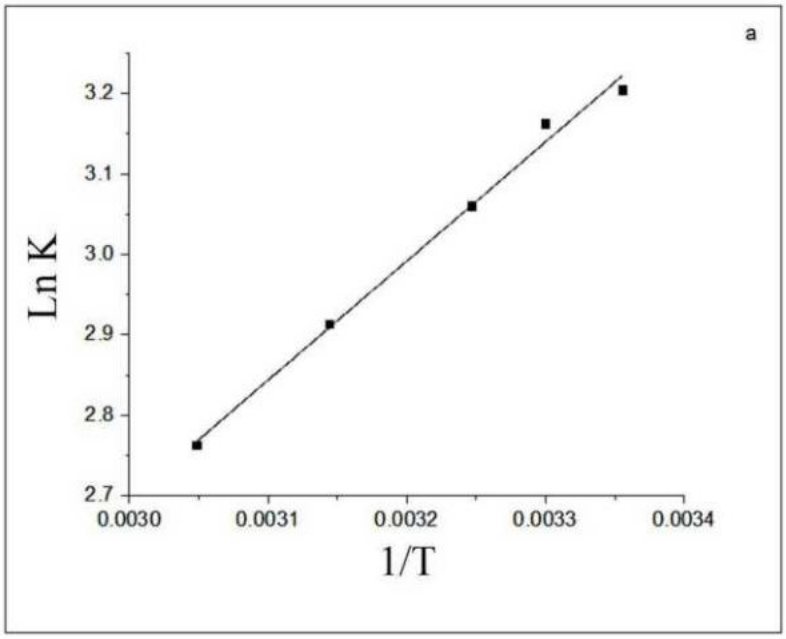

a2
Log (qe-qt)
t (min)

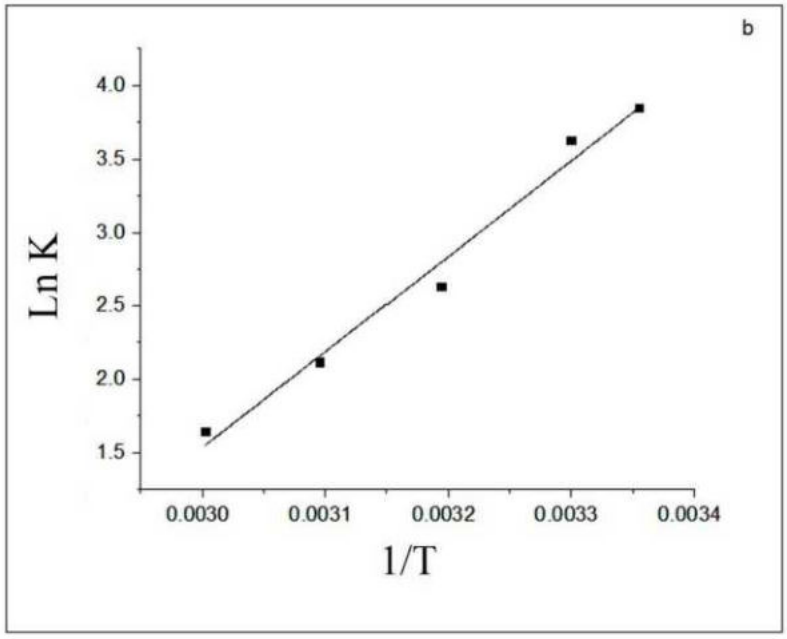

b1
t/qt
t (min)

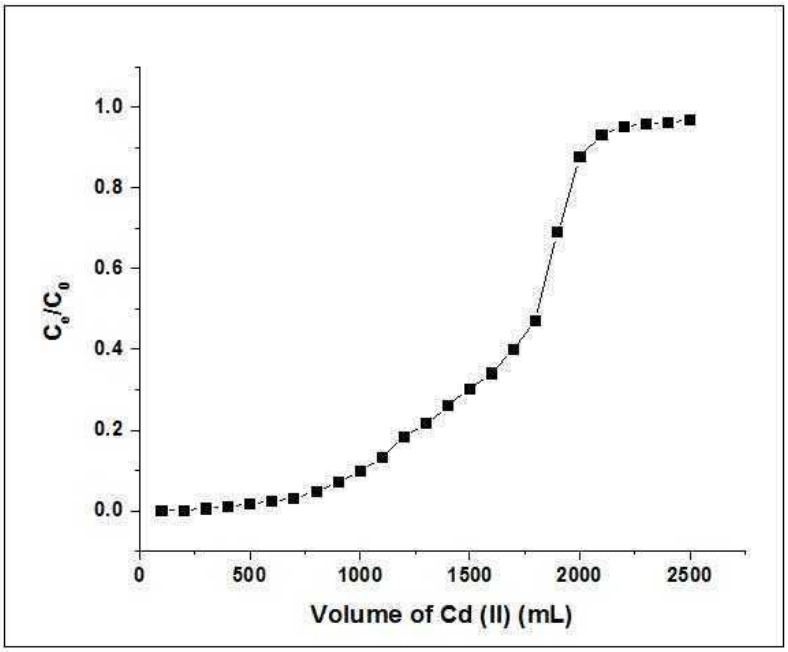

b2
t/qt
t (min)

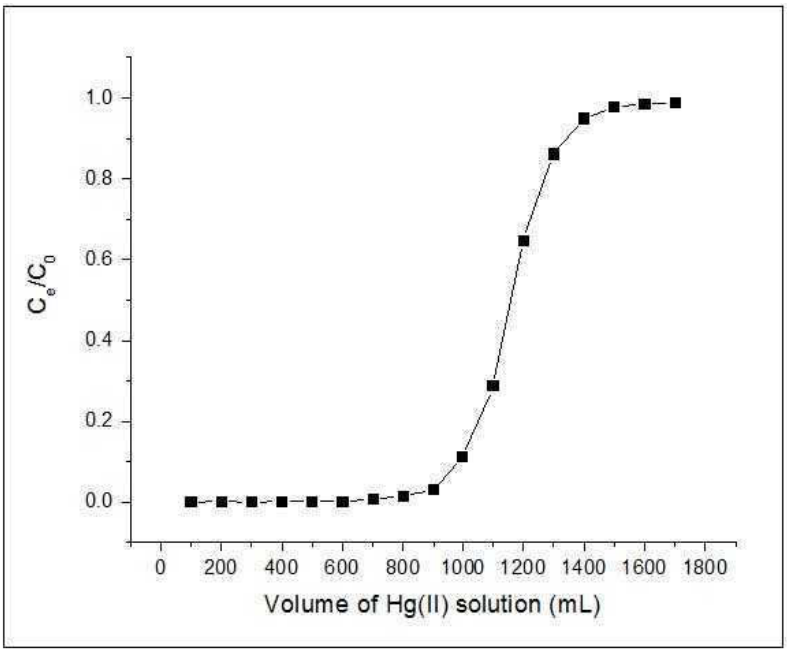

c1
qt
t1/2

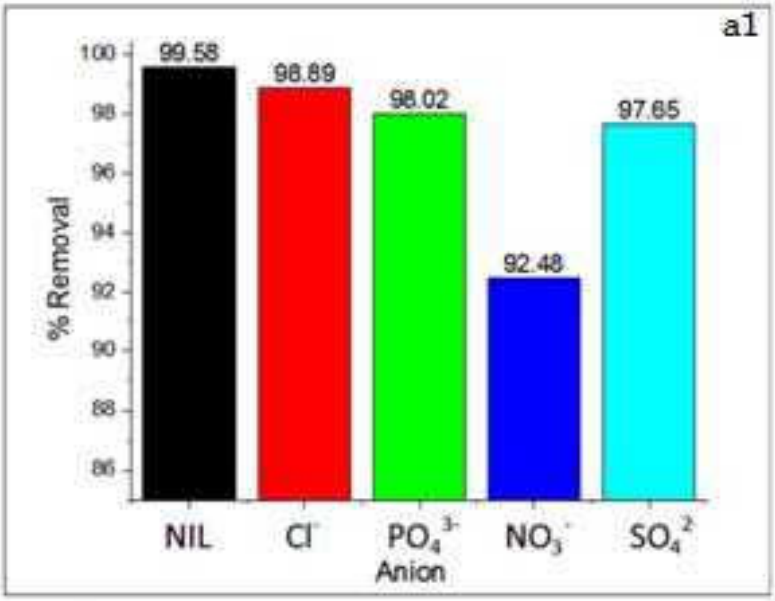

c2
qt
t1/2

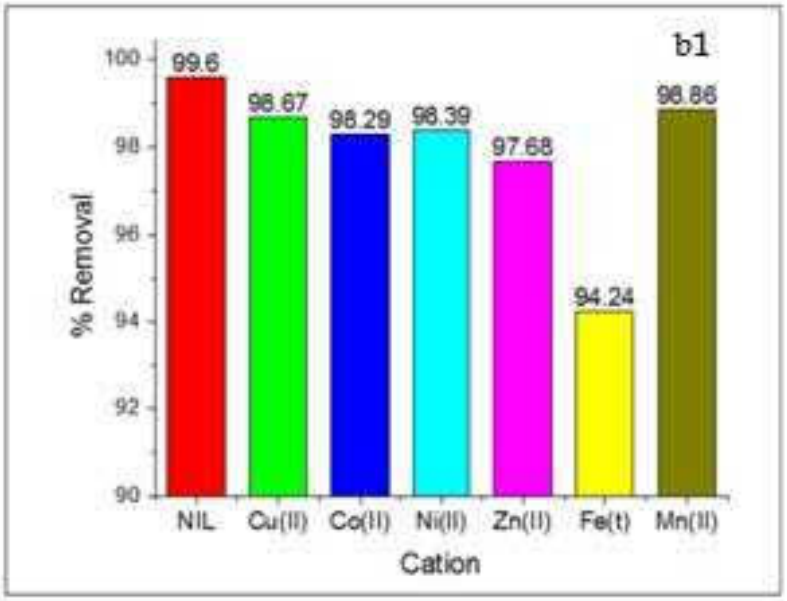

a
Ln K
3.2
3.1
3.0
2.9
2.8
2.7
0.0030
0.0031
0.0032
0.0033
0.0034
1/T

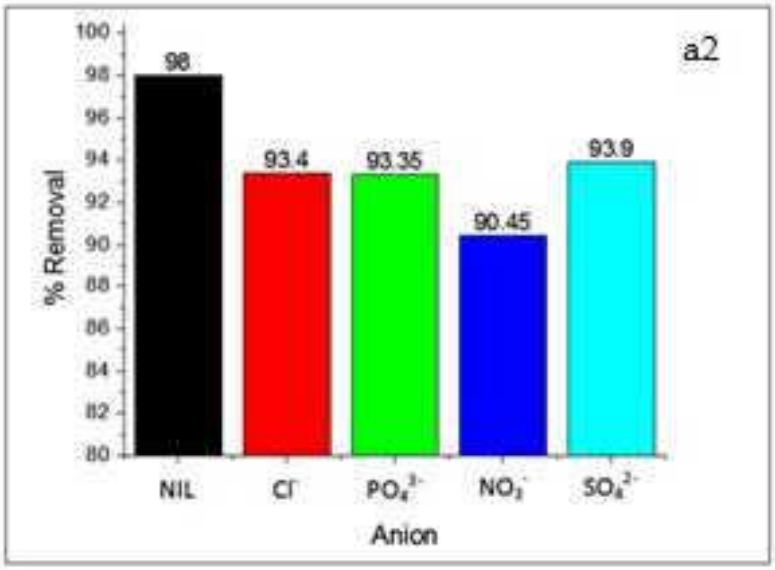

b
Ln K
4.0
3.5
3.0
2.5
2.0
1.5
0.0030
0.0031
0.0032
0.0033
0.0034
1/T

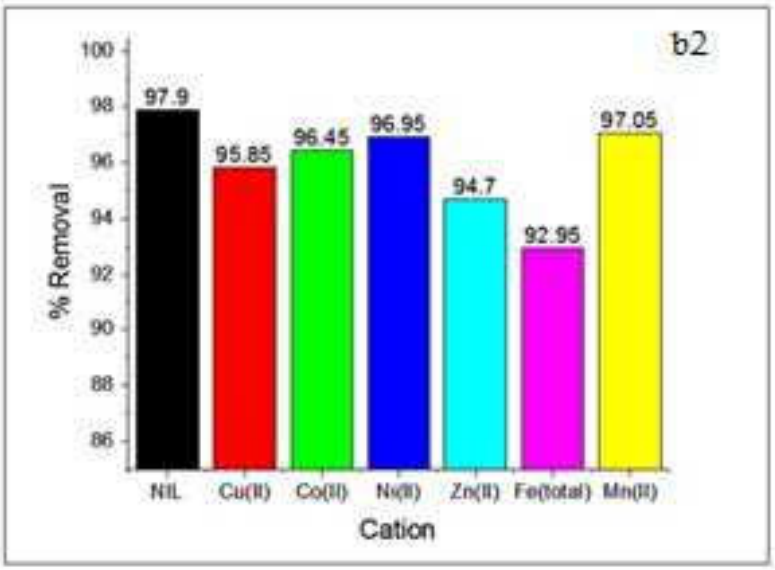

1.0
0.8
0.6
0.4
0.2
0.0
C_e/C_0
0
500
1000
1500
2000
2500
Volume of Cd (II) (mL)

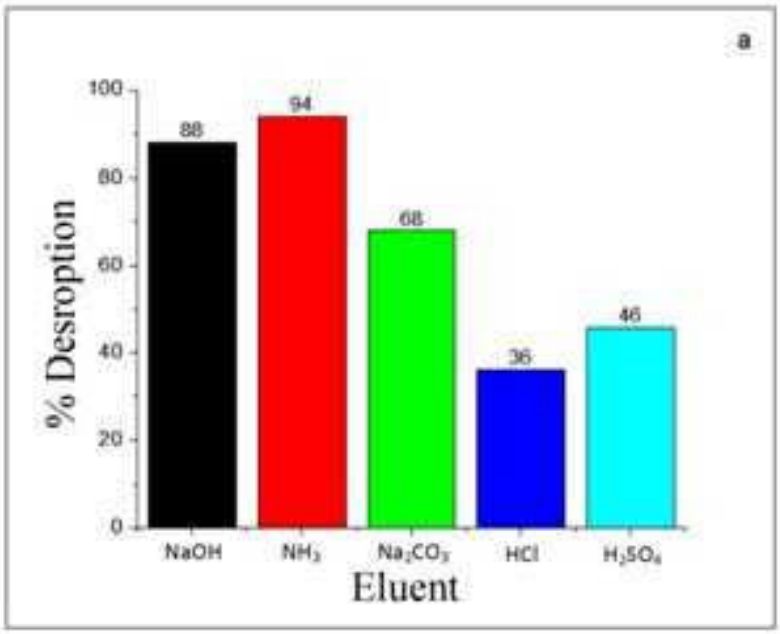

1.0
0.8
0.6
0.4
0.2
0.0
C_e/C_0
0
200
400
600
800
1000
1200
1400
1600
1800
Volume of Hg(II) solution (mL)

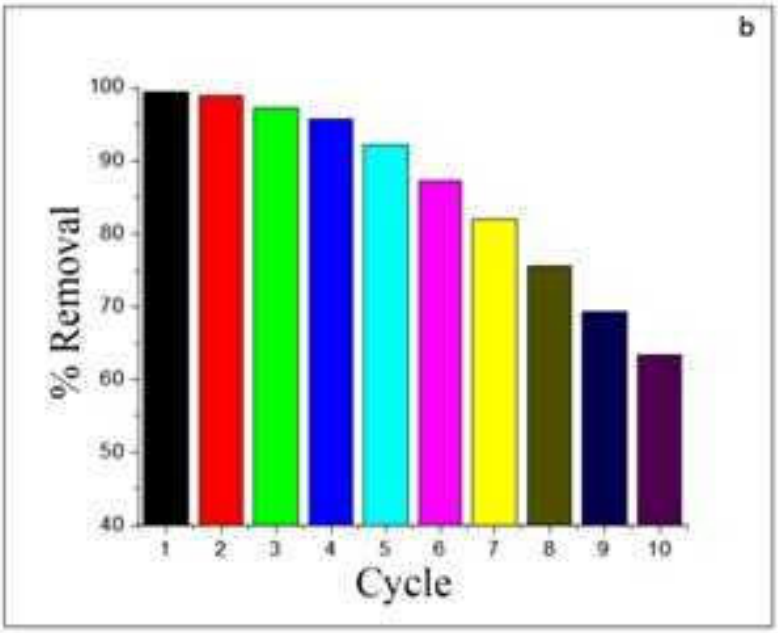

a1
% Removal
100
98
96
94
92
90
88
86
99.58
98.89
98.02
92.48
97.65
NIL
Cl-
PO4 3-
NO3-
SO4 2-
Anion

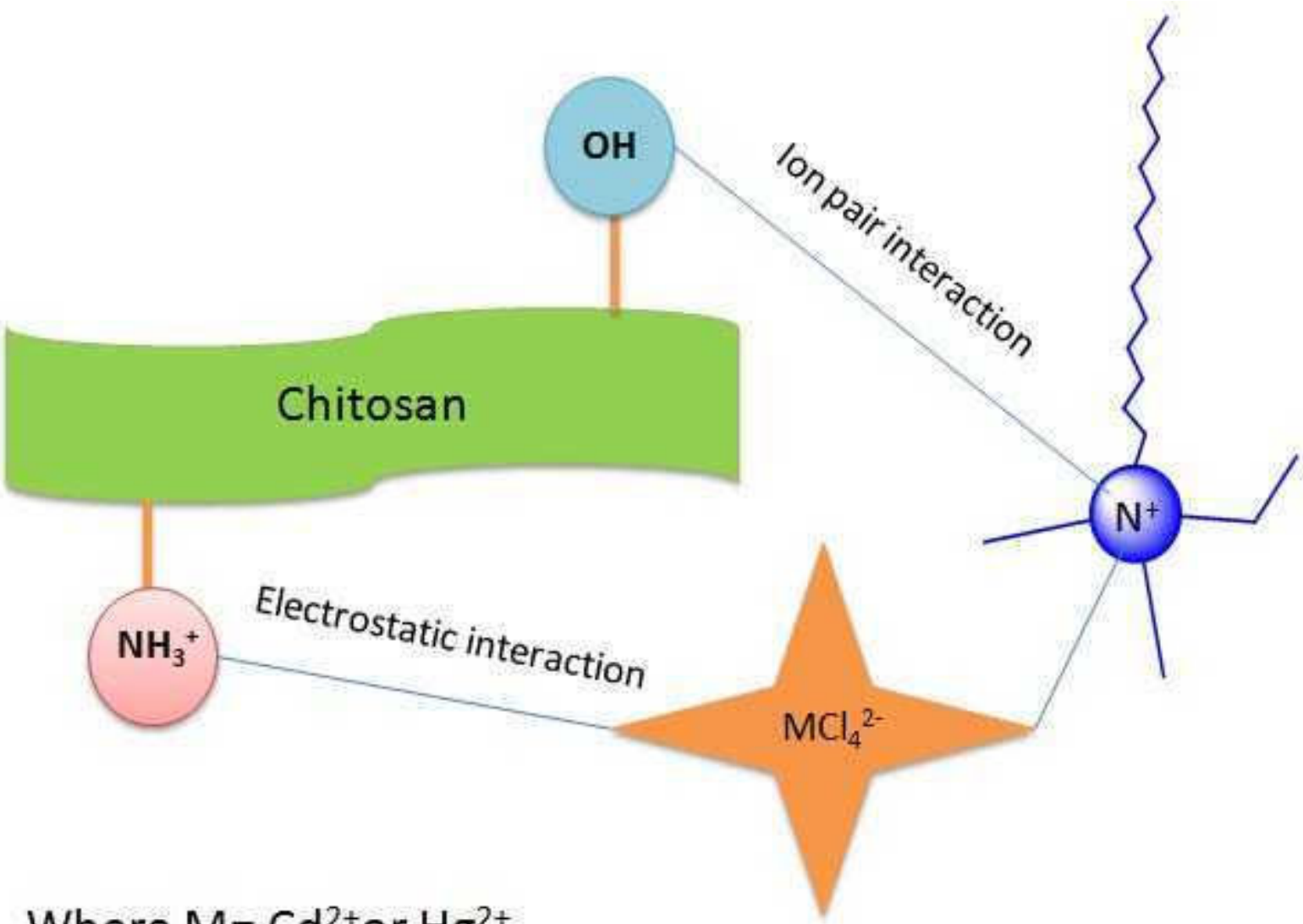

b1
% Removal
100
98
96
94
92
90
99.6
98.67
98.29
98.39
97.68
94.24
98.86
NIL
Cu(II)
Co(II)
Ni(II)
Zn(II)
Fe(t)
Mn(II)
Cation


a2
% Removal
100
98
96
94
92
90
88
86
84
82
80
98
93.4
93.35
90.45
93.9
NIL
Cl-
PO4 3-
NO3-
SO4 2-
Anion


b2
% Removal
100
98
96
94
92
90
88
86
97.9
95.85
96.45
96.95
94.7
92.95
97.05
NIL
Cu(II)
Co(II)
Ni(II)
Zn(II)
Fe(total)
Mn(II)
Cation


a
% Desroption
100
80
60
40
20
0
88
94
68
36
46
NaOH
NH3
Na2CO3
HCl
H2SO4
Eluent


b
% Removal
100
90
80
70
60
50
40
1
2
3
4
5
6
7
8
9
10
Cycle



Where M= Cd^{2+}or Hg^{2+}

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Kinetics and Mechanism of Oxidation of Tartaric Acid by N-Chloronicotinamide (NCN)

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ABSTRACT

The oxidation of tartaric acid by N-chloronicotinamide in the presence of H_2SO_4 is studied. First order kinetics with respect to NCN is observed. The kinetics results indicate fractional order dependence about [tartaric acid]. Inverse first order in [nicotinamide] and inverse fractional order about $[H^+]$ are noted. Rate of the reaction increases with a decrease in the percentage of acetic acid. The values of rate constants observed at four different temperatures were utilized to calculate the activation parameters. A suitable mechanism consistent with the experimental findings has been proposed.

Keywords: Tartaric acid, N-Chloronicotinamide, oxidation, mechanism

INTRODUCTION

The kinetics of the oxidation of hydroxy acids has been studied with a number of oxidizing agents like potassium bromate, hexamethylenetetraminebromine, sodium N-chlorobenzenesulfonamide, N-bromoacetamide, ditelluratocuprate(III), 2,2- bipyridium chlorochromate, benzo-dipteridine etc. Although hydroxy acids have been utilized for a number of catalyzed reactions, nobody has examined the role of catalysts in NBN oxidation of hydroxy acids. Malic acid is a key intermediate in the major biochemical energy-producing cycle in cells, known as the Kreb's cycle, it takes place in the cells mitochondria in most living organisms. The body synthesizes malic acid during the process of converting carbohydrates to energy. Preliminary evidence suggests that individuals with the disease fibromyalgia (a disorder that involves fatigue and pain in the muscles) might have difficulty in creating or utilizing malic acid . Such a deficiency could interfere with normal muscle function. A.K. Singh [1] studied the kinetics and mechanism of oxidation of some hydroxy acids by N-bromoacetamide. Chand Waqar [2] investigated the

mechanism of Ru(III)-catalysed oxidation of glycollic and mandelic acids with N-bromosuccinimide in acidic media**.** Pradeep K. Sharma [3] reported the oxidation of some α-hydroxy acids by tetraethyl ammonium chlorochromate.Ajaya Kumar Singh[4] followed the kinetic and mechanistic study on the oxidation of hydroxy acids by N-bromophthalimide in the presence of a micellar system. E.V. Sundaram[5] explained the oxidation of α-hydroxy acids with Quinolinium Dichromate .Asim K Das[6] studied the micellar effect on the reaction of Chromium(VI) oxidation of some representative alpha-hydroxy acids in the presence and absence of 2,2'-bipyridyl in aqueous acid media. A perusal of literature shows that the reactivity of N-chloronicotinamide (NCN) could be compared with other N-haloimide such as N-bromosuccinimide (NBS) and N-bromosaccharin (NBSa). There are several reports available in the literature on the oxidation of alpha-hydroxy acids by oxidants such as N-bromosuccinimide, N-bromoacetamide , potassium bromate , N-bromobenzenesuphonamide , and iodate[7] However, the details of oxidation of tartaric acid by N-chloronicotinamide are yet to be explored. This encouraged the systematic kinetic study on the oxidation of tartaric acid by NCN in aqueous acetic acid medium.

Materials and methods

Abbreviations

NCN N-Chloronicotinamide

TA Tartaric acid

NA Nicotinamide

Preparation and standardisation

N-Chloronicotinamide (NCN) was prepared by the reported method [8]. Standard solution of NCN was prepared afresh in water and its purity was checked iodometrically. Tartaric acid ((Merck) was used. $HClO_4$ (A.R. grade) diluted with double distilled water and was standardized via acid–base titration. All other standard solutions of $NaClO_4$, KCl, KBr and nicotinamide were prepared using double distilled water. Double distilled water was distilled over $KMnO_4$ in an all glass (Pyrex) distillation set up. Distilled acetic acid was used throughout the experiment.

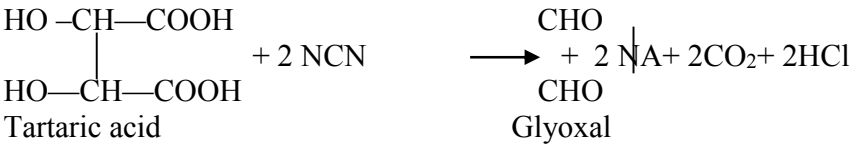
Kinetic Measurements

The solution of tartaric acid and oxidant were kept in black coated bottles separately. These solutions were kept in the thermostat to attain the thermostatic temperature. The appropriate quantity of oxidant was added to the substrate containing other reagents and the reaction bottle was shaken well. The reaction was followed potentiometrically by

setting up a cell made up of the reaction mixture into which the platinum electrode and reference electrode(SCE) were dipped. The e.m.f of the cell was measured periodically using a Equip-Tronics (EQ-DGD) potentiometer. The reactions were studied at constant temperature 35°C. Different studies such as variation of tartaric acid, oxidant (NCN), sulphuric acid, sodium perchlorate, nicotinamide and temperature were carried out. The reaction was carried out under pseudo-first order condition ([tartaric acid] >>[NCN]). The pseudo-first order rate constants computed from the linear ($r^2 > 0.9990$) plots of log (E_t–E_∞) against time. Duplicate kinetic runs showed that the rate constants were reproducible within ±3%. The course of the reaction was studied for more than two half-lives.

Stoichiometry

The reaction mixture containing a known excess of [NCN] >> [tartaric acid] was kept in the presence of H_2SO_4 and $Hg(OAc)_2$ at 40°C for 72 h. After completion of the reaction, the unconsumed NCN was calculated iodometrically. It was found that nearly 2 moles of NCN were consumed for each mole of tartaric acid.



Product Analysis

The presence of glyoxal as the main oxidation product was detected by the spot test [9] and the 2,4-dinitrophenylhydrazine method [10].

Results

The kinetic results for the oxidation of tartaric acid by
N-Chloronicotinamide (NCN) can be summarized as follows. The kinetic studies were carried out under pseudo-first order conditions with [tartaric acid] >> [NCN].

The kinetics of the oxidation of tartaric acid by NCN in presence of $HClO_4$ was investigated at several initial concentrations of the reactant. The reaction was of first order linearity of a plot of log [NCN] versus time for tartaric acid. The rate constants at different initial [NCN] are reported.

Table 1- Effect of variation of [NCN] on reaction rate

[Tartaric acid]=0.03mol dm^{-3}, $[H_2SO_4]$=0. 1mol dm^{-3},

AcOH:H_2O (1:4), [$NaClO_4$]=0.1mol dm^{-3}, Temp. =308 K

[NCN] 10^4 moldm^{-3}	**10^5 k_{obs} sec^{-1}**
1.0	35.01
1.5	23.45
2.0	17.43
2.5	14.05
3.0	11.84
4.0	9.06
5.0	7.14

Table 1 summarizes the pseudo first order rate constant's dependence on the NCN concentration. It was observed that, with the increase in initial NCN concentration, the value of rate constant decreased . At a constant value of NBN, H_2SO_4, the rate constant was determined at different initial concentrations of tartaric acid ranging from 5×10^{-3} to 50×10^{-3} mol dm^{-3}. Table 2 summarizes the pseudo first order rate constant's dependence on tartaric acid concentration. The rate constant, increased with increasing [tartaric acid]. The plot of log k versus log [tartaric acid] was linear with a slope of less than unity showing fractional order dependence on [tartaric acid]. Furthermore, a plot of log k versus [tartaric acid] was linear with an intercept on y axis, confirming the fractional order dependence on substrate. The rate constant k decreased with increase in [H_2SO_4] from 5×10^{-3} to 50×10^{-3} mol dm^{-3} (Table 2) . This may be due to protonation of the substrate. The plot of log k versus log[H_2SO_4] is linear with negative slope. The slope being less than unity indicates inverse fractional order dependence on [H_2SO_4]. Successive addition of nicotinamide (as one of the oxidation products of NCN) to the reaction mixture showed a decreasing effect on the rate of oxidation of tartaric acid. Addition of $NaClO_4$ (to study the effect of ionic strength) in the reaction mixture showed an insignificant effect on the rate of oxidation. In order to find the effect of dielectric constant (polarity) of the medium on the rate, the oxidation of tartaric acid by NCN was studied in aqueous acetic acid mixtures of various compositions (Table 2). The data clearly reveal that the rate of reaction increases with a decrease in the percentage of acetic acid, i.e., increasing dielectric constant or polarity of the medium leads to the inference that there is a charge development in the transition state involving a more polar activated complex than the reactants [11].

Table 2- Effect of variation of [Tartaric acid], [$HClO_4$] and the dielectric constant on reaction rate

[NCN]=0.00015 mol dm^{-3} [$NaClO_4$]=0.1mol dm^{-3},
Temp. =308K

10^3[TA]	10^3[H_2SO_4]	CH_3COOH %(v/v)	10^5 $k_{(obs)}$ sec^{-1}
5	10	20	5.56
10	10	20	9.74
20	10	20	16.75
25	10	20	19.91
30	10	20	23.55
40	10	20	29.01
50	10	20	34.74
30	5	20	34.41
30	10	20	23.52
30	20	20	16.49
30	25	20	14.68
30	30	20	13.25
30	40	20	11.35
30	50	20	10.01
30	10	20	23.55
30	10	25	20.90
30	10	30	18.11
30	10	40	13.14
30	10	50	8.56

In the present case, KBr has no effect on the reaction rate where as the rate of reaction increased with an increasing concentration of KCl.

Effect of temperature

Increase in temperature increases the rate of oxidation and plot of log k_{obs} Vs reciprocal of temperature is linear. The oxidation of tartaric acid by NCN was studied at different temperatures (303K to 323K) (Table 3) and the activation parameters were evaluated (Table 4). Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place.

Table 3-Effect of Temperature on reaction rate

[Tartaric acid]=0.03 mol dm^{-3} $[H_2SO_4]$=0.01mol dm^{-3},
[NCN]=0.0015 mol dm^{-3} $[NaClO_4]$=0.1mol dm^{-3},
AcOH:H_2O (1:4)

Temperature K	**10^5 k_{obs} sec^{-1}**
303	18.85
308	23.31
313	28.52
318	34.96
323	42.61

Substrate	**E_a kJmol^{-1}**	**$\Delta H^{\#}$ kJmol^{-1}**	**$\Delta S^{\#}$ J K^{-1}mol^{-1}**	**$\Delta G^{\#}$kJmol^{-1}**
Tartaric acid	14.32	16.88	– 168.7	66.22

Table 5- Activation Parameters

Test for Free Radicals

To test for the presence of free radicals in the reaction, the reaction mixture containing acrylamide was kept for 24 h in an inert atmosphere. When the reaction mixture was diluted with methanol, the formation of a precipitate was not seen. This suggests that there is no possibility of formation of free radicals in the reaction.

Mechanism

It has been reported [12] earlier that NCN is a stable oxidizing and chlorinating agent because of the large polarity of the N–Cl bond. NCN, like other similar N-haloimides, may exist in various forms in an acidic medium, that is, free NCN, protonated NCN, Cl^+, HOCl, $(H_2OCl)^+$ according to the following equilibria.

$$NCN + H_2O \rightleftharpoons HOCl + NA \quad (1)$$

$$NCN + H^+ \rightleftharpoons NA + Cl^+ \quad (2)$$

$$NCN + H^+ \rightleftharpoons [NCNH]^+ \quad (3)$$

$$HOCl + H^+ \rightleftharpoons [H_2OCl]^+ \quad (4)$$

Addition of nicotinamide to the reaction mixture decreases the rate of oxidation in acidic media suggesting that the pre-equilibrium step involves a process in which nicotinamide is one of the products. When NCN or $(NCNH)^+$ is assumed as the reactive species, the derived rate laws fail to explain the negative effect of nicotinamide, hence neither of these species can be considered as reactive species. When $(H_2OCl)^+$ is taken as the reactive species, the rate law obtained shows first order kinetics with respect to hydrogen ion concentrations contrary to the observed negative fractional order in H_2SO_4, although it fully explains the negative effect of nicotinamide. Therefore, the possibility of cationic bromine (Cl^+) as a reactive species is also ruled out. Thus, the only choice left is HOCl, which, when considered as the reactive species of NCN, leads to a rate law capable of explaining all the kinetics observations and other effects. Hence, in the light of kinetic observations, HOCl can safely be assumed to be the main reactive species of NCN for the

present reaction. On the basis of the above experimental findings and taking HOCl to be the most reactive species of NBN, the following scheme can be proposed for the kinetics of oxidation of tartaric acid by NCN in acidic medium.

$$NCN + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} HOCl + NA \quad (5)$$

$$HOCl + TA \overset{K_2}{\rightleftharpoons} X^- + (H_3O)^+ \quad (6)$$

$$X^- \xrightarrow[\text{Rate controlling step}]{k} \text{Products} \quad (7)$$

According to above scheme, the rate of disappearance of NBN is given as

$$-\frac{d[NBN]}{dT} = \frac{kK1K2[TA][NBN]TOTAL}{[NA][H+] + K1K2[TA]}$$

where

$[NCN]_{TOTAL} = [NCN]\,[NA]\,[X^-]$

The above rate law is in good agreement with the experimental results.

Conclusion

At the end of this study, it is evident that the reaction rates are enhanced by increase in [tartaric acid] and temperature. Added nicotinamide retards the rate. HOCl is the reactive intermediate leading to product. Glyoxal is the product of oxidation. Suitable mechanism in compliance with experimental observations was proposed and the rate law was derived.

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Synthesis, characterization, crystal structure, *in-vitro* anti-inflammatory and molecular docking studies of 5-mercapto-1-substituted tetrazole incorporated quinoline derivative

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ABSTRACT

A novel 5-mercapto-1-substituted tetrazole incorporated quinoline analog was synthesized. The compound 2-Cyclopropyl-4-(4-fluorophenyl)-3-{1-[2-(4-methoxybenzyloxy)ethyl]1*H*-tetrazol-5-ylsulfanylmethyl} quinoline was characterized by IR, Mass, ^{1}H and ^{13}C NMR spectroscopic techniques. Molecular structure was confirmed by using single crystal X-ray diffraction technique. Thermal behavior was studied by using TGA and DSC techniques. Further, *in vitro* anti-inflammatory and *in silico* docking analysis has been carried out to study the activity of the compound.

1. Introduction

Heterocyclic compounds are well known to possess diverse pharmacological properties, such as antimicrobial, antimalarial and anticancer activities. Recently heterocyclic compounds are gaining more attention and playing vital role in the design and development of biologically potent molecules or lead compounds. Heterocyclic compounds play an important role in designing new classes of medicinally important structural entities. Particularly, the quinoline derivatives continuously gain attention due to its structural features [1]. Quinoline nucleus occurs in several natural compounds, which exhibit wide range of biological activity such as anti-inflammatory [2], antimalarial [3], HIV-1 replication inhibitors [4,5], antituberculosis [6,7] and anthelmintic [8]. Interestingly, quinoline scaffold is prevalent in a variety of biologically active compounds as well as in medicinally important naturally products [9]. In addition, quinoline and its derivatives have been observed as promising nuclei to exhibit anticonvulsant properties [10,11]. Moreover, quinoline scaffolds are also utilized in the synthesis of biologically active molecules such as antitumor [12], antiproliferative [13], anticancer [14] and antiparasitic agents [15]. Aforementioned studies unveiled the biological significance and plethoric applications of quinoline derivatives. So we envisioned to synthesis quinoline based molecule in order to examine its anti-inflammatory activity.

Tetrazoles, a unique five membered heterocycles, possess multifarious applications in medicinal, biochemical and biological chemistry [16–20]. Particularly, 1-substituted tetrazole and 5-mercapto substituted tetrazole derivatives have been used in the preparation of pharmacologically active drugs [21–30]. As pharmaceutical compounds, tetrazoles have cholinesterase inhibitor

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activity [31] and it could be a potential bioisostere for carboxylic acid [32]. The tetrazole scaffolds are known to be superior in resisting metabolic degradation [33–36]. Further, tetrazoles are highly flexible ligands, which can serve as pharmacophore replacement of carboxylic acids in medicinal chemistry as well as in supramolecular chemistry, and it can easily adapt to different binding modes [37–40]. Interestingly1-(2-hydroxyethyl)-5-mercapto tetrazole is the pivotal fragment of flomoxef, a cephalosporin drug, due to its significance in antibacterial activity [41]. Studies have shown that, quinoline and tetrazole fused molecules, resulted in wide variety of biological activities such as anti-inflammatory [42], anti-bacterial [43], antimicrobial [44] and antituberclosis [45].

Based on highly promising biological activities of quinoline and tetrazole derivatives, we envisioned to synthesize quinoline and tetrazole fused analog. Herein, we report the synthesis, characterization, single crystal XRD and anti-inflammatory activity of a novel 5-mercapto-1-substituted tetrazole incorporated quinoline derivative. Molecular docking study was also performed on 2-Cyclopropyl-4-(4-fluorophenyl)-3-{1-[2-(4-methoxybenzyloxy)-ethyl]1*H*-tetrazol-5-ylsulfanylmethyl}quinoline with the targeted Human Histamine H1 Receptor (H1R).

2. Experimental

2.1. Materials and methods

All the raw materials and reagents used for synthesis were procured and used without purification. The compound was prepared as per the synthetic method provided in the experimental section.

Progress of the reaction was monitored by Thin Layer Chromatography (TLC) using a mixture of *n*-Hexane:Ethyl acetate (7:3) as eluent. Analytical TLC was performed on pre-coated aluminium sheets of silica gel 60 F254 of 0.20 mm thickness (Merck, Germany) and compounds were visualized with UV radiation. The melting point was determined by open capillary tube method on a Buchi melting point apparatus and is uncorrected. FT-IR analysis was done over 4000–400 cm^{-1} with 4 cm^{-1} resolution on a Perkin-Elmer spectrum 65 FT-IR Spectrometer. Eight scans were applied to each sample and the average spectra in transmittance mode is collected and processed through Spectrum software. A mass spectrum was recorded on a PE-SCIEX API-300 LC-MS/MS with Turboion spray mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer using $CDCl_3$ as solvent with TMS (tetramethyl silane) as internal standard.

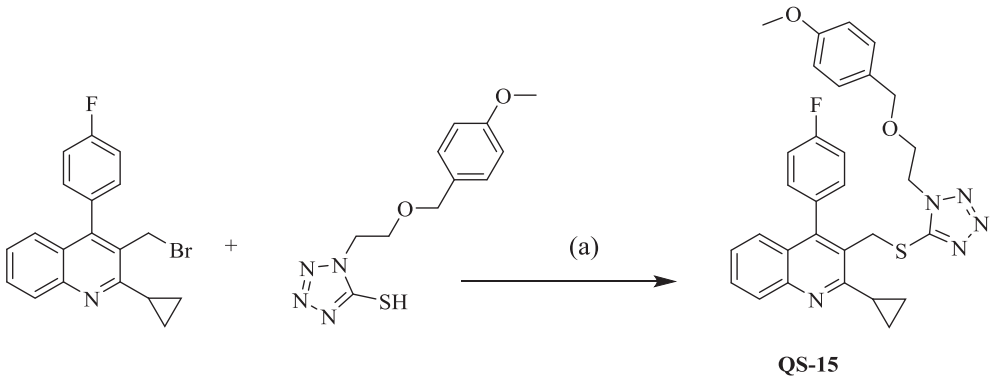
Calorimetric response of the sample was measured using DSC (TA Instruments DSC1000, USA), operating with Universal software (version 4.5A). Prior to analysis, calibration of the instrument was performed using piece of indium (In). The sample (≈2.0–3.0 mg) was weighed and transferred into an aluminum pan and sealed with pin-holed lid. The sample was equilibrated and heated at a rate of 10 °C/min from 25 to 250 °C under nitrogen purge at 40 ml/min.

Thermo gravimetric analysis was performed using TGA (TA Instruments TGA Q500), with Universal software (version 4.5A). TGA system was purged with nitrogen gas at the flow rate of 100 ml/min (60 ml/min for sample and 40 ml/min for balance). About 10 mg of sample was transferred to Aluminium pan and analyzed in the range of 30–350 °C at 10 °C/min temp ramp. Weight calibration of balance was done with certified weights (100 mg and 1000 mg) and temperature calibration was done by using Alumal and Nickel metals. Dry nitrogen was used as a purge gas (sample purge 60 ml/min, balance purge 40 ml/min).

2.2. Synthesis

2.2.1. Preparation of 2-Cyclopropyl-4-(4-fluorophenyl)-3-{1-[2-(4-methoxybenzyloxy)- ethyl]1H-tetrazol-5-ylsulfanylmethyl} quinoline (QS-15)

Anhydrous potassium carbonate (7.76 g, 0.056 mol, 2 eq.) was added to a solution of 3-(bromomethyl)-2-cyclopropyl-4-(4-fluorophenyl)quinoline (10 g, 0.028 mol, 1 eq.) and 1-{2-[(4-methoxybenzyl)oxy]ethyl}-1*H*-tetrazole-5-thiol (7.47 g, 0.028 mol, 1 eq.) in acetone (150 ml) at RT. The reaction mixture was stirred at room temperature for 24 h. The progress of the chemical reaction was monitored by TLC and by completion of the reaction, the reaction mixture was filtered to remove insoluble materials and the clear filtrate was concentrated to thick mass under vacuum at 45–50 °C. The concentrated mass was dissolved in ethyl acetate and washed twice with demineralized water. The organic layer was dried over sodium sulfate and concentrated the clear solution under vacuum at 50–55 °C. To residue methanol (80 mL) was added and the clear solution was stirred for 1 h. The precipitated compound was filtered and washed with chilled methanol (20 mL), which yields 12.8 g (84%) of the final product. The melting point of the compound was determined as 130–132 °C by open capillary method.



QS-15

(a) Reagents and conditions: Anhydrous K_2CO_3, Acetone at RT

Reaction Scheme 1

2.2.2. Crystallization

A supersaturated solution was prepared by dissolving the compound in dichloromethane-cyclohexane mixture (1:1) at ambient temperature. The prepared solution was filtered, slightly warmed and allowed to evaporate slowly at room temperature. After about one week, good quality transparent crystals appeared were allowed to grow to a maximum possible dimension and then harvested. The single crystal obtained was used for X-ray diffraction studies.

2.3. Single crystal X-ray diffraction studies

X-ray diffraction intensity data were collected for compound on Bruker axs Kappa ApexII single crystal X-ray diffractometer equipped with graphite monochromated MoKα (λ = 0.7103 Å) radiation and CCD detector. Crystals were cut to suitable size and mounted on a glass fibre using cyanoacrylate adhesive. The unit cell parameters were determined from 36 frames measured (0.5° phi-scan) from three different crystallographic zones and using the method of difference vectors. The intensity data were collected with an average four-fold redundancy per reflection and optimum resolution (0.75 Å). The intensity data collection, frames integration, Lorentz and polarization correction and decay correction were done using SAINT-NT [46] software. Empirical absorption correction (multi-scan) was performed using SADABS [46] program. The compound crystallized in the monoclinic system. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry indicating space group $P2_1/c$ for compound.

Crystal structure was solved by direct methods using SHELXS-97 [47] and refined by the full-matrix least-squares method using SHELXL-97 [47]. All the non-hydrogen atoms were first refined isotropically and then with anisotropic displacement parameters for compound. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk) as supplementary publication number CCDC 1508929.

2.4. Molecular docking studies

2.4.1. Target protein identification

Target protein was identified using the DINIES server (Drug-target Interaction Network Inference Engine based on Supervised Analysis) which predicts the potential interactions between drug molecules and target proteins based on drug data and omics-scale protein data. Chemogenomic approach with learning on Kyoto Encyclopedia of Genes and Genomes (KEGG) were employed to mine the existing similar drugs against the title compound. We found that, among the predicted results astemizole has similar scaffold as the synthesized compound with high similarity-score of 0.47 [48]. Interestingly, astemizole is known for anti-allergic activity and antagonist for histamine H1 receptor, and in recent days it gained importance in designing in anti-cancer drugs [49,50]. Further studies shows that Tetrazolo [1,5-*a*] quinoline derivative possess anti-inflammatory activity [42]. Thus in this study we have used human histamine H1 target as protein receptor to perform molecular docking analysis. Three-dimensional structural co-ordinates of human histamine H1 receptor (H1R) in complex with doxepin [51] were obtained from RCSB Protein Data Bank (PDB id: 3RZE); the binding site of doxepin was used as the docking site in the present study.

2.4.2. Target protein and ligand structure preparation

All computational works were performed using the molecular modeling software MAESTRO, developed by Schrödinger [52]. The compounds used in the docking study were built using builder panel in MAESTRO and ligand preparation was carried out for these compounds using the Ligprep suite of GLIDE-5.6 (Grid-based Ligand Docking with Energetics) software [53]. Ligprep performs addition of hydrogens, 2D to 3D conversion, realistic bond lengths and bond angles, low energy structure with correct chiralities, ionization states, tautomers, stereochemistries and ring conformations. A utility script named 'hetgrp_ffgen' available within the Schrödinger molecular modeling package was used to generate OPLS2005 force field parameters for each compound. To perform docking, the target protein molecule, human histamine H1 receptor, was prepared by building missing residues/atoms, adding hydrogen atoms, assigning correct bond orders and fixing the orientation of various groups. All amino acid flips were assigned and H-bonds were optimized. Non-hydrogen atoms were minimized using steepest descent algorithm followed by conjugate gradient method until it reached an RMS (root mean square) gradient of 0.001 kcal/mol.

2.4.3. Molecular docking

Molecular docking was performed using Induced Fit Docking (IFD) procedure in which receptor and ligand are kept flexible, so that receptor's side-chain/backbone undergoes conformational changes, which allow the receptor for better binding according to the shape and binding mode of the ligand. The prepared protein was loaded in the workspace and the grid was generated for 5 Å around the active site (experimental binding site of doxepin) of protein to perform IFD. The van der Waal's radii of nonpolar receptor and ligand atoms were scaled by a default factor of 0.50. IFD calculations were carried out for the compound QS-15, astemizole, doxepin and diclofenac sodium with the human histamine H1 receptor. IFD computes 20 docked conformational poses, from which the best conformational pose was selected based on the docking score, glide energy, glide emodel values and non-bonded interactions.

All the molecular modeling simulations were carried out using OPLS-2005 (Optimized Potential Liquid Simulations) force field. PyMOL [54], Chimera [55] and "Ligand Interaction Diagram" of the GLIDE software were used for graphical visualization, analyzing hydrogen bonds and hydrophobic contacts between protein and ligand.

2.5. In vitro anti-inflammatory activity (anti-denaturation assay)

We have followed the previously reported experiment to check the anti-inflammatory activity with minor modification [56]. The standard drug (diclofenac sodium) and the synthesized compound are dissolved in minimum quantity of dimethyl formamide (DMF) and diluted with phosphate buffer (0.2 M, PH 7.4). The final concentration of DMF was maintained at <2.5% in all solutions. The test solution (4 mL) containing different concentrations of drug was mixed with 1 mL of 1 mM albumin solution in phosphate buffer and incubated at 37 °C in incubator for 15 min. Denaturation was induced by keeping the reaction mixture at 70 °C in water bath for 15 min. After cooling, the turbidity was measured at 660 nm. Percentage of inhibition of denaturation was calculated using following formula, from the control where no drug was added.

$$\% \text{ of Inhibition} = 100 \times (A_t - A_c)/A_t$$

where, A_t = O.D. of test solution, A_c = O.D. of control.

3. Results and discussions

The present study describes the synthesis and structural characterization of tetrazole incorporated quinoline analog. The

tetrazole derivative QS-15 was synthesized by the coupling of 3-(bromomethyl)-2-cyclopropyl-4-(4-fluorophenyl)quinoline with 1-{2-[(4-methoxybenzyl)oxy]-ethyl}-1*H*-tetrazole-5-thiol in the presence of anhydrous potassium carbonate. The formation of tetrazole and quinoline fused derivative was confirmed by spectral data and single crystal XRD. The results are presented in the experimental section.

3.1. Structural assignments using spectroscopic data

The compound QS-15 was characterized using IR, Mass and NMR spectral data. The assignment of signals in ^{1}H NMR and ^{13}C NMR spectra for the compound QS-15 was achieved from signal multiplicities, integral values and chemical shifts as well as from the correlations in two-dimensional H–H COSY and ^{1}H–^{13}C heteronuclear HSQC.

3.2. IR spectra analysis

IR spectrum of compound exhibited an absorption band at 1611 cm^{-1} accounted for C=N stretching for aromatic quinoline ring. An absorption band at 670 cm^{-1} was assigned to stretching absorption of C–S group. Besides, a band at 3065–3001 cm^{-1} indicates the aromatic C–H stretching vibrations (Fig. S1).

IR (KBr, υ, cm^{-1}): 3434 ($\upsilon_{aliphatic\text{-}C\text{-}N\text{-}tetrazole}$), 3067, 3045, 3001 ($\upsilon_{aromatic\ =C-H}$), 2954, 2906, 2862, 2833 (υ_{C-H}), 1611 ($\upsilon_{C=N}$), 1578 & 1512 ($\upsilon_{C=C}$), 1450(υ_{CH2}), 1389 (υ_{CH3}), 1302($\upsilon_{-N-N=N-}$), 1248 & 1041(υ_{C-O}), 840 ($\upsilon_{CH\ bend}$), 761 ($\upsilon_{Aliphatic\ CH}$).

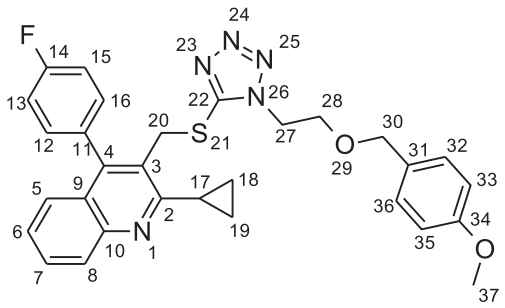
3.3. Mass spectra analysis

MS data was acquired in positive ionization FIA mode and is displayed in Fig. S4. The ESI mass spectrum of the compound (QS-15) displayed the protonated molecular ion at *m/z 542.2*. Therefore the molecular weight of this compound would be 541.0 amu. The mass number showed the presence of odd number of nitrogen atom in the compound.

ESI-MS: *m/z* 542.2 $[M+H]^{+}$.

3.4. ^{1}H and ^{13}C NMR analysis

In addition to ^{1}H and ^{13}C spectrum for QS-15 compound, ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSQC spectra were recorded to confirm the assignments (Figs. S5–S14).



Structure of the compound QS-15

^{1}H NMR spectrum of QS-15 shows a singlet at 3.75 ppm. This is due to the methyl protons attached at C-37. A multiplet at 2.41 ppm shows methine protons at C-17 and is further confirmed by H–H COSY correlations (vicinal coupling partner is confirmed by observing a cross peak between the methine protons at C-17 and attached methylene protons at C-18 & C-19). A singlet centered at 4.70 ppm corresponds to the methylene protons at C-20, flanked by electronegative sulphur atom. Appearance of singlet further confirms there is no adjacent vicinal protons and it does not have any cross peaks in H–H COSY experiment. The triplet at 3.76 ppm with coupling constant 5.5 Hz, indicates the methylene protons at C-28, splitting pattern shows the adjacent two vicinal protons and is further confirmed by the H–H COSY cross peaks. The triplet at 4.33 ppm with a coupling constant of 5.5 Hz indicates the methylene protons at C-27 and its vicinal protons further confirmed by H–H COSY correlation.

A multiplet at 2.43 ppm in ^{1}H NMR corresponds to –CH proton of cyclopropane ring, which was confirmed by H–H COSY experiment in which it couples with $-CH_2$ protons of cyclopropane ring. The corresponding carbon signal was assigned by HSQC experiment and also it exhibits a positive signal in DEPT-135. The $-CH_2$ protons of cyclopropane ring at 10.10 ppm exhibit a negative signal in DEPT-135.

The two multiplets at 1.06 ppm and 1.35 ppm shows the two methylene protons at C-18 and C-19, and their multiplicity are due to the coupling of germinal as well as vicinal protons. The fact is concordance with the observation of cross peaks in H–H COSY experiment. The singlet centered at 4.36 ppm is assigned for methylene protons at C-30. The doublet of doublet in the most downfield region of about 7.97–7.98 ppm is due to aromatic ring proton at C-8 position of heterocyclic ring. The two multiplets at 7.62–7.65 ppm and 7.31–7.35 are due to aromatic ring protons at C-7 and C-6 respectively.

In ^{13}C NMR spectrum of the compound QS-15, there are two signals in the region of 163.7 ppm and 161.8 ppm. These are characteristic for ring carbon attached to fluorine atom. The signals in the region of 114–164 ppm are due to aromatic carbons. Among this the less intense signals with higher chemical shift values in the region of 124–164 ppm are characteristic for *ipso* carbons. The positive signal at δ 14.94 corresponds to methane –CH of cyclopropyl ring. The positive signal at δ 55.25 corresponds to methyl carbon of $-OCH_3$ group, which is attached to phenyl ring.

From the HSQC spectrum of compound QS-15, it is evident that the contour of aromatic =C–H protons (6.78–6.81 ppm) attached at C-33 and C-35 shows correlation with 113.9 ppm in carbon spectrum and hence the unambiguous assignment is completed. Similarly the contour of HSQC spectrum showing the correlation of 2.41 ppm in ^{1}H NMR spectrum with 14.9 ppm in ^{13}C NMR spectrum, confirming the carbon chemical shift of methine group (C-17). These HSQC of compound QS-15 correlations are further confirmed by DEPT-135 spectrum where the carbon signals are observed for those having the attached protons. The methyl and methine carbons are observed as positive peak and methylene carbons are observed as negative peak at the respective chemical shift of ^{13}C NMR spectrum. The presence of six negative signals in DEPT-135 experiment confirmed the presence of six methylene protons. The ten positive signals in DEPT-135 correspond to twelve aryl carbons in which two of them appeared as single signal. The ten extra

Table 1
Correlation in HOMOCOSY and HSQC of compound QS-15 (δ, ppm).

^{1}H NMR signal	DEPT-135	Correlation in HOMOCOSY	Correlation in HSQC
1.06(H(18))	Negative	1.35(H(19)), 2.41(H(17))	10.10(C(18))
1.35(H(19))	Negative	1.06(H(18)), 2.41(H(17))	10.10(C(19))
2.41(H(17))	Positive	1.06(H(18)), 1.35(H(19))	14.90(C(17))
3.75(H(37))	Positive	–	55.25(C(37))
3.76(H(28))	Negative	4.33(H(27))	66.82(C(28))
4.33(H(27))	Negative	3.76(H(28))	47.50(C(27))
4.36(H(30))	Negative	–	72.88(C(30))
7.32(H(6))	Positive	7.63(H(7)), 7.22(H(5))	125.85(C(6))
7.63(H(7))	Positive	7.32(H(6)), 7.98(H(8))	129.60(C(7))
7.98(H(8))	Positive	7.63(H(7))	129.01(C(8))

Table 2
Crystal data and structure refinement.

Parameters	Values
Empirical formula	C_{30} H_{28} F N_5 O_2 S
Formula weight	541.63
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 15.6975(12) Å b = 9.4080(6) Å c = 18.5514(12) Å β = 101.615(2)°
Volume	2683.6(3) $Å^3$
Z, Calculated density	4, 1.341 Mg/m^3
Absorption coefficient	0.165 mm^{-1}
F(000)	1136
Crystal size	0.40 × 0.35 × 0.35 mm
Theta range for data collection	2.242 to 26.343°
Limiting indices	$-19 \le h \le 19$ $-11 \le k \le 11$ $-23 \le l \le 23$
Reflections collected/unique	32382/5463
[R_{int}]	0.0346
Completeness to θ = 25.242	99.90%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5463/0/353
Goodness-of-fit on F^2	1.04
Final R indices [I > 2σ(I)]	R1 = 0.0671, w*R*2 = 0.1457
R indices (all data)	R1 = 0.1058, w*R*2 = 0.1720
Largest diff. peak and hole	1.062 and −0.916 e A^{-3}

signals in ^{13}C NMR other than DEPT-135 experiment correspond to quaternary carbon.

With the help of all these experiments, all the signals are assigned without ambiguity and complete skeleton of the molecular structure is established. Correlation in HOMOCOSY and HSQC of compound QS-15 is given in Table 1.

3.4.1. ^1H NMR ($CDCl_3$, 500 MHz) δ ppm

1.06–1.08(m, 2H), 1.35–1.38(m, 2H), 2.41–2.45(m, 1H, 17-CH), 3.75(s, 3H, 37-CH_3), 3.76–3.78(t, 2H, 28-CH_2, J = 5 Hz), 4.33–4.35(t, 2H, 27-CH_2, J = 5 Hz), 4.36(s, 2H, 30-CH_2), 4.69(s, 2H, 20-CH_2), 6.78–6.81(m, 2H, 33-CH & 35-CH), 7.07–7.10(m, 2H, 32-CH & 36-CH), 7.15–7.19(m, 2H, 13-CH & 15-CH), 7.22–7.27(m, 3H), 7.31–7.35(m, 1H, 6-CH), 7.61–7.65(m, 1H, 7-CH), 7.97–7.98(dd, 1H, 8-CH).

3.4.2. ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm

10.10(C18 & C19), 14.94(C17), 33.77(C20), 47.50(C27), 55.25(C37), 66.82(C28), 72.88(C30), 113.86(C33 & C35), 115.70 (C13), 115.87(C15), 124.52(C10), 125.85(C6), 126.24(C31), 126.31(C5), 129.01(C8), 129.13(C3), 129.18(C32 & C36), 129.60(C7), 130.93(C12), 130.99(C16), 131.80(C11), 147.35(C4), 147.65(C9), 154.27(C34), 159.42(C2), 161.57(C22), 161.75 & 163.72 (C14).

3.5. Thermal analysis

Thermal behavior of the compound QS-15 has been investigated using TGA and DSC techniques.

3.5.1. TGA

TGA thermogram (Fig. S2) shows that there is no weight loss up to 200 °C that clearly illustrates the absence of physically adsorbed and lattice water. Further, there is a stepwise weight loss observed at about 235 °C which indicates the decomposition of compound.

3.5.2. DSC

DSC thermogram (Fig. S3) shows a sharp endothermic peak at about 131.5 °C and an exothermic peak at about 226.1 °C. The endothermic peak corresponds to melting of the compound. The exothermic peak corresponds to decomposition of the compound.

3.6. Crystal structure analysis

The title compound (C_{30} H_{28} F N_5 O_2 S) was crystallized in $P2_1/c$, monoclinic space group with cell constants: a = 15.6975(12)Å, b = 9.4080(6)Å, c = 18.5514(12)Å, β = 101.615(2)°. The asymmetric unit contains only one molecule of the compound. The relevant crystal data and the structural refinement parameters of QS-15 are presented in Table 2. Selected bond lengths, bond angles and torsion angles are given in Table 3 and hydrogen bonding interactions

Table 3
Selected bond lengths, bond angles and torsion angle.

Atoms	Length(Å)	Atoms	Angle(°)	Atoms	Angle(°)	Atoms	Angle(°)
C2–N1	1.318(4)	N1–C2–C3	122.4(3)	N1–C2–C3–C4	0.4(4)	N5–C18–N2–N3	0.7(4)
C6–N1	1.366(4)	N1–C2–C29	116.9(3)	N1–C2–C3–C17	−178.2(3)	S1–C18–N2–N3	−179.9(3)
C14–F1	1.356(3)	N1–C6–C5	122.6(3)	C10–C5–C6–N1	−179.0(3)	C18–N2–N3–N4	0.0(4)
C17–S1	1.822(3)	N1–C6–C7	117.9(3)	C4–C5–C6–N1	0.4(4)	N2–N3–N4–N5	−0.8(4)
C18–N2	1.319(4)	C15–C14–F1	118.1(3)	N1–C6–C7–C8	179.1(3)	N2–C18–N5–N4	−1.2(4)
C18–N5	1.329(4)	F1–C14–C13	118.9(3)	C12–C13–C14–F1	180.0(3)	S1–C18–N5–N4	179.4(2)
C18–S1	1.723(3)	C3–C17–S1	109.9(2)	F1–C14–C15–C16	−180.0(3)	N2–C18–N5–C19	−178.8(3)
C19–N5	1.455(4)	N2–C18–N5	109.0(3)	C4–C3–C17–S1	101.1(3)	S1–C18–N5–C19	1.8(5)
C20–O1	1.308(6)	N2–C18–S1	127.1(3)	C2–C3–C17–S1	−80.4(3)	N3–N4–N5–C18	1.2(4)
C21–O1	1.325(6)	N5–C18–S1	123.9(2)	N5–C19–C20–O1	−61.5(7)	N3–N4–N5–C19	179.1(3)
C25–O2	1.366(4)	N5–C19–C20	112.7(4)	O1–C21–C22–C27	−98.2(6)	C20–C19–N5–C18	87.4(5)
C28–O2	1.403(5)	O1–C20–C19	108.5(5)	O1–C21–C22–C23	84.7(6)	C20–C19–N5–N4	−90.0(5)
N2–N3	1.357(4)	O1–C21–C22	117.2(4)	C23–C24–C25–O2	−178.9(4)	C19–C20–O1–C21	174.1(5)
N3–N4	1.284(4)	C24–C25–O2	124.5(3)	O2–C25–C26–C27	179.5(4)	C22–C21–O1–C20	54.2(9)
N4–N5	1.352(4)	O2–C25–C26	116.0(3)	N1–C2–C29–C30	13.3(5)	C24–C25–O2–C28	0.6(6)
		C18–N2–N3	105.2(3)	N1–C2–C29–C31	−54.8(4)	C26–C25–O2–C28	−177.7(4)
		N4–N3–N2	111.3(3)	C3–C2–N1–C6	1.0(4)	N2–C18–S1–C17	−10.7(3)
		N3–N4–N5	106.3(3)	C29–C2–N1–C6	178.7(3)	N5–C18–S1–C17	168.6(3)
		C18–N5–N4	108.1(3)	C5–C6–N1–C2	−1.4(4)	C3–C17–S1–C18	143.4(2)
		C18–N5–C19	131.6(3)	C7–C6–N1–C2	−179.7(3)		
		N4–N5–C19	120.2(3)				
		C20–O1–C21	124.1(5)				
		C25–O2–C28	118.2(3)				
		C18–S1–C17	99.68(15)				

Table 4
Identified hydrogen bonding interactions [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
C12–H12···N1[a]	0.93	2.59	3.479(4)	161
C19–H19B···O2[b]	0.97	2.55	3.329(5)	137
C21–H21B···F1[c]	0.97	2.40	3.302(6)	154
C17–H17B···N2	0.97	2.39	2.933(4)	115
C15–H15···Cg3[d]	0.93	2.82	3.734(4)	166

D-donor; A-Acceptor; H-hydrogen.
Symmetry Equivalent Positions:
[a] 1-x,1-y,1-z.
[b] -x,-y,-z.
[c] 1-x,1/2 + y,1/2-z.
[d] 1-x,-1/2 + y,1/2-z.

are given in Table 4. The three dimensional structure of the compound (Fig. 1) shows that the main moiety of the title compound, quinoline ring [N1/C2–C10] and other moieties, fluorophenyl [C11–C16/F1] and cyclopropyl ring [C29–C31] adopts the planar conformation. The fluorophenyl and cyclopropyl rings are in equatorial and axial orientation with respect to the quinoline ring; the corresponding dihedral angles are, 0.32(12)° and 81.3(3)°.

The tetrazole ring [C18/N2–N5] is observed in planar conformation with the maximum deviation of atom (C7) 0.007(3)Å. Further, the tetrazole ring is oriented axial with quinoline and equatorial with methoxybenzene ring, with the dihedral angle values of 75.35(15)° and 29.27(11)° respectively. The methoxybenzyl group [C22–C27/O2/C28] is found in planar conformation. Further, the methoxy group [O2/C28] lie in a plane which are evidenced by torsion angle values of [C24–C25–O2–C28=] 0.6(6)° and [C26–C25–O2–C28=] −177.7(4)°. The crystal packing is stabilized by C–H···O, C–H···N and C–H···F types of intra and inter molecular interaction and also C–H···π and van der Waals forces. The C–H···N and C–H···O interaction forms a $R^{22}(14)$ and $R^{22}(20)$ dimers which running along c-axis as shown in Fig. 2 [57].

3.7. Molecular docking studies

Human histamine receptors belong to the superfamily of G-protein-coupled-receptor (GPCR) and are classified into four major types, namely, H1, H2, H3 and H4. Of these H1 type has involved in the inflammation pathway, which can be inhibited by antihistamine class of compounds [47,48]. The quinoline derivative (QS-15) was analyzed for the binding affinity with H1R along with astemizole and diclofenac sodium. Further, co-crystallized ligand of the protein human histamine H1 receptor [51] (PDB id: 3RZE), doxepin was also docked using the same procedure to compare its binding

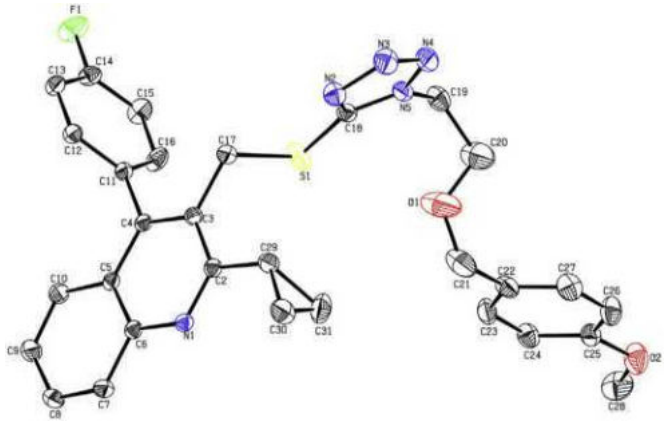


Fig. 1. ORTEP diagram of non-hydrogen atoms of the compound QS-15 are drawn at 20% probability level.

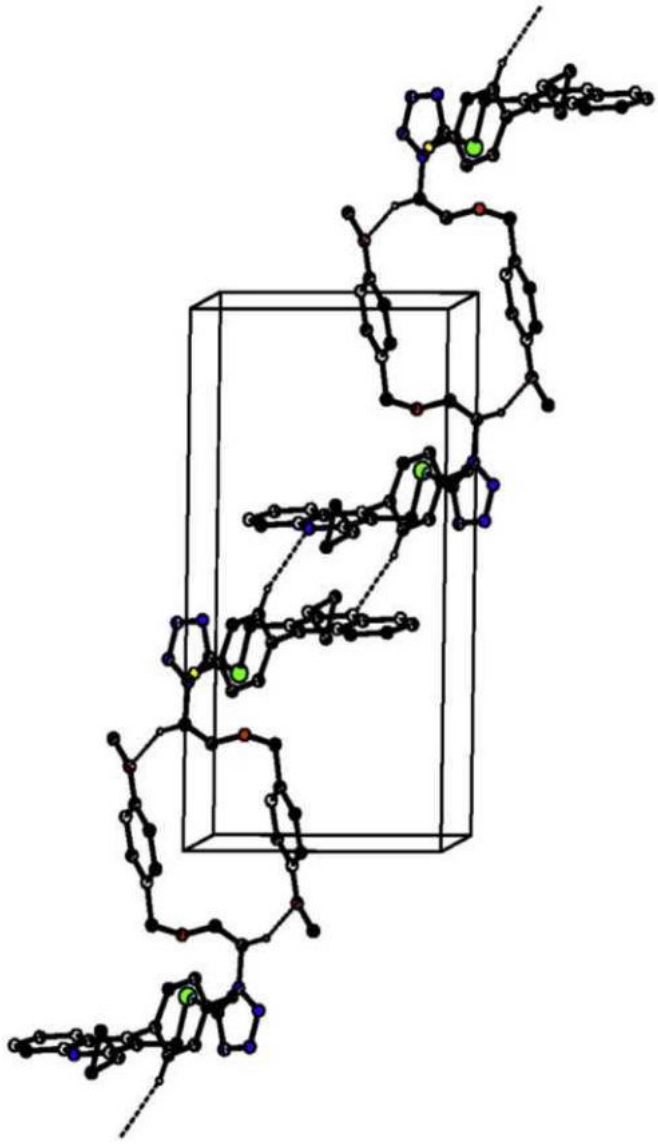


Fig. 2. C–H···N & C–H···O type of hydrogen bonding interactions of $R^{22}(14)$ and $R^{22}(20)$ dimer.

Table 5
Docking Score, energy and hydrogen bonding interactions of ligands with H1R (PDB ID: 3RZE).

Compound	Docking score	Glide energy (kcal/mol)	Type of interaction	Bond length (Å)
QS-15	−10.720	−76.490	(TRP 428) N–H···N	2.9
			(ASP 107) O–H···N	3.1
Astemizole	−12.936	−72.050	(TYR 431) O–H···N	2.9
Doxepin (Co-crystallized compound)	−10.777	−50.989	(THR 112) O–H···O	2.7
			(ASP 107) O–H···N	2.8
Diclofenac sodium	−10.136	−42.281	(ASP 107) O–H···O	2.7

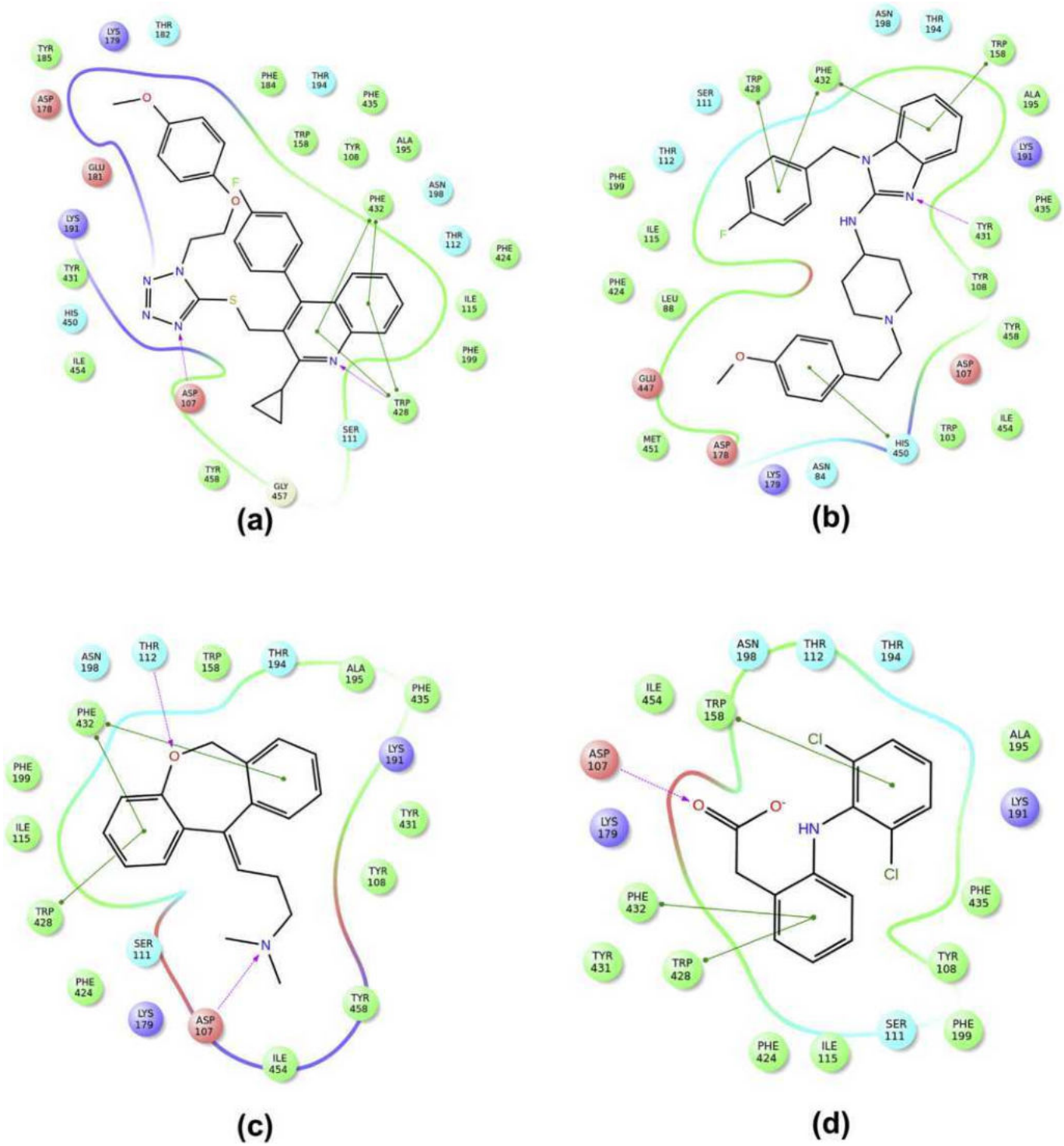


Fig. 3. Schematic diagrams of docking interactions between human histamine H1 receptor and the ligands (a) QS-15 (b) astemizole (c) doxepin (d) diclofenac sodium. The diagrams are prepared using the "Ligand Interaction Diagram" of the GLIDE software [53]. The hydrophobic residues were shown in green, the polar residues were in cyans, Oxygen and OH groups are depicted in red and nitrogen in blue. The hydrogen bonds and pi-pi stacking interactions were in magenta arrows and green lines respectively. The residues in black text show the kind of intramolecular or intermolecular interaction they have with respect to the ligand. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

affinity parameters. The conformation of doxepin in both crystal structure and docked structure are highly similar. The inhibitory mechanism of tetrazol-quinoline derivative was analyzed from docking score, glide energy and hydrogen mediated interactions.

The glide energy of QS-15 (−76.49 kcal/mol), is significantly better than the binding of astemizole, doxepin and diclofenac sodium ligands which clearly indicating the stability of the histamine-QS-15 complex (Table 5). Ligand Interaction module in the Schrodinger suite was used to analyze and display the ligand-protein interactions (Fig. 3). Docking studies shows that

Table 6
Anti-inflammatory activity of QS-15 (Concentration vs % inhibition of denaturation).

Compound	Concentration (μg)	Absorbance	% inhibition (Denaturation)
QS-15	100	0.107	14.01
	200	0.152	39.47
	300	0.183	49.72
	400	0.256	64.06
	500	0.319	71.15
	1000	0.362	74.58
	Control	0.092	
Diclofenac Sodium	100	0.126	26.98
	200	0.248	62.91
	300	0.382	75.91
	400	0.583	84.22
	500	0.824	88.83
	1000	1.412	93.48
	Control	0.092	

compounds QS-15, doxepin and diclofenac sodium were stabilized by the hydrogen bonding interaction with the highly conserved active site residue Asp107, which is not observed in astemizole. The

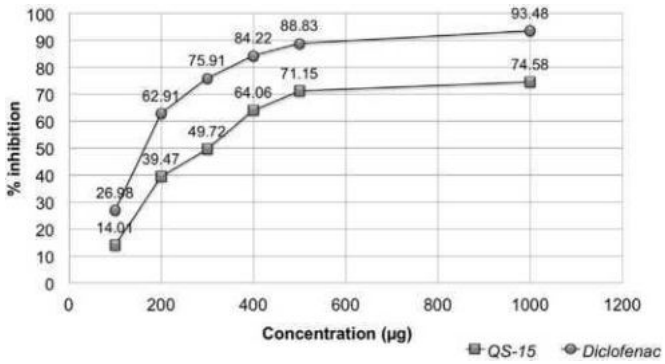


Fig. 4. Comparison of anti-inflammatory activity between the compound QS-15 Vs (filled square) Diclofenac sodium (filled circle).

N-atom of tetrazole ring and *N*-atom of quinoline ring of QS-15 interacts with the Asp107 and Trp 428 residues respectively as shown in the Fig. 3.

Further QS-15 and doxepin were stabilized by π-π stacking interactions with Trp 428 and Phe 432 residues. Whereas, astemizole and doxepin are stabilized by stacking interactions with Tyr431 and Thr112 respectively. Interestingly Trp158, Trp 428 and Phe 432 residues forms π-π stacking interactions with both astemizole and diclofenac sodium compounds which maintains its stability with H1R. The docking score, glide energy and interaction patterns suggests that quinoline derivative (QS-15) can have good binding with histamine receptor H1R and possess anti-inflammatory property compared to doxepin and the standard drug molecule, diclofenac sodium, which was supported by *in vitro* anti-inflammatory activity.

3.8. Anti-inflammatory activity

The synthesized compound shows significant anti-inflammatory activity, which was evaluated using BSA assay. The *in vitro* anti-inflammatory activity (Anti-denaturation assay) of synthesized compound is comparable to that of the standard drug (Diclofenac sodium) used in the study; the results are shown in Table 6 and in Fig. 4. Solutions of QS-15 and Diclofenac sodium after denaturation at various concentrations are shown in Fig. 5.

4. Conclusion

In the present study, novel 5-mercapto-1-substituted tetrazole incorporated quinoline compound, 2-Cyclopropyl-4-(4-fluorophenyl)-3-{1-[2-(4-methoxybenzyloxy)-ethyl]-1*H*-tetrazol-5-ylsulfanylmethyl}quinoline has been prepared and characterized by 2D-NMR and single-crystal XRD. Single crystal XRD revealed that the main moiety of title compound, quinoline ring and other moieties, flurophenyl, cyclopropane ring and tetrazole ring are in planar conformation. The molecular docking results showed that the compound QS-15 has comparably good binding with histamine receptor H1R and possess anti-inflammatory property. The *in-vitro*

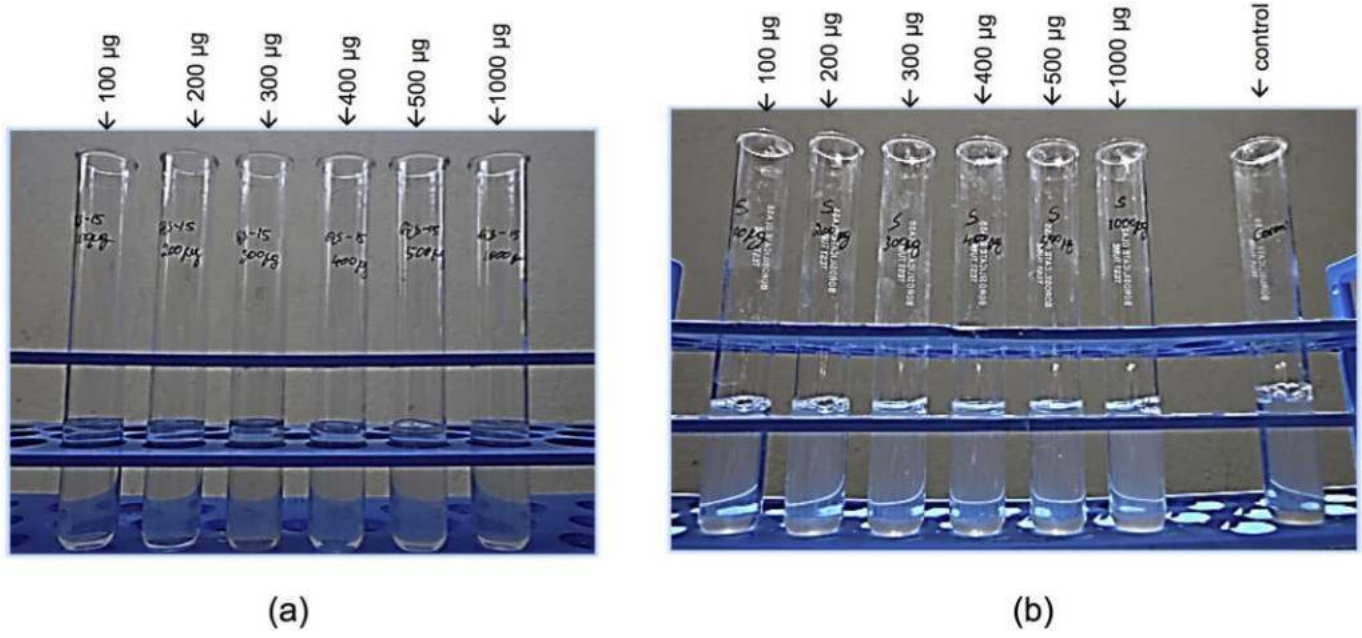


Fig. 5. Solutions of (a) QS-15 and (b) Diclofenac sodium, after denaturation at different concentration in the anti-denaturation assay.

evaluation of anti-inflammatory activity revealed that QS-15 exhibits significant activity when compared with standard drug diclofenac sodium. The results we obtained suggested intriguing directions, which are currently under active investigation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2017.05.085.

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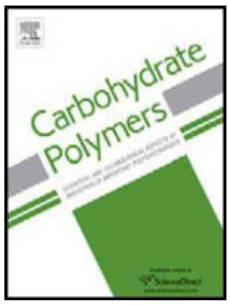

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Tin(IV) cross-linked chitosan for the removal of As(III)

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Highlights

- Sn(IV) crosslinked chitosan (Sn-Ch)
- Sn-Chis used for adsorption ofAs(III).
- Adsorption capacity of Sn-Ch towards As(III)was found to be 17.10 mg/g.
- The material was tested for applicability, regeneration and reusability.

Abstract

Chitosan, a potent amino polysaccharide, has been cross-linked with Sn(IV) chloride. The material was thoroughly characterized using FT-IR, XRD, SEM, EDX, TGA-DTA and BET studies. This Sn(IV) chloride cross-linked chitosan (Sn-Ch) has been exploited for As(III) adsorption . Various parameters like pH, amount of adsorbent, adsorption time etc have been optimized to achieve maximum adsorption efficiency. Under optimum conditions of pH 7.0±0.2, adsorption time of 45 min and adsorbent dose 200 mg, Sn-Ch was found to have adsorption capacity of 17.10 mg/g at 298 K. Adsorption of As(III) by Sn-Ch follow non-linear Freundlich isotherm model. The equilibrium studies showed that the experimental data fits well with non-linear pseudo-second-order kinetic model. Adsorption process was found to be exothermic and spontaneous. Column study proves the applicability of Sn-Ch to the

larger sample volumes. It was found to be recyclable material and could be regenerated and reused multiple times adding a greener dimension.

Keywords: stannic chloride crosslinked chitosan; adsorption; As(III).

1. Introduction

Arsenic is one of the most toxic element which is also the most diffused pollutants in the wastewater. Inorganic arsenic gives rise to severe hazards to human health, especially on the gastrointestinal and respiratory tracts, skin, liver, cardiovascular and nervous system (Smith & Lingas, 2000; Brown & Ross, 2002). Arsenic is generally present as pentavalent (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$) and trivalent (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$) oxidation states. As(III) is more toxic, more mobile and more difficult to remove than As(V) for arsenic extraction processes, as it exists in uncharged form in pH range 2-6. (Yamani ,Miller, Spaulding & Zimmerman, 2012). The European Commission, USEPA(U.S. Environmental Protection Agency, 2002) and W.H.O. (WHO, 2004) have revised the maximum permissible concentration limit for arsenic in drinking water by decreasing it from 50 µg/L to 10 µg/L.

Many technologies such as precipitation (Bhattacharya, Jumawan & Grieves, 1979), coagulation (Sancha, 2000), chemical oxidation (Bissen & Frimmel, 2003), ion exchange (Viraraghavan, Subramanian & Tanjore, 1996) and adsorption (Sharma et al. 2014) have been applied for the removal of arsenic. Among all these, adsorption has greater significance. This technique can be used in such regions where water is inadequate. It is also affordable by developing countries as it is less energy demanding, and no additional chemicals are required for treating the wastewater. Although activated carbon (Chuang et al., 2005; Gu, Fang & Deng, 2005) is still the most used compound for the toxic elements removal from the aqueous medium, there is avid research on alternative adsorbents, especially polysaccharides

which are abundant, biodegradable, eco-friendly, renewable and non-toxic. Among them, chitosan plays a prominent role.

Iron oxides, manganese oxides, Fe–Mn binary oxide, Fe(III)-Sn(IV) binary oxide powders (Oscarson, Huang, Defosse & Herbillon1981; Zhang, Qu, Liu, Liu & Li, 2007; Lafferty, Ginder-Vogel & Sparks, 2010; Ghosh, Bandyopadhyay, Manna & Mandal , 2006) were also extensively studied because they could effectively remove arsenate and arsenite. However, they cannot be used in fixed-bed or other flow-through systems because of their weak mechanical strength and proclivity to aggregate. (Sarkar, Guibal, Quignard & Sen Gupta, 2012; Li et al., 2012). To overcome these margins, the powdered materials needed to be immobilized. The main ways for immobilization are coating, loading, crosslinking, impregnation or entrapment of active components in/on certain carriers to yield better sorbents.

Chitosan, an aminopolysaccharide, obtained by the deacetylation of chitin in alkaline medium, can be easily formulated into beads and films (Gerente, Lee, LeCloirec & McKay 2007). Moreover, it is inexpensive, biodegradable, biocompatible, and nontoxic to environment (Gupta, Chauhan & Sankararamakrishnan, 2009). Thus, it has been used as a host material for immobilization of fine powders and nanoparticles (Sankar et al., 2013). Chitosan had been employed for the removal arsenic from water, but it showed rather low sorption capacity for As(V) and even less capacity for As(III) (Elson,Davies & Hayes ,1980; Miller and Zimmerman, 2010), which limited its application.

Based on the facts, present study reports preparation of stannic chloride crosslinked chitosan (Sn-Ch) for excellent sorption of arsenic(III). This study is focused on evaluating the parameters such as contact time, solution pH, and common coexisting anions which affect arsenic removal by Sn-Ch. The feasibility of reuse has also been examined. Moreover, removal performance has been estimated for arsenic-spiked water using column tests.

2. Materials and Methods

2.1 Materials

A stock solution of As(III) (1000 mg/L) was prepared by dissolving 1.3200 g of As_2O_3 in 25 mL of 1.0 M NaOH. The solution was diluted to about 100 mL with double distilled water, and two drops of 0.2% phenolphthalein were added. It was then neutralized with 1.0 M HCl and further diluted to 1 L. This stock solution was diluted to obtain a standard solution of 5

mg/L As(III). Chitosan with 85% of degree of deacetylation and molecular weight 120 KD was supplied by Uniloid Bio-Chemicals India Limited, Hyderabad. All the reagents were of analytical grade and used without further purification.

2.2 Preparation of tin(IV) crosslinked chitosan (Sn-Ch)

In a two naked round bottom flask, 5 g chitosan was added with 50 mL of ethanol to form a slurry. To it, a solution of 2 mL anhydrous Sn (IV) chloride in 25 mL ethanol was added dropwise with the help of dropping funnel. It was stirred for 1 hour at room temperature. The reaction leads to generation of HCl which was neutralized with 5% ammonia-ethanol (v/v) mixture. The residue was filtered and washed with double distilled water till negative test of chloride. The Sn-Ch adsorbent was dried in oven at 60 ^{0}C. Supplementary Fig.1 shows preparative schematic diagram of Sn-Ch.

2.3 Batch adsorption experiments

For batch absorption studies, 5-100 mg/L As(III) solutions were equilibrated with 200 mg Sn-Ch in stoppered conical flasks. Each systemwas stirred for 45 min. The amount of As(III) adsorbed (mg /g) on Sn-Ch at equilibrium (q_e) can be given by-

$$q_e = \frac{C_0 - C_e}{W} \times V \qquad (1)$$

Also the percent removal capacity was calculated as-

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

where C_0 and C_e refer to the initial and equilibrium liquid phase concentrations in mg /L of As(III), V is the volume of As(III) solution in litre and W is the weight of Sn-Ch adsorbent in gram. All the batch adsorption experiments were performed in triplicate and mean concentrations have been reported. The analysis of the data was carried out using ORIGIN 8.5 software.

2.4 Physicochemical characterization of Sn-Ch adsorbent

Structural details of Sn-Ch could be explained on the basis of FT-IR spectra recorded using Bruker *Alpha* spectrometer with ZnSe ATR crystal in the wavelength range 500-4000 cm^{-1}.

The XRD spectra were recorded by X-ray diffractometer system Righaku-Miniflex 300 in 2θ range 3.0 to 90.0^0 employing copper Kα radiation. Surface morphology of adsorbent was studied using Scanning Electron Microscope (SEM) model TESCAN VEGA 3 SBH. Energy dispersive X-ray (EDX) analysis was performed for elemental composition using X- ray analyzer Oxford INCA Energy 250 EDS System during SEM studies. Thermal analysis of Sn-Ch was carried out using Hitachi TG-DTA 7200 analyzer in temperature range 50 - 900 ^{0}C with heating rate of 20 ^{0}C/min in nitrogen medium. The Brunauer–Emmet–Teller (BET) surface area estimation was carried out by nitrogen adsorption–desorption method on single point surface area analyzer model Smart Sorb 92/93.

2.5 Analysis

The concentration of the arsenic in the aqueous solutions was measured using ICP-AES.

3. Results and discussion

3.1 Characterization of Sn-Ch

The FT-IR spectrum of chitosan showed characteristic broad peak corresponding to O-H and N-H stretching vibrations in the region 3300 cm^{-1} and 3500 cm^{-1} respectively (Fig.1). The bending vibration of N-H bond was observed around 1545 cm^{-1}. The peaks obtained around 2890 cm^{-1} and 1017 cm^{-1} were of C-H and the C-O stretching bands respectively. In Sn-Ch, the peak around 750 cm^{-1} is assigned to Sn-Cl vibration and peak at 606 cm^{-1} is attributed to Sn-N vibrational mode (Yearwood, 2014). In XRD pattern, characteristic diffraction peaks of chitosan were observed at $2\theta = 10.94^0$ and 21.99^0 matching with the reported values. In Sn-Ch, the diffraction peaks at $2\theta = 26.5^0$ and 51.5^0 of Sn confirms impregnation of tin on chitosan (Hemalatha, Illakkiya, Oommen & Usha Rajalakshmi, 2014). The TGA curve of chitosan showed two-step degradation. Initial degradation observed between 60 to 100 ^{0}C with weight loss of 5% which corresponds to dehydration. The second degradation occurred in the range of 250–350 ^{0}C and could be attributed to the degradation of the polysaccharide structure of the molecule, including the degradation of polysaccharide rings and the decomposition of the acetylated and deacetylated units of chitosan (Pereira, Agostini, Job & González, 2013). At the end of 900 ^{0}C, chitosan loses 71% of its weight. In TGA curve of Sn-Ch weight loss has been observed at slightly lower temperature with same decomposition pattern as that of chitosan. In case of Sn-Ch, the percent weight loss has been reduced

substantially from 71% to 55%. This is mainly due to remnants of tin containing ash in Sn-Ch at the end of 900 ^{0}C. In the DTA curve of chitosan, there is a strong exothermic peak at 288.66 ^{0}C which is due to the thermal decomposition of chitosan. This exothermic peak gets shifted to lower temperature in Sn-Ch which might be due to lower thermal stability of Sn-Ch structure compared to that of pure chitosan. Apart from this, there are two endothermic peaks at 120 ^{0}C and 230 ^{0}C which may be attributed to the degradation behaviour of Sn-Ch.

SEM micrographs of chitosan, Sn-Ch and Sn-Ch with adsorbed As(III) were recorded to understand subsequent change in surface morphology (Fig. 2). The chitosan seems to have a smooth surface morphology. In case of Sn-Ch, it shows porous and rough morphology due to the crosslinking of Sn(IV). After adsorption of As(III), the surface of Sn-Ch became less porous. The EDX spectrum of chitosan shows the peaks for carbon, oxygen and nitrogen (Fig. 2a). After impregnation with Sn(IV), a peak of Sn appeared in the range 3 to 4 eV which confirms the successful loading of Sn onto the chitosan matrix (Fig. 2b). Also the presence of chlorine peak in Sn-Ch ascertains the fact that tin is encumbered in the form of tin chloride and not tin oxide. The adsorption of As(III) was confirmed from the EDX spectrum which shows the presence of arsenic along with the other major peaks (Fig. 2c). BET surface area and pore volume of chitosan and Sn-Ch were measured by nitrogen adsorption-desorption method. The decrease in surface area from 3.47 to 3.02 m^2/g and pore volume from $6.0 \times 10^{-3}$to $5.2 \times 10^{-3} cm^3/g$ of Sn-Ch is mainly due to metal ion incorporation and crosslinking which reduces the diffusion of N_2 gas.

3.2 Effect of time on As(III) adsorption

The effect of contact time on the % removal of As(III) by Sn-Ch was studied by varying the contact time in the range 5-60 min with initial As(III) concentration of 5 mg/L with 200 mg Sn-Ch at 298 K. The % removal efficiency of As(III) was found to be higher at the start and reaches equilibrium in about 45 min (Supplementary Fig. 2a). This is because of availability of more adsorption sites on Sn-Ch surface in the beginning which consequently get loaded with As(III) with increasing time. Also, the decrease in concentration gradient with time leads to equilibrium state.

3.3 Effect of adsorbent dose on As(III) adsorption

The effect of adsorbent dose on % removal efficiency was studied by equilibrating 5 mg/L As(III) solution with varying dose of Sn-Chat room temperature (298 K) and at optimum pH 7 for 45 minutes. It can be seen that the % removal of As(III) increases linearly as the amount of adsorbent increases from 50 to 300 mg (Supplementary Fig. 2b). When the dose of Sn-Ch increases further a plateau was obtained probably due to unavailability of adsorbate in the solution for incoming escalating adsorbent surface. Thus beyond 200 mg dose of Sn-Ch adsorbent there was no remarkable change in % removal efficiency of As(III) due to attainment of equilibrium.

3.4 Effect of pH on As(III) adsorption

The pH of adsorption medium is the most important parameter influencing the adsorption capacity. Based on oxidizing and reducing conditions, arsenic is sensitive to pH in ground waters (pH 6.5–8.5). Redox potential and pH are the most important factors regulating arsenic speciation. The functional groups of adsorbents and the arsenic species (adsorbates) are strongly pH dependent. The solutions of varying pH from 2.0 to 9.0 at initial As(III) concentration of 5 mg/ L were equilibrated with 200 mg of Sn-Ch for contact time of 45 min at 298 K. It is obvious from Supplementary Fig. 2d, that the % removal increases and reaches maximum at pH 7.0 followed by a decrease in the extent of adsorption. In highly acidic medium, where the adsorbent surfaces are highly protonated and As(III) mostly exists in the form of neutral H_3AsO_3 species. This situation is not favorable for As(III) adsorption. In neutral to alkaline medium, the negative charged $H_2AsO_3^-$ species starts dominating and surface tends to acquire negative charge. The pH_{PZC} of Sn-Ch is 7.1 (Supplementary Fig. 2c). Therefore, the percentage of removal starts increasing and reaches maximum at pH 7.0. This tendency of acquiring negative charge of the adsorbate species and adsorbent surface continues to increase with increase of pH in alkaline medium resulting into gradual increase in the repulsive forces between the surface and adsorbate species (Singh, Prasad, Rupanwar& Singh,1988).

3.5 Isotherms study for adsorption of As(III)

Adsorption isotherms gives insight of adsorption mechanism as well as help in evaluating the adsorption performance. In the present study non-linear Langmuir and Freundlich isotherm models were studied at three different temperatures (Langmuir, 1918; Freundlich, 1906).
The Langmuir isotherm assumes adsorption sites are identical and energetically equivalent, and monolayer adsorption onto an adsorbent surface. The non-linear expression of Langmuir isotherm equation can be expressed by the following equation

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where C_e (mg/L) is the equilibrium As(III) concentration, q_e (mg/g) is the equilibrium adsorption capacity, bis the Langmuir isotherm constant which related to the strength of adsorption, q_m (mg/g) is the maximum adsorption capacity.

The Freundlich model assumes that the adsorbent owns heterogeneous surfaces and the distribution of adsorption site energy is not equivalent and independent. The non-linear expression of Freundlich isotherm equation can be expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is the constant of the Freundlich isotherm, 1/n is the constant which related to the adsorption capacity and the adsorption intensity.
From Table 1, it is clear that in case of Freundlich isotherm model the value of correlation coefficient is close to unity and hence a best fit model for adsorption of As(III) by Sn-Ch.

3.6 Adsorption kinetics

Kinetics of adsorption of As(III) on to Sn-Ch was studied to understand the time dependency of adsorption process. At three different temperatures, non-linearized pseudo-first-order and pseudo-second-order kinetic models were studied to understand adsorption kinetics.
The studies were carried out using 50 mL 5 mg/L As(III) solution at pH 7.0. It was equilibrated with 200 mg of Sn-Ch adsorbent for different time intervals of 5 to 60 min.

The non-linearized pseudo-first-order kinetics is given by the equation

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

The non-linearized pseudo-second-order equation is given as

$$q_t = \frac{k_2 q_e{}^2 t}{1 + k_2 q_e t} \quad (6)$$

The kinetic plots of adsorption of As(III) by Sn-Ch had been shown in supplementary Fig. 4 a,b and corresponding results were depicted in Table 2. From the value of correlation coefficient it is clear that for pseudo-second-order model it is close to unity and hence a best fit model to describe the adsorption of fluoride by Sn-Ch. Also the same can be seen from the values of experimental q_e obtained in pseudo-second-order rate model as they had close agreement with that of calculated q_e indicating the fitment of experimental data in non-linearized pseudo-second-order rate model.

Weber–Morris model (Weber & Morris, 1963) was studied to understand intraparticle diffusion is the rate determining step or not.

$$q_t = k_{\text{int}}.t^{1/2} + C \quad (7)$$

If the plot of q_t verses $t^{1/2}$ (Supplementary Fig. 4c) passes through origin and is linear, then intraparticle diffusion is the only rate-limiting step. The slope gives the intraparticle rate constant k_{int} (Table 2.) and non-zero intercept showed that diffusion is not the only rate-limiting step for adsorption of fluoride by Sn-Ch. Rate of adsorption of As(III) may be influenced by external mass transfer of As(III) from solution phase to solid phase, pore diffusion and at interior sites of the adsorbent. Thus the adsorption of As(III) by Sn-Ch was controlled by boundary layer as well as diffusion process (Kahu, Saravanan & Jugade 2014).

3.7 Thermodynamics of adsorption

Effect of temperature on adsorption of As(III) by Sn-Ch was studied to obtain relevant thermodynamic parameters at 298 K, 308 K, 318K and 328 K. The free energy change of adsorption (ΔG^0) (Shekhawat, Kahu, Saravanan, & Jugade, 2015) is given by

$$\Delta G^0 = -RT\ln K \quad (8)$$

van't Hoff equation which relates entropy (ΔS^0) and enthalpy (ΔH^0) changes is given by

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

where R is the gas constant (8.314 J mol/K). The value of equilibrium constant K has been evaluated from the ratio of concentration of As(III) adsorbed to that in the solution phase. The values of ΔH and ΔS (Table 3) were obtained from slope and intercept of the plot of ln K against 1/T (Supplementary Fig. 5) respectively. The negative free energy change indicates the spontaneous nature, negative enthalpy change indicates the exothermic nature of adsorption process while negative entropy change indicates the decrease in randomness of arsenites it passes from solution to adsorbed state.

3.8 Column Studies

Column adsorption studies were performed in order to prove the applicability of Sn-Ch adsorbent for As(III) removal of larger sample volumes. For this, a column (30 cm length, 1 cm inner diameter) was packed with 1 g of Sn-Ch. 10 mg/L As(III) solution maintained at pH 7.0 was passed through the column at a flow rate of 5 mL/min. The eluent was collected after every 10 min interval and it was analyzed for As(III) content. The column eluent was also tested for possible leaching of tin but the results were negative. The various column parameters were calculated using following formulas and results have been depicted in Table 4 (Supplementary Fig.6).

$$\text{Breakthrough Capacity}\,(mg/g) = \frac{\text{Breakthrough Volume (L)} \times \text{Inlet concentration}\,(mg/L)}{\text{Wt. of adsorbent (g)}} \quad (10)$$

$$\text{Exhaustion Capacity} = \frac{\text{Exhaustion Volume (L)} \times \text{Inlet concentration}\,(mg/L)}{\text{Wt. of adsorbent (g)}} \quad (11)$$

$$\text{Degree of column utilization}\,(\%) = \frac{\text{Breakthrough Volume}}{\text{Exhaustion Volume}} \times 100 \quad (12)$$

3.8 Effect of co-anions on adsorption of As(III)

The real waste water contains variety of anions which compete for available active sites on adsorbent. The effect of these diverse anions on As(III) adsorption capacity of Sn-Ch was

studied with 10 mg/L As(III) solution and 100 mg/L co-anions such as SO_4^{2-}, Cl^-, PO_4^{3-} and NO_3^-. From Supplementary Fig 7, it is clear that chloride ions have higher interference in adsorption of As(III) by Sn-Ch adsorbent. However, these observations were obtained at ten times higher concentration of Cl^- as compared to As(III).

3.9 Regeneration and reusability of adsorbent

Various reagents such as sodium chloride, sodium nitrate, sodium sulphate and sodium carbonate were examined for desorption studies of Sn-Ch loaded with As(III). The best results were obtained with 5% (w/v) sodium chloride solution (Supplementary Fig. 8a). The chloride ions in NaCl causes ion exchange at this high concentration with the adsorbed As(III) of Sn-Ch leading to desorption of As(III) . The regenerated Sn-Ch was tested for fifteen adsorption-desorption cycles and it was observed (Supplementary Fig. 8b) that there is decrease in adsorption efficiency as compared to original Sn-Ch. Upto 8 cycles, the adsorption efficiency was found to be more than 90% which decreased subsequently after it.

3.10 Mechanism of adsorption of As(III) on Sn-Ch

Tin (IV) chloride binds amino groups of chitosan at room temperature with loss of HCl. Sn-Ch thus obtained is insoluble in dilute HCl and acetic acid indicating that there were no free amino groups in Sn-Ch adsorbent. The presence of chloride ions on Sn-Ch was detected in EDX spectra of adsorbent. At pH 7.0, chloride ions on Sn-Ch adsorbent gets exchange with arsenite ions (Fig.3) resulting into an increase in adsorption capacity of Sn-Ch.

3.11 Comparison with other related adsorbents

The adsorption capacity is the most important parameter for describing an adsorbent and it distinguishes the adsorbent with the other adsorbents. A comparison of Sn-Ch with other adsorbents is mentioned in Table 5.

Conclusion

Chitosan has been crosslinked with tin(IV) chloride to give an excellent As(III) adsorbent Sn-Ch. The polymeric chains found to get crosslinked by covalent bonding with Sn(IV) with the loss of HCl molecule. The resultant material has a number of chloride ions that can

exchange with As(III) of the eluent. The Sn-Ch adsorbent shows high As(III) adsorption capacity of 17.10 mg/g at 298K. The adsorption process follows non-linear Freundlich adsorption isotherm. The kinetics studies indicate that the experimental data fits well in non-linear pseudo-second order kinetics. Column studies clearly indicated that the material can be used to treat larger sample volumes. Applicability towards real sample, recycling and reusability are the most encouraging properties of Sn-Ch adsorbent.

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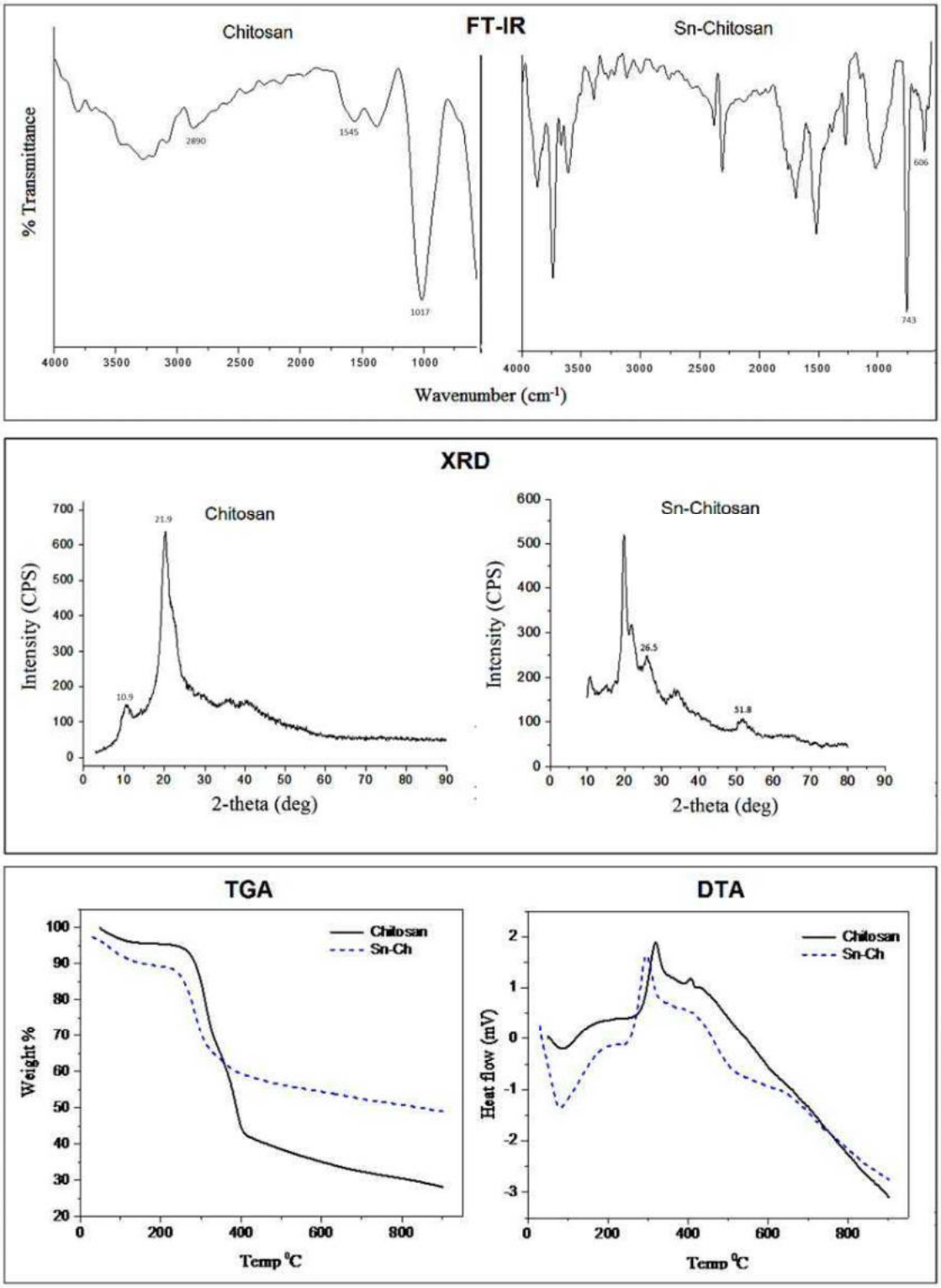

Fig. 1 Characterisation of Sn-Ch.

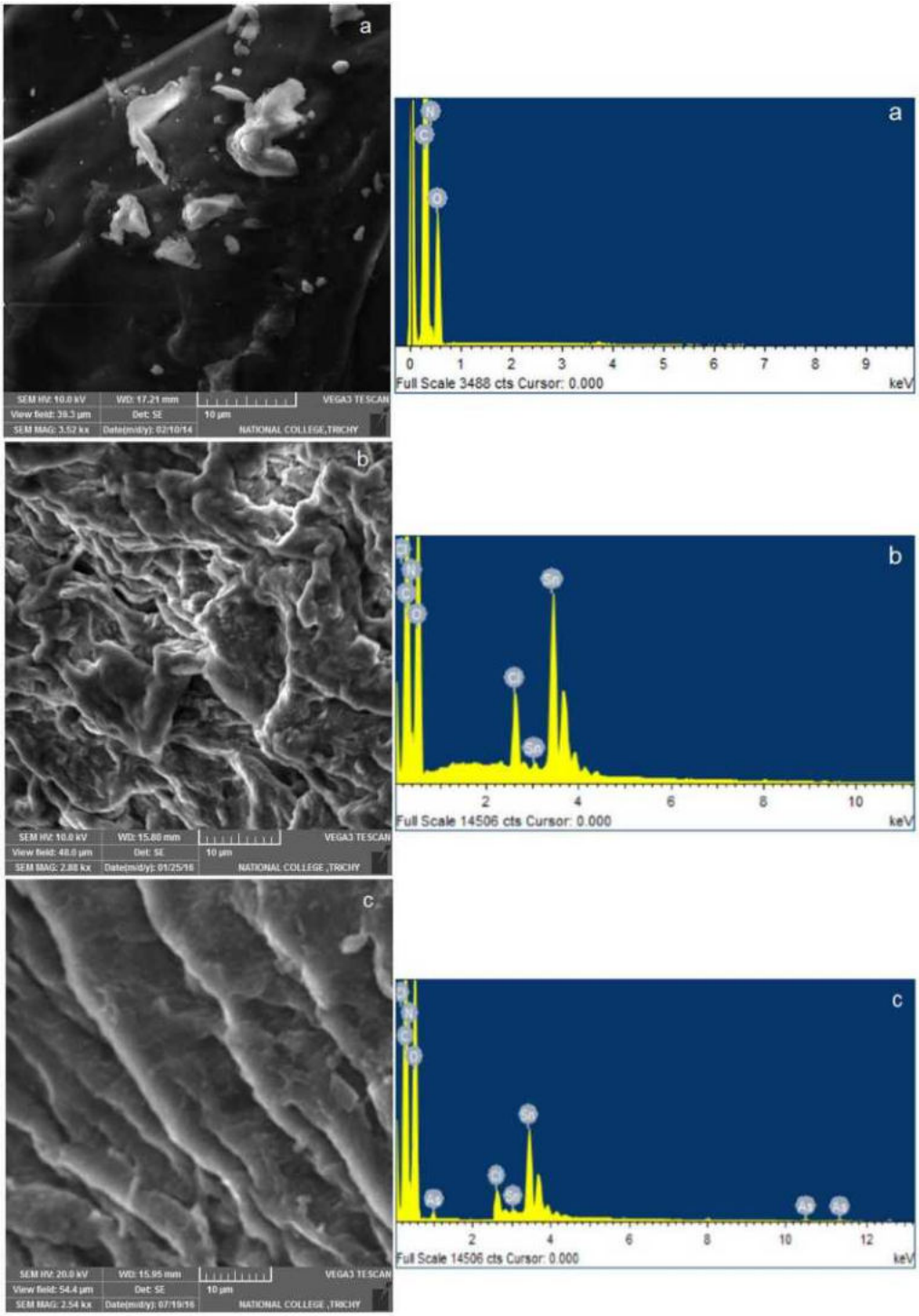

Fig. 2 SEM Images and EDX spectra of (a) chitosan, (b) Sn-Ch and (c) Sn-Ch with adsorbed Arsenic.

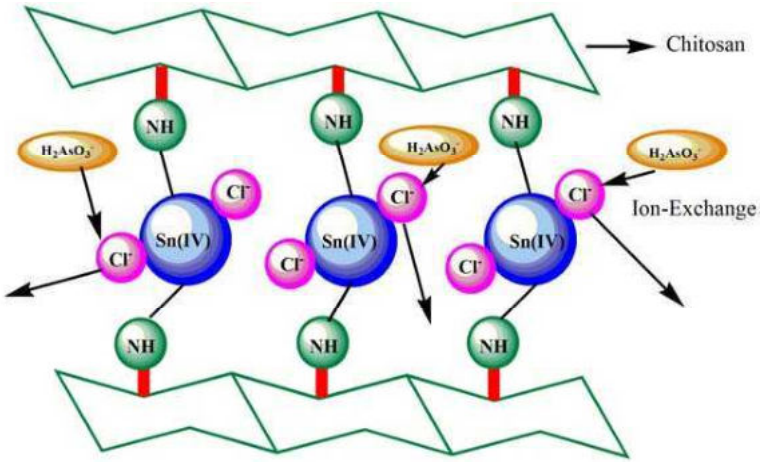

Fig. 3 Adsorption mechanism of As(III) by Sn-Ch.

Table 1 Isotherm model

S. No.	Isotherm	Parameters	Temperature		
			298 K	**308 K**	**318 K**
1	Langmuir	q_m(mg/g)	17.103	15.613	15.393
		b(L /mg)	0.146	0.133	0.090
		r^2	0.956	0.955	0.929
2	Freundlich	K_F ($mg^{1-1/n}$ $L^{1/n}$/g)	3.545	3.082	2.334
		n	2.436	2.423	2.184
		r^2	0.995	0.985	0.971

Table 2 Kinetic data associated with adsorption process.

Sl. No.	Rate model	Parameters	Temperatures		
			298 K	308 K	318 K
1	Pseudo-first-order kinetics	K_1	0.197	0.137	0.097
		q_{eexp} (mg/g)	1.186	1.183	1.170
		q_{ecal} (mg/g)	1.220	1.202	1.185
		r^2	0.779	0.935	0.983
2	Pseudo-second-order	K_2	0.252	0.143	0.081
		q_{eexp} (mg/g)	1.289	1.329	1.385
		q_{ecal}(mg/g)	1.220	1.202	1.185
		r^2	0.941	0.972	0.993
3	Intraparticle diffusion	K_{int}	0.071	0.096	0.123
		r^2	0.84	0.83	0.89

Table 3 Thermodynamic parameters

Temperature	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol/K)
298K	-8.788	-49.230	-0.143
308K	-4.867		
318K	-3.224		
328K	-1.358		

Table 4 Column parameters

Parameter	Result
Inlet As(III) concentration	10 mg/L
Breakthrough volume	1200 mL
Exhaustion volume	1800 mL
Breakthrough Capacity	12 mg/g
Exhaustion Capacity	18 mg/g
Degree of column utilization	66.67

Table 5 Comparison of Sn-Ch with reported adsorbents.

Sorbents	Adsorption capacity (mg/g)	References
Chitosan	1.83	Elson, Davies & Hayes, 1980
Molybdate impregnated chitosan beads	1.98	Chassary, Vincent &Guibal, 2004
Titanium dioxide impregnated chitosan beads	6.40	Miller & Zimmerman , 2010
Iron impregnated chitosan beads	6.48	Gang, Deng & Lin, 2010
Iron coated chitosan flakes	16.15	Gupta, Chauhan & Sankararamakrishnan, 2009
Iron crosslinked chitosan	13.40	dos Santos, Demarchi, Rodrigues, Greneche, Nedelko & Slawska -Waniewska, 2011
Sn-Ch	17.10	Present Study

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Synthesis of Mercapto Heterocyclic Derivatives of 1-(4-((4-Chlorophenyl)(phenyl)methyl)piperazin-1-yl)-2-thio-propan-1-one and its Biological Activities

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Abstract

In the present study, a new series of mercapto heterocyclic derivatives of 1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)-2-thio-propan-1-one derivatives are synthesized. The chemical structures were confirmed by IR, ^{1}H-NMR and mass spectral analysis. The compounds were screened for antibacterial and antifungal activity. It shows good antibacterial and antifungal activity for most of synthesized compounds.

Keywords: *Antibacterial; Antifungal; Chlorophenyl; Piperazine.*

1. INTRODUCTION

The main objective of organic and medicinal chemistry is to provide molecules having value as human therapeutic agents. Compounds with heterocyclic structures are getting special attention as they belong to a class of compounds with proven utility in medicinal chemistry. Piperazine is a heterocyclic compound containing four carbon atoms and two nitrogen atoms at 1 and 4 positions (as called 1, 4-hexahydropyrazine) which are important building blocks in drug discovery. Piperazines are a broad class of chemical compounds with many important pharmacological properties with a more number of positive hits during biological screening. Piperazine and substituted piperazine nuclei had constituted an attractive pharmacological scaffold present in various potent marketed drugs and piperazine has the chemical resemblance with piperidine. Nitrogen in piperazine ring plays an important role in biological research and drug manufacturing and the incorporation of piperazine in the compounds is an important synthetic strategy in drug discovery due to its easy modification, water solubility, the capacity for the formation of hydrogen bonds and adjustment of molecular physicochemical properties.

The piperazine skeleton contained molecules are found to be biologically active compounds in different therapeutic areas (Guo *et al*. 2004; Berkheij et a. 2005; Kuldeep Singh *et al*. 2015). A broad range of biological active compounds displaying antibacterial (Foroumadi *et al* 2006; Lohray *et al*. 2006; Foroumadi *et al*. 2007; Phillips *et al*. 2008), antifungal (Upadhayaya *et al*. 2004; Watkins *et al*. 2007), anticancer (Gillet *et al*. 1998; Hulme *et al*. 1999; Gabriel *et al*. 2000; Rokosz *et al*. 2005; Chen *et al*. 2006; Shami *et al*. 2006), antiparasitic (Mayence *et al*. 2004; Cunico *et al*. 2009) antihistamin (Smits *et al* 2008), psychotolytic (Penjišević *et al*. 2007), antidepressants (Nee Kosoczky Bolya Balla *et al*. 1975; Becker *et al*. 2006) and HIV protease inhibitors (Dorsey *et al* 1994; Askin *et al*. 1994; Rosen *et al*. 1995) have been also found to contain this versatile core. In particular, 1-(1-naphthylmethyl)-piperazine compound as the efflux pump inhibitor, could employ positive effect on tetracyclines and ciprofloxacin against their resistant bacteria (Bean and Wareham, 2009; Coban *et al*. 2009). Also, benzotriazole-based piperazine derivatives and N,N'-bis(alkyloxymethyl)piperazines had moderate antibacterial and antifungal activities against pathogenic bacterial strains and fungal strains (Chaudhary *et al*. 2006; Farzaliev *et al*. 2009). Betalactam antibiotics are a class of broad-spectrum antibiotics, includes penicillin derivatives (penams), cephalosporins (cephems), and carbapenems contain a beta-lactam ring. Most β-lactam antibiotics are with heterocyclic thiol side chains and are the most widely used group of antibiotics and more than half of all commercially available antibiotics in use was β-lactam compounds. Due to the higher contribution of piperazine and heterocyclic thiol side chains in drug synthesis, fusing of these moieties may result wide variety of biological activities such as anti-bacterial and antimicrobial. Therefore, it was envisioned that a

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new series of mercapto heterocyclic derivatives of 1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)-2-thio-propan-1-one3(a-j) would result in compounds of potential biological activities.

In view of above, the present study with a series of 2-bromo-1-(4-((4-chlorophenyl)(phenyl) methyl) piperazin-1-yl) propan-1-one are synthesized by the reaction of 1-((4-chlorophenyl)(phenyl)methyl) piperazine with 2-bromopropanoyl bromide. Mercapto heterocyclic derivatives of 1-(4-((4-chlorophenyl)(phenyl)methyl) piperazin-1-yl)-2-thio-propan-1-one are synthesized by reaction of 2-bromo-1-(4-((4-chlorophenyl) (phenyl) methyl)piperazin-1-yl) propan-1-one with and mercapto heterocyclic side chains. The chemical structures were confirmed by means of IR, 1H-NMR and mass spectral data. Antibacterial and antifungal activity of the above synthesized compounds was screened. The results are good for most of the compounds and for few compounds moderately good.

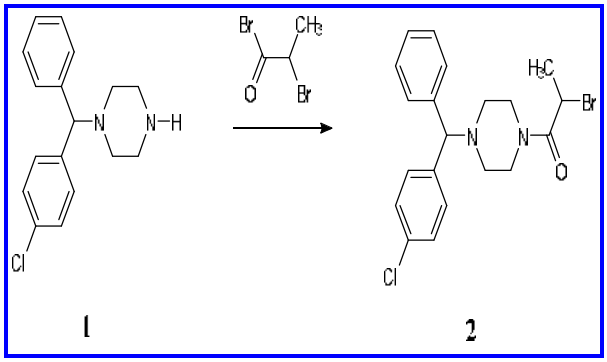
2. MATERIALS & METHODS

All the Chemical and solvents used in the preparation of compounds are Sigma-Aldrich and Alfa-Aesar. All the reported melting points were determined using an electrically heated block with calibrated thermometer; samples are taken in open capillaries and were uncorrected. The IR Spectra were taken from Alpha Bruker IR spectrophotometer by using KBr pallets. Molecular weights of all the synthesized compounds were determined using Mass SCIEX 3000API instrument. ^{1}H-NMR spectra were recorded in DMSO – d6 on Bruker NMR (400 MHz) using tetramethylsilane (TMS) as an internal standard.

In vitro antibacterial activities of synthesized compounds are done with disc diffusion method by two-fold serial dilution method and Ciprofloxacin is used as standard for comparison. In vitro antifungal activities were evaluated for the synthesized compounds with disc diffusion method by two-fold serial dilution method and Amphotericin B is used as standard for comparison.

2.1 Procedure for the synthesis of 2-bromo-1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl) propan-1-one [2].

To a stirred solution of 1-((4-chlorophenyl)(phenyl)methyl)piperazine (25 g, 0.087 moles, 1.0 equ) in dichloromethane (100 mL), triethyl amine (9.7 g, 0.095 moles, 1.1 equ.) was added followed by slow addition of 2-bromopropanoyl bromide (28.2 g, 0.130 moles, 1.5 equ.) at 0-5 °C. The mixture was stirred at 0-5°C till completion of reaction and the progress of the reaction was monitored by TLC. After completion of reaction, water was added to the mass at 2-5°C, the pH was adjusted to 7.0 to 7.5 using sodium bicarbonate solution and the layers were separated. The organic layer was washed with water, evaporated the dichloromethane till thick mass. Diisopropyl ether was added and distilled and the solid of title compound was obtained by crystallization with diisopropyl ether. The preparation of 2-bromo-1-(4-((4-chlorophenyl)(phenyl)methyl) pipera zin-1-yl)propan-1-one by condensation of 1-((4-chlorophenyl)(phenyl)methyl)piperazine with 2-bromopropanoyl bromide, triethyl amine and dichloromethane as the solvent as shown in scheme 1.



Scheme 1

Mass analysis of compound 2 shows m/z 421 $(M+1)^+$ peak which confirms formation of compound 2.

^{1}H NMR (δ ppm)–$CDCl_3$: 1.80 (d, 3H, CH_3), 2.31 (m, 4H, $2CH_2$), 3.43 (m, 4H, $2CH_2$), 4.22 (s, 1H, CH), 4.48 (m, 1H, CH), 7.19 - 7.37 (m, 9H ,aromatic)

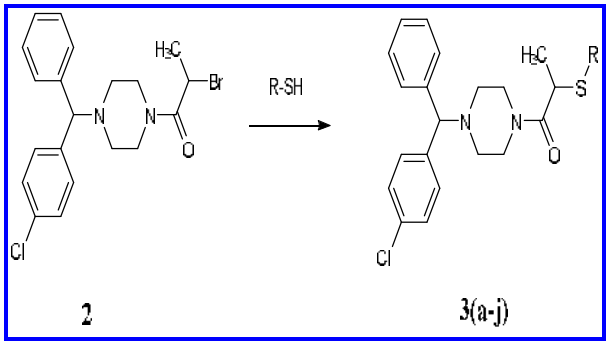
2.2 Procedure for Synthesis of Mercapto Heterocyclic Derivatives of 1-(4-((4-Chlorophenyl) (phenyl) methyl) piperazin-1-yl)-2-thio-propan-1-one derivatives 3(a-j)

2.2.1 Procedure for the Synthesis 1-(4-((4-Chlorophenyl)(phenyl)methyl)piperazin-1-yl)-2-((5-phenyl-1,3,4-oxadiazol-2-yl)thio)propan-1-one 3(a)

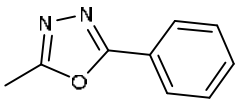
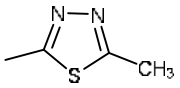
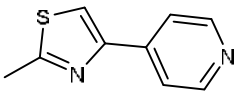
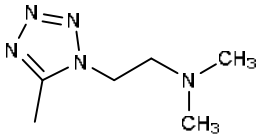
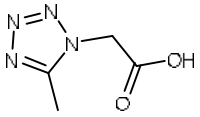
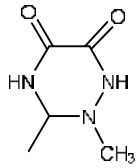
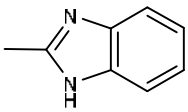
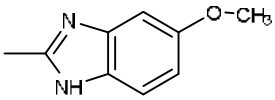
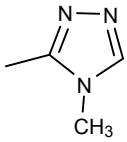
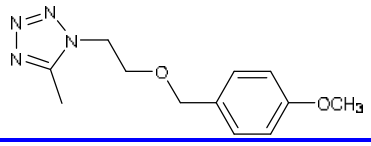
To a stirred solution of 2-bromo-1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)propan-1-one (**2**) (5 g, 0.011 moles, 1 eq.) in acetone (100 ml), 5-phenyl-1,3,4-oxadiazole-2-thiol (2.1 g, 0.0118 moles, 1 eq.) and anhydrous potassium carbonate (3.2 g, 0.0237 moles, 2 eq.) were added. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was filtered to remove insoluble materials and the clear filtrate was concentrated to thick mass under vacuum at 45 °C - 50 °C. The concentrated mass was dissolved in ethyl acetate and washed twice with demineralized water. The organic layer was dried over sodium sulfate and concentrated the clear solution under vacuum at 50 °C - 55 °C. The crude product was purified with silica gel column chromatography with ethyl acetate and

n-heptane (3:7 mixture) yielded the product 1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)-2-((5-phenyl-1,3,4-oxadiazol-2-yl)thio)propan-1-one (3a).

The preparation of compounds of 3(a-j) is shown in Scheme 2.



Scheme 1

Compound	R
3a	
3b	
3c	
3d	
3e	
3f	
3g	
3h	
3i	
3j	

IR (KBr) (cm^{-1}) γ 692 (C-S-C), 758 (C-Cl), 992 (C-H Aromatic), 1071, 1288 (C-O-C), 1446 (CH_2), 1634 (C=O), 2803 (C-H)

Mass analysis of compound 3a shows m/z 563.3 $(M+HCOO)^-$ peak which confirms formation of synthesized compound 3a with 518 mass.

^{1}H NMR (δ ppm)–$CDCl_3$: 1.72 (d, 3H, CH_3), 2.38 (m, 4H, $2CH_2$), 3.57 (m, 4H, $2CH_2$), 4.23 (s, 1H, CH), 4.93 (t, 1H, CH), 7.18 - 7.98 (m, 14H, aromatic).

The compounds 3(b-j) synthesized similarly from 2-bromo-1-(4-((4-chlorophenyl) (phenyl) methyl) piperazin-1-yl) propan-1-one with different thiol compounds.

2.3.2 1-(4- ((4-Chlorophenyl) (phenyl) methyl) piperazine-1-yl)-2-((5-methyl-1,3,4-thiadiazol-2-yl)thio)propan-1-one (3b)

Prepared from 2-bromo-1-(4-((4-chlorophenyl) (phenyl)methyl)piperazin-1-yl)propan-1-one with 5-methyl-1,3,4-thiadiazole-2-thiol

IR (KBr) (cm^{-1}) γ 699 (C-S-C), 753 (C-Cl), 991 (C-H Aromatic), 1077, 1288 (C-O-C), 1433 (CH_2), 1633 (C=O), 2804 (C-H).

Mass analysis of compound (3b) shows m/z 473.3 (M+) peak which confirms formation of product.

^{1}H NMR (δ ppm)– $CDCl_3$: 1.65 (s, 3H, CH_3), 2.35 (m, 4H, $2CH_2$), 2.63 (s, 3H, CH_3), 3.54 (m, 4H, $2CH_2$), 4.26 (s, 1H, CH), 4.96 (t, 1H, CH), 7.20 – 7.95 (m, 9H, aromatic).

2.3.3 1- (4- ((4 - Chlorophenyl) (phenyl) methyl) piperazin-1- yl) -2- ((4- (pyridin-4-yl) thiazol-2-yl) thio) propan-1-one (3c)

Prepared from 2-bromo-1-(4-((4-chlorophenyl) (phenyl) methyl)piperazin-1-yl)propan-1-one with 4-(pyridin-4-yl)thiazole-2-thiol.

IR (KBr) (cm^{-1}) γ 697 (C-S-C), 754 (C-Cl), 1000 (C-H Aromatic), 1083, 1288 (C-O-C), 1433 (CH_2), 1635 (C=O), 2807 (C-H).

Mass analysis of compound (3c) shows m/z 579.5 $(M+HCOO)^-$ peak which confirms formation of product.

^{1}H NMR (δ ppm)– $CDCl_3$: 1.68 (d, 3H, CH_3), 2.32 (m, 4H, $2CH_2$), 3.55, 3.70 (m, 4H, $2CH_2$), 4.17(s, 1H, CH), 4.92 (d, 1H, CH), 7.20 – 8.64 (m, 14H, aromatic).

2.3.4 1-(4-((4-Chlorophenyl)(phenyl)methyl) piperazin-1-yl)-2-((1-(2-(dimethylamino)ethyl)-1H-tetrazol-5-yl)thio)propan-1-one (3d)

Prepared from 2-bromo-1-(4-((4-chlorophenyl)(phenyl) methyl)piperazin-1-yl)propan-1-one with 1-(2-(dimethylamino)ethyl)-1H-tetrazole-5-thiol.

IR (KBr) (cm^{-1}) γ 701 (C-S-C), 755 (C-Cl), 996 (C-H Aromatic), 1190 (C-O-C), 1439 (CH_2), 1635 (C=O), 2804 (C-H).

Mass analysis of compound (3d) shows m/z 558.4 $(M+HCOO)^-$ peak which confirms formation of product.

^{1}H NMR (δ ppm)- $CDCl_3$:1.63 (d, 3H, CH_3), 2.23 (S, 6H, $2CH_3$), 2.36 (m, 4H, $2CH_2$), 2.71 (t, 2H, CH_2), 3.54 (m, 4H, $2CH_2$), 4.23 (m, 3H, CH_2 and CH), 5.01 (m, 1H, CH), 7.17 - 7.36 (m, 9H, aromatic).

2.3.5 2-(5-((1-(4-((4-Chlorophenyl)(phenyl)methyl) piperazin-1-yl)-1-oxopropan-2-yl)thio)-1H-tetrazol-1-yl)acetic acid (3e)

Prepared from 2-bromo-1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)propan-1-one with 2-(5-mercapto-1H-tetrazol-1-yl)acetic acid.

IR (KBr) (cm^{-1}) γ 704 (C-S-C), 760 (C-Cl), 1034 (C-H Aromatic), 1091, 1290 (C-O-C), 1439 (CH_2), 1640 (C=O), 2987 (C-H).

Mass analysis of compound (3e) shows m/z 499 (M^-) peak which confirms formation of product.

^{1}H NMR (δ ppm) - $CDCl_3$: 1.53 (t, 3H, CH_3), 2.74 (m, 4H, $2CH_2$), 3.63 (m, 4H, $2CH_2$), 4.72 (s, 1H, CH), 4.85 (m, 2H, CH_2), 5.04 (d, 1H, CH), 7.29 - 7.56 (m, 9H, Aromatic).

2.3.6 3-((1-(4-((4-Chlorophenyl)(phenyl)methyl) piperazin-1-yl)-1-oxopropan-2-yl)thio)-2-methyl-1,2,4-triazinane-5,6-dione (3f)

Prepared from 2-bromo-1-(4-((4-chlorophenyl)(phenyl) methyl)piperazin-1-yl)propan-1-one with 3-mercapto-2-methyl-1,2,4-triazinane-5,6-dione.

IR (KBr) (cm^{-1}) γ 700 (C-S-C), 754 (C-Cl), 995 (C-H Aromatic), 1084, 1292 (C-O-C), 1430 (CH_2), 1634 (C=O), 2808 (C-H).

Mass analysis of compound (3f) shows m/z 498 (M^-) peak which confirms formation of product.

^{1}H NMR (δ ppm) - $CDCl_3$:0.90 (t, 3H, CH_3), 1.44 (d, 2H, CH_2), 3.0, 3.42 (m, 2H, CH_2), 3.53 (d, 1H, CH), 4.52 (t, 1H, CH), 4.62 (t, 1H, CH), 7.22 - 7.35 (m, 7H, aromatic).

2.3.7 2-((1H-benzo[d]imidazol-2-yl)thio)-1-(4-((4-Chlorophenyl)(phenyl)methyl)piperazin-1-yl)propan-1-one (3g)

Prepared from 2-bromo-1-(4-((4-chlorophenyl)(phenyl) methyl)piperazin-1-yl)propan-1-one with 1H-benzo[d]imidazole-2-thiol.

IR (KBr) (cm^{-1}) γ 703 (C-S-C), 744 (C-Cl), 994 (C-H Aromatic), 1081, 1257 (C-O-C), 1432 (CH_2), 1619 (C=O), 2804 (C-H).

Mass analysis of compound (3g) shows m/z 489.3 (M^-) peak which confirms formation of product.

^{1}H NMR (δ ppm) - $CDCl_3$: 1.60 (d, 3H, CH_3), 2.28 (m, 4H, $2CH_2$),3.52 (m, 4H, $2CH_2$), 4.15 (s, 1H, CH), 4.50 (t, 1H, CH), 7.20 - 7.65 (m, 13H, aromatic), 11.1 (s, 1H, NH).

2.3.8 1-(4-((4-Chlorophenyl)(phenyl)methyl) piperazin-1-yl)-2-((5-methoxy-1H-benzo[d]imidazol-2-yl)thio)propan-1-one (3h)

Prepared from 2-bromo-1-(4-((4-chlorophenyl)(phenyl) methyl)piperazin-1-yl)propan-1-one with 5-methoxy-1H-benzo[d]imidazole-2-thiol.

IR (KBr) (cm^{-1}) γ 705 (C-S-C), 752 (C-Cl), 994 (C-H Aromatic), 1088, 1287 (C-O-C), 1434 (CH_2), 1621 (C=O), 2809 (C-H).

Mass analysis of compound (3d) shows m/z 519 (M^-) peak which confirms formation of product.

^{1}H NMR (δ ppm) - $CDCl_3$: 1.57 (d, 3H, CH_3), 2.21 (m, 4H, $2CH_2$),3.52 (m, 4H, $2CH_2$), 3.82 (s, 3H, CH_3), 4.10 (d, 1H, CH), 4.51 (s, 1H, CH), 7.18 - 7.51 (m, 12H, aromatic), 11.1 (d, 1H, NH).

2.3.9 1-(4-((4-Chlorophenyl)(phenyl) methyl) piperazin-1-yl)-2-((4-methyl-4H-1,2,4-triazol-3-yl)thio) propan-1-one (3i)

Prepared from 2-bromo-1-(4-((4-chlorophenyl)(phenyl) methyl)piperazin-1-yl)propan-1-one with 4-methyl-4H-1,2,4-triazole-3-thiol.

IR (KBr) (cm^{-1}) γ 694 (C-S-C), 754 (C-Cl), 1000 (C-H Aromatic), 1084, 1290 (C-O-C), 1436 (CH_2), 1629 (C=O), 2809 (C-H).

Mass analysis of compound (3i) shows m/z 500.4 $(M+HCOO)^-$ peak which confirms formation of product.

^1H NMR (δ ppm) - $CDCl_3$: 1.59 (d, 3H, CH_3), 2.37 (d, 4H, $2CH_2$), 3.55 (m, 3H, 4H, CH_3,$2CH_2$), 4.22 (s, 1H, CH), 4.85 (m, 1H, CH), 7.19 – 8.13 (m, 10H, aromatic)

2.3.10 1- (4 - ((4 - Chlorophenyl) (phenyl)methyl) piperazin-1-yl) -2 - ((1 - (2 - ((4-methoxybenzyl) oxy) ethyl) - 1H - tetrazol-5-yl)thio) propan -1 -one (3j)

Prepared from 2-bromo-1-(4-((4-chlorophenyl)(phenyl) methyl)piperazin-1-yl)propan-1-one with 1-(2-((4-methoxybenzyl)oxy)ethyl)-1H-tetrazole-5-thiol.

IR (KBr) (cm^{-1}) γ 702 (C-S-C), 755 (C-Cl), 996 (C-H Aromatic), 1093, 1294 (C-O-C), 1439 (CH_2), 1634 (C=O), 2814 (C-H).

Mass analysis of compound (3j) shows m/z 651 $(M+HCOO)^-$ peak which confirms for mation of product.

^1H NMR (δ ppm) - $CDCl_3$: 1.60 (d, 3H, CH_3), 2.35 (d, 4H, $2CH_2$), 3.49 (m, 4H, $2CH_2$), 3.75 (m, 5H, CH_2, CH_3), 4. 12 (s, 1H, CH), 4.37 (d, 4H, $2CH_2$), 6.8 - 7.35 (m, 13H, aromatic).

3. RESULTS & DISCUSSION

3.1 Spectroscopic characterization

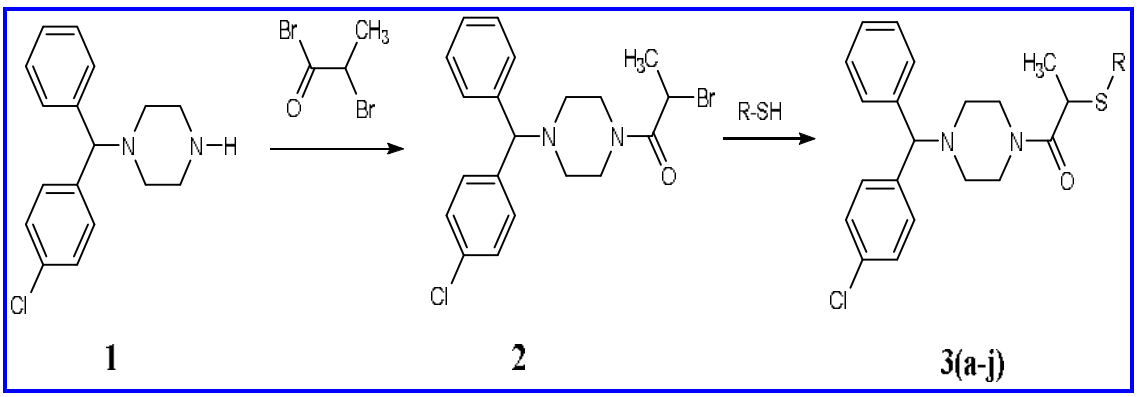
2- bromo -1 -(4 -((4 - chlorophenyl) (phenyl)methyl) piperazine-1-yl) propan-1-one (**2**) was prepared by the reaction of 1-((4-chlorophenyl)(phenyl)methyl) piperazine with 2-bromopropanoyl bromide triethyl amine as a base in dichloromethane as the solvent. The mass spectra of compound 2 show m/z values 421 which confirm the formation of compound 2 with molecular weight 420. Proton and carbon NMR of compound also confirms the formation of compound 2.

The reaction of 2-bromo-1-(4-((4-chlorophenyl) (phenyl)methyl)piperazin-1-yl)propan-1-one (**2**) with different heterocyclic thiol side chains compounds in acetone and anhydrous potassium carbonate resulted mercapto heterocyclic derivatives of 1-(4-((4-chlorophenyl) (phenyl) methyl) piperazin-1-yl)-2-thio-propan-1-one3(a-j). The overall synthesis of navel piperazine derivatives 3(a–j) from 1-((4-chlorophenyl)(phenyl)methyl)piperazine were presented in scheme-3. The compounds 3(a-j) are confirmed by 1H NMR and Mass and IR techniques and the analytical data corresponds to the nature of substituents are provided in table 1.

The IR spectrum of compounds 3 (a–j) show an absorption band at IR (KBr) (cm^{-1}) γ 692, 758, 992, 1071, 1288, 1446, 1634 and 2803 are due to corresponding C-S-C, C-Cl, C-H, Aromatic C-O-C, CH_2, C=O and C-H functional groups respectively. The ^1H NMR spectrum of compounds 3(a–j) show a doublet at 1.72 ppm attributed to CH_3 protons, 2.38, 3.57 ppm corresponds to $4CH_2$ protons at piperazine ring, 4.23 ppm attributed to CH proton at C-S position and 4.93 ppm attributed to CH proton at Benzhydryl group.

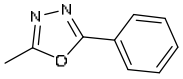
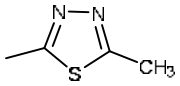
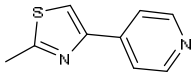
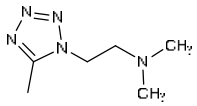
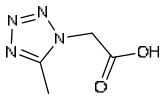
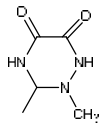
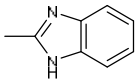
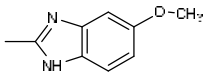
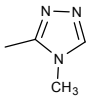
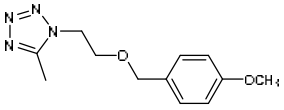
3.2 Antibacterial Activity

The synthesized mercapto heterocyclic derivatives of 1-(4-((4-chlorophenyl) (phenyl) methyl) piperazin-1-yl)-2-thio-propan-1-one 3(a-j) compounds were screened for their in vitro antibacterial activity by disc diffusion method. MIC values were determined by two-fold serial dilution method. Ciprofloxacin was used as a standard for the comparison of the antibacterial activity, and the MIC results are reported in Table 2.



Scheme 1

Table 1. Analytical Data for Compounds 3(a-j)

Compounds	R	Molecular Weight	Yield (%)	Decomposition Temperature (°C)
3a		518	85	78
3b		472	89	64
3c		534	78	72
3d		513	75	55
3e		500	67	171
3f		501	87	144
3g		490	85	120
3h		520	90	117
3i		455	84	50
3j		606	90	49

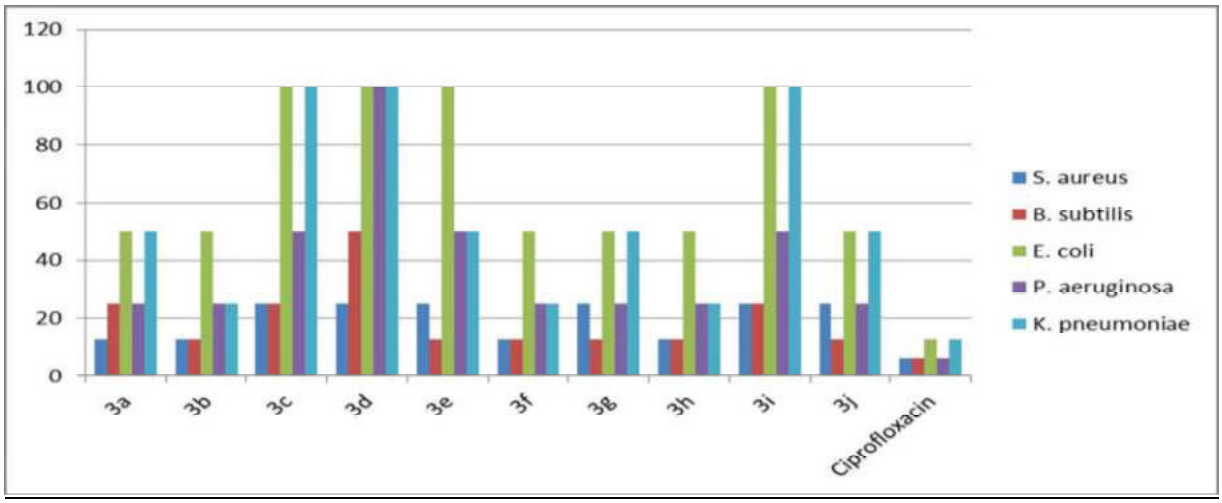


Fig. 1: Bar Diagram for Antibacterial Study for the Synthesised Compounds 3(a-j)

Table 2. In Vitro Antibacterial Activities of 3(a-j)

Compounds	Minimum inhibitory concentrations (µg/mL)				
	S. aureus	B. subtilis	E. coli	P. aeruginosa	K. pneumoniae
3a	12.5	25	50	25	50
3b	12.5	12.5	50	25	25
3c	25	25	100	50	100
3d	25	50	100	100	100
3e	25	12.5	100	50	50
3f	12.5	12.5	50	25	25
3g	25	12.5	50	25	50
3h	12.5	12.5	50	25	25
3i	25	25	100	50	100
3j	25	12.5	50	25	50
Ciprofloxacin	6.25	6.25	12.5	6.25	12.5

The antibacterial activity data showed that compound 3a, 3b, 3f and 3h exhibited good activity and 3c, 3d, 3e, 3g, 3i and 3j exhibited moderate activity against *S. aureus.* Most of the compound in this series 3(a-j) are showing good activity against *B. subtilis* and showed moderate activity against *E. coli* and *P. aeruginosa*. Compound 3b, 3f and 3h are exhibited good activity against *K. pneumoniae.*

5-methyl-1,3,4-thiadiazole-2-thiol , 2-(5-mercapto-1H-tetrazol-1-yl)acetic acid and 5-methoxy-1H-benzo[d]imidazole-2-thiol subtituted compunds in 1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)propan-1-one moiety showed good antibacterial activity.

The obtained antibacterial results revealed that the nature of the substituents and the substitution pattern on the 1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl) propan-1-one moiety have considerable impact on the antibacterial activities.

3.3 Antifungal Activity

All the synthesized mercapto heterocyclic derivatives of 1-(4-((4-chlorophenyl) (phenyl) methyl) piperazin-1-yl)-2-thio-propan-1-one 3(a-j) compounds were screened for in vitro antifungal activity. The antifungal activities were evaluated against different fungal strains, such as Candida albicans, Candida tropicalis, Candida guilliermondii, Candida parapsilosis and Candida glabarata. MIC values were determined by two-fold serial dilution method. Amphotericin B was used as a standard for the comparison of antifungal activity. DMSO was used as solvent control. The MIC values of the tested compounds are presented in Table 3.

Synthesised compounds 3a, 3b, 3f, 3h and 3j showed a good activity and 3c, 3d, 3e, 3f and 3i exhibited moderate activity against *Candida albicans.* Most of these compounds showed moderate activity against *Candida tropicalis*. The synthesised compounds (3a, 3f and 3h) have good activity against *Candida guilliermondii, Candida parapsilosis* and *Candida glabarata*. The antifungal activity of compounds (3a, 3f and 3h) against the tested fungal strains was significantly increased due to the introduction of 5-phenyl-1,3,4-oxadiazole-2-thiol, 3-mercapto-2-methyl-1,2,4-triazinane-5,6-dione and 5-methoxy-1H-benzo[d]imidazole-2-thiol respectively

.

Table 3. In Vitro antimicrobial Activities of 3(a-j)

Compounds	Minimum inhibitory concentrations (µg/mL)				
	Candida albicans	Candida tropicalis	Candida guilliermondii	Candida parapsilosis	Candida glabarata
3a	25	50	25	12.5	50
3b	25	100	50	25	25
3c	50	100	50	25	100
3d	50	100	50	50	50
3e	50	100	50	50	100
3f	25	100	25	25	25
3g	50	100	50	25	100
3h	25	50	25	12.5	25
3i	50	100	100	25	100
3j	25	100	50	50	50
Amphotercin-B	12.5	25	12.5	12.5	25

** Mean, ± = Standard deviation Inculdind disc 6 mm)

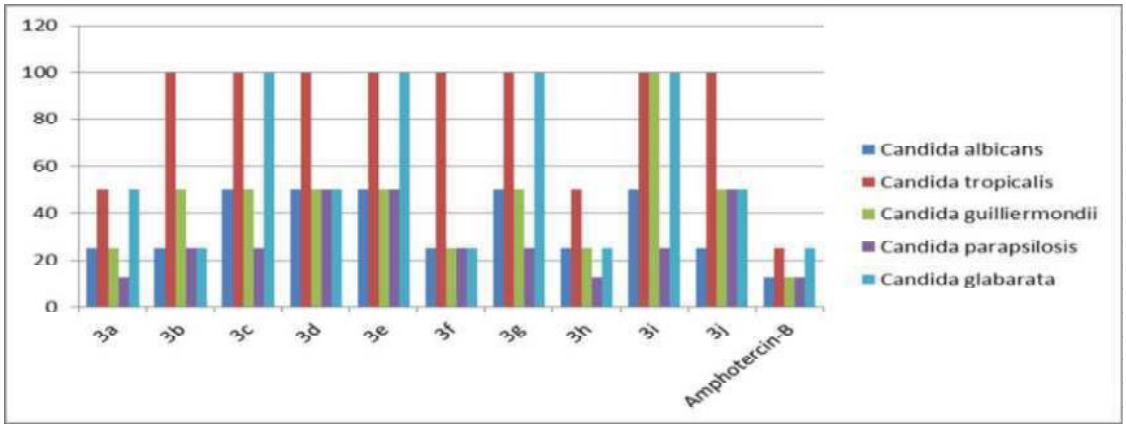


Fig.5: Bar Diagram for Antifungal study for the Sunthesised Compounds 3(a-j).

4. CONCLUSION

The main objective of the present study is to synthesize new mercapto heterocyclic derivatives of 1-(4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)-2-thio-propan-1-one 3(a-j), characterize and examine the antimicrobial and antifungal activity. The synthesised compounds 3 (a-j) containing with the hope of discovering new structures serving as potential broad spectrum antimicrobial and antifungal agents. The synthesized compounds are characterized by IR, mass, proton and carbon NMR spectra. Antibacterial study revealed that the compounds (3b, 3f and 3h) showed good antimicrobial activity. Antifungal study shows that the compounds (3a, 3f and 3h) showed good antifungal activity and compound (3h) being the best of synthesized six compounds.

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PERFORMANCE OF COMMERCIAL BANKS THROUGH INSTITUTIONAL FINANCE TO DALIT ENTREPRENEURS IN TIRUNELVELI DISTRICT

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Abstract

Dalit entrepreneurship is recent and innovation concept in our country, now-a-days most of the dalit entrepreneurs tend to start the business in all over India in between communal clauses. So, the most of the dalit people as well as dalit entrepreneurs face the problems through upper caste peoples and also entrepreneurs. Dalits are socially, economically, politically backward. They are facing the problems of untouchability, poverty, social prejudice, and lack of participation in decision making etc. most of the dalit entrepreneurs don't have own funds, so they are depends upon the outsiders fund. Hence, this paper shows performance of commercial banks through institutional finance to dalit entrepreneurs in Tirunelvelidistrict.

Keywords: *Dalit, Dalit Entrepreneurs, Institutional Finance, Commercial Banks.*

Introduction

Dalit entrepreneurship is one of the emerging concepts, which decide not only the economic development, but also the social sustainability of the country. Encouragement of entrepreneurship is the only substitute to provide employment opportunities, taking away the regional imbalances and promoting the life style of the educated youth, particular to the downtrodden society. Dalit are the most vulnerable caste group of India as well as TamilNadu. Tamil Nadu is one of the well-developed states of the country, with socio-economic infrastructure. It is the birth place of social reformer ThanthaiPeriyarbut even there are honour killing, double dumber system, dalit not allowing the car pulling festival, and separate place and so on. They are facing many problems, violation, and discrimination among the upper caste people. So, that situation in similar dalit entrepreneurs are owning the new business concern in all over India, they are not come back from business heredity family and they are does not have own funds to invest the new business concern. So this type of situation commercial banks are provide financial assistance to dalit entrepreneurs in Tirunelveli district. The given below the role and performance of commercial banks and how the financial assistance provided by commercial banks.

Meaning of Dalit

The word Dalit comes from Sanskrit it means Ground, Suppressed, Gushed or Broken to pieces. AdiDravida, Adi-Karnataka, Adi-Andhra are words used in the states of Tamil Nadu, Karnataka, and Andhra Pradesh respectively, it is identify the former untouchables for official documents.

Dalit Entrepreneurs

Dalit owning a business concern is called dalit entrepreneurs. Now-a-days most of the dalit entrepreneurs tend to start the business concern all over India. Dalit entrepreneurs are of low average of literacy level and they need to improve the business traits and they are untrained in particular field. Dalit owned enterprises are below average in India as per the report of MSMEs. But now the scenario has been changing fast with modernization, urbanization, and

development of education. But still it cannot be made to plan and develop and the need for providing appropriate awareness and environment to promote entrepreneurship is of vital importance.

Table.1 Commercial Banks in Tirunelveli District

Year	Public Sector Banks	Private Sector Banks	RRB	Total
2009-2010	18	10	1	29
2010-2011	19	10	1	30
2011-2012	19	10	1	30
2012-2013	19	10	1	30
2013-2014	23	10	1	34
2014-2015	23	10	1	34
2015-2016	24	10	1	35

Source: Lead Bank in Tirunelveli (Indian Overseas Bank)

Table 4.3 displays the commercial banks in Tirunelveli district. In the year 2009-10, totally 29 commercial banks were in the district and 18 are public sector banks. In the year 2010-11, one more public sector bank was introduced and the count increased to 30 banks in which 19 are public sector banks. The same status was maintained till the year 2012-13. In the year 2013-14, four more public sector banks were launched and the total count improved to 34 banks in the district and it was the same in 2014-15. In the year 2015-16, one more public sector bank was established in the district and the total number of banks was 35. In particular, there have been 10 private sector banks and one regional rural bank in the district since 2009-10.

Table.2 Commercial Banks' finance to Scheduled Caste entrepreneurs

Year	SC (Rs. In. 000's)
2009-2010	2596282
2010-2011	15858341
2011-2012	16019484
2012-2013	3967545
2013-2014	4167955
2014-2015	6236321
2015-2016	9721963

Source: Lead Bank in Tirunelveli (Indian Overseas Bank)

Table 4.5 illustrates the commercial banks' finance to schedule caste entrepreneurs in Tirunelveli district. In the year 2009-10, Rs.2596282 thousand was financed to SC. In the year 2010-11, Rs.15858341 thousand was financed to SC. In the year 2011-12, Rs.16019484 thousand was financed to SC. In the year 2012-13, Rs.3967545 thousand was financed to SC. In the year 2013-14, Rs.4167955 thousand was financed to SC. In the year 2014-15,

Rs.6236321 thousand was financed to SC. In the year 2015-16, Rs.9721963 thousand was financed to SC.

Table.3 Commercial Banks' finance to MSE & Retail Trade

(Amount in. 000's)

No. of Banks	MSME	MSE	R.T	Total
State Bank Group				
State Bank of India	384200	216500	301200	4359900
State Bank of Travancore	1222600	886200	318200	2108800
Nationalised Banks				
Allahabad Band	33700	28200	200	62100
Andhra Bank	112600	51300	2000	165900
Bank of Baroda	155100	68300	0	223400
Bank of India	190100	15390	37100	242590
Bank of Maharastra	4500	1600	16800	22900
Canara Bank	1829700	1199100	0	3028800
Central Bank of India	22689	1361	0	24050
Corporation Bank	1070400	945900	25700	204200
Dena Bank	12000	6000	0	18000
IDBI	79700	49700	16300	145700
Indian Bank	1945493	345600	431571	2722664
Indian Overseas Bank	3320000	208548	0	3528548
Oriental Bank of Commerce	-	-	-	-
Punjab National Bank	538000	496200	1000	1035200
Syndicate Bank	279700	51500	220500	551700
Uco Bank	78000	18600	136400	206700
Union Bank of India	244800	199800	110100	554700
United bank of India	0	0	700	700
Vijaya Bank	58100	31700	5629	95429
Pirvate Sector Bank				
Axis Bank	1188600	815400	0	2004000
City Union Bank	556223	274401	45000	875624
Federal Bank	21000	-	1500	88500
HDFC Bank	1022955	64375	0	1120330
ICICI Bank	370000	303000	6300	3763300
Karnataka Bank	6000	3600	0	9600
KarurVysya Bank	238700	7706	377835	624241
Lakshmi Vilas Bank	325700	678900	96000	1100600
South Indian Bank	117000	126500	32300	275800
Tamil Nadu Mercandile Bank	6213000	1800000	2726600	10739600
Regional Rural Bank				
PandianGrama Bank	166400	1525600	851000	2543000

Source: Lead Bank in Tirunelveli (Indian Overseas Bank)

Table No 3 indicates the commercial banks' finance to MSME, MSE and Retail Trade. State Bank of India disbursed Rs.4359900 thousand on the whole and in that MSME gained

Rs.384200 thousand, MSE Rs.216500 thousand and retail and trade Rs.301200 thousand. State Bank of Travancore expended totally Rs.2108800 thousand, in which MSME records Rs.1222600 thousand, MSE Rs.886200 thousand and RT Rs.318200 thousand. Allahabad Bank totally disbursed Rs.62100 thousand and in that MSME got Rs.33700 thousand, MSE Rs.28200 thousand and retail and trade Rs.200 thousand. Andhra Bank completely financed Rs.165900 thousand, of which MSME gained Rs.112600 thousand, MSE Rs.51300 thousands and to RT Rs.2000 thousand. Bank of Baroda provided Rs.223400 thousand, of which MSME received Rs.33700 thousand, to MSE Rs.28200 thousand and retail and trade Rs.200 thousand. Bank of India completely financed Rs.242590 thousands, of which MSME gained Rs.190100 thousands, MSE Rs.15390 thousands and to RT Rs.37100 thousand. Bank of Maharashtra offered Rs.22900 thousands, of which MSME received Rs.4500 thousand, MSE Rs.1600 thousand and retail and trade Rs.16800 thousand. Canara Bank completely financed Rs.3028800 thousand, of which MSME gained Rs.1829700 thousand and MSE Rs.1199100 thousand. Central Bank of India provided Rs.24050 thousand, of which MSME received Rs.22689 thousands and MSE Rs.1361 thousand. Corporation Bank completely financed Rs.204200 thousand, of which MSME gained Rs.1070400 thousand, MSE Rs.945900 thousand and RT Rs.25700 thousands. Dena Bank offered Rs.18000 thousand, of which MSME received Rs.12000 thousand and MSE Rs.6000 thousand. IDBI completely financed Rs.145700 thousand, of which MSME gained Rs.79700 thousand, to MSE Rs.49700 thousand and to RT Rs.16300 thousand. Indian Bank offered Rs.2722664 thousand, of which MSME received Rs.1945493 thousand, to MSE Rs.345600 thousand and retail and trade Rs.431571 thousand. Indian Overseas Bank completely financed Rs.3528548 thousand, of which MSME gained Rs.3320000 thousand and MSE received Rs.208548 thousand. Punjab National Bank assisted Rs.1035200 thousand, which of MSME received Rs.538000 thousand, to MSE Rs.496200 thousand and retail and trade Rs.1000 thousand. Syndicate Bank completely financed Rs.551700 thousand, of which MSME gained Rs.279700 thousand, to MSE Rs.51500 thousand and RT Rs.220500 thousand.UCO Bank gave an assistance of Rs.206700 thousand, of which MSME received Rs.78000 thousand, MSE Rs.18600 thousand and retail and trade Rs.136400 thousand. Union Bank of India completely financed Rs.554700 thousand, of which MSME gained Rs.244800 thousand, MSE Rs.199800 thousand and RT Rs.110100 thousand. United Bank of India provided Rs.700 thousand and it totally allotted retail and trade. Vijaya Bank completely financed Rs.95429 thousand, of which MSME gained Rs.58100 thousand, MSE Rs.31700 thousand and RT Rs.5629 thousand. Axis Bank offered Rs.2004000 thousand, of which MSME received Rs.1188600 thousand and MSE received Rs.815400 thousand. City Union Bank completely financed Rs.875624 thousand, of which MSME gained Rs.556223 thousand, MSE Rs.274401 thousands and RT Rs.45000 thousand. Federal Bank gave Rs.88500 thousand, of which MSME received Rs.21000 thousand and retail and trade got Rs.1500 thousand. HDFC Bank completely financed Rs.1120330 thousand, of which MSME gained Rs.1022955 thousand and MSE obtained Rs.64375 thousand. ICICI Bank offered Rs.376300 thousand, which of MSME received Rs.37000 thousand, MSE Rs.303000 thousand and retail and trade Rs.6300 thousand. Karnataka Bank completely financed Rs.9600 thousand, of which MSME gained Rs.6000 thousand and MSE obtained Rs.3600 thousand. KarurVysya Bank gave an assistance of Rs.624241 thousand, which of MSME received Rs.238700 thousand, MSE Rs.7706 thousand and retail and trade Rs.377835 thousand. Lakshmi Vilas Bank completely financed Rs.1100600 thousand, of which MSME gained Rs.325700 thousand, MSE

Rs.678900 thousand and RT Rs.96000 thousand. South Indian Bank provided Rs.275800 thousand, of which MSME received Rs.117000 thousands, MSE Rs.126500 thousand and retail and trade Rs.32300 thousand. Tamil Nadu Mercantile Bank completely financed Rs.10739600 thousand, of which MSME gained Rs.6213000 thousand, MSE Rs.1800000 thousand and RT Rs.2726600 thousand. PandianGrama Bank offered Rs.2543000 thousand, of which MSME received Rs.166400 thousand, MSE Rs.1525600 thousand and retail and trade Rs.851000 thousand.

Conclusion

Entrepreneurship is one of the most effective economic activities which provide not only employment opportunities but also become the economic empowerment of young talented personalities. Dalit entrepreneurs face violations by the co-entrepreneurs, customers, suppliers, employees and government officers. Without removing this kind of destruction against dalit entrepreneurs, economic development through entrepreneurial growth may not be possible. Hence, the government and policy makers should consider and implement more promotional schemes to encourage the dalit entrepreneurs through various financial institutions. The higher caste peoples do not allow the dalit in commercial activities. If they have a chance to get more financial assistance and moral support from the ruling parties, they will show their advanced talents and innovative skills to the society.

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ANALYSIS AND COMPARISON OF CRACK DETECTION IN METAL IMAGES USING BILATERAL FILTER AND DIFFUSION TECHNIQUE

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ABSTRACT

The streak image caused by metal implants degrades the image quality and limits the applications of metal that results in loss of image quality. The proposed method uses bilateral filter and it is compared with diffusion technique and fractional wavelet transformation to extract the texture features. Diffusion method used in this previous work is inefficient for detecting the pitting and laminating defects. By using Gradient Magnitude and structure coherence, the exact level of defect is found. For this purpose, an automatic defect detection and classification technique using enhanced bilateral filter is proposed to ensure the better quality of metal in manufacturing process as well as production rate. In this proposed methodology for crack detection in metal images, bilateral filter method is used to acquire the knowledge about the pattern of defects within a very short period of time and so that the defected metal may not be mixed with the fresh metal.

KEYWORDS: Diffusion, Lamination, Bilateral filter (BLF).

INTRODUCTION

Iron machines and materials square measure utilized in most of the production industries. These iron materials inherit contact with humidness and pollution which will increase the rust of iron. Corrosion takes place once in the mechanical materials, As a result of the attack of the corrosion, these mechanical materials ensure the fatigue that affects the integrity of the argentiferous surfaces. This rust caused by corrosion leads to the wastage of iron materials, reduction in potency and dear maintenance. Different departments use materials that square measure created from iron. In Civil department, for maintaining the great quality of steel bridges, it is necessary to sight rust defects. By detecting rust defects with this acne, bridge managers can make important decisions whether to paint bridges immediately or later [1]. Metallic objects like dental implants, surgical clips, or steel-hip prostheses lead to severe shadow and streak artifacts in CT images that superimpose the structures of interest and deteriorate image quality. The reason is that metallic objects have a very high density in the human body, which creates a barrier to the transmitted x-ray beam during CT examination. It results a lack of data in the projection data that lead to the production of streak in CT images. This photo deficiency caused by metallic object would become more severe under low dose scanning. During the last decade, many approaches have been proposed to reduce these artifacts. These methods can be roughly classified into iterative and interpolation-based methods [2]. If material is heated with infrared radiators, the temperature of the surface will rise suddenly. The speed at which the heat front is subsequently dissipated depends on different thermal properties of the material such as density, heat capacity, thermal conductivity and the bonding quality between top surface layer and the base material.

A defect in the sub-surface creates a barrier for the heat diffusion process and therefore the surface temperature above the defect will decrease more slowly than the temperature in other regions. The region above such a defect will show a hot area much longer than the surrounding containing good quality bonding. This causes a problem in quality assurance.[3]. Component-based representation with LDA is carried out based on a full metal image analysis [5]. The image is partitioned into several metal components to simplify the modeling of image statistics. The components are encoded by LDA to compensate for the effect of illumination and expression variation. LDA is then applied to the collection of the component-based LDA representations yielding a compact description referred to as 'cascaded LDA'. The decomposition of the face image and its re-combination in the LDA space effectively solves the problem of face retrieval and person identification.[4]. The proposed system analyses automatic crack detection in metal using famination and pitching process is explained in this paper. The paper is categorized as six sections. The first section is introduction, followed by description of the proposed system. The third section depicts the existing system and next section explains about the results and discussion. The final section states the conclusion.

Metallic rod is an important joining process in modern industries. Metallic rod with cracks is regarded as in the worst condition based on many standards in the world, which may lead to fatal accidents and cause great losses [6]. The classification is a processing step, which is decoupled from the feature definition and extraction. Any classifier in the related literature could be used for the classification of defects and the field would obviously benefit from more advanced classification methods [7]. To minimize the chance of removing or breaking cracks

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at this step, the threshold level was slightly overestimated initially, which also caused the cracks thicknesses. A simple erosion with a cross structuring element could be used to correct the thicknesses, but again could cause crack breaking [8]. Hierarchical approach to detecting weld defects is proposed. Comparing with existing techniques, different thresholds are selected to control the scales of defects that make it more flexible to meet various requirements. By using proper parameters, it is easy to locate most of defects from the radiographic image at a desired scale. However in practice, it still is a difficult problem to depict "false" defects from "true" [9]. To ensure low deformation of profile region, corroded surfaces were covered with an epoxy resin before cutting and mounting with phenolic resin for mechanical polishing. A bilateral filter is a non-linear, edge-preserving and noise-reducing smoothing filter for images. The intensity value at each pixel in an image is replaced by a weighted average of intensity values from nearby pixels. This weight can be based on a Gaussian distribution. Crucially, the weights depend not only on Euclidean distance of pixels, but also on the radiometric differences (e.g. range differences, such as color intensity, depth distance, etc.). This preserves sharp edges by systematically looping through each pixel and adjusting weights to the adjacent pixels accordingly. A representative number of 1260-960-8 bit digital images [10].

Noise filters to remove the noise due to the complexity of welding environment. Comparison of three noise filters (Bilateral filter) was made to find out the optimal noise filtering algorithm. The result showed that the Median filter algorithm is the preferred method, as not only this algorithm performance provided lower MSE (Mean Square Error) and RMSE (Root Mean Square Error) values than those of Gaussian filter and Wiener filter, but also the values of the PSNR (Peak Signal-to-Noise Ratio) and SNR (Signal-to-Noise Ratio) were higher. Therefore, the Median filter can be considered to have a better enhancement effect than the other two filters [11]. In Linear Discriminant Analysis (LDA), the proposed method finds most of the discriminative set of image processing operations to increase training samples. We analyzed the lamination and pitting defects using Diffusion methods [12].

In this proposed methodology, the bilateral filter is used in Crack Detection in Metal process. This filter may be a non-linear technique that may blur a picture whereas respecting robust edges. Its ability to decompose a picture into completely different scales while not inflicting haloes when modification has created it present in process photography applications similar to tone mapping, vogue transfer, relighting, and denoising. This text provides a graphical, intuitive introduction to bilateral filtering, a sensible guide for economical implementation and an outline of its varied applications, likewise as mathematical analysis.

PROPOSED SYSTEM

In the proposed system these images are mainly subjected to two different operations in the proposed analysis system. The first step is to preprocess and the second step is to identity the edges. The image of the metal surface has many features that need to be treated as such and all the information present in the image are analyzed.

In order to detect the crack automatically using Bilateral Filter and diffusion method and also using the texture classification and segmentation are analyzed.

An optimal spatial kernel for the bilateral filter, which is represented by a line spread function with an orientation and scale adjusted adaptively to the metal structure. Morcover, this approach can also be served as a preprocessing tool for improving the accuracy of the filter detection technique.

The proposed system implement the concept as Fractional Wavelet Transform. The proposed transform not only inherits the advantages of multi resolution analysis of the WT-Wavelet Transform, but also has the capability of signal representations in the fractional domain which is similar to the FRWT.

Edge-preserving methods and bilateral filter were proposed to overcome the loss of prominent edges. For example, the anisotropic diffusion filter and the weighted least squares filter attempt to smooth images while preserving edges based on measuring the image gradient. The nonlocal means filter computes filtered result relying on the similarity of intensity and the order of pixel in their neighborhoods. BLF is distinguished for its edge-preserving ability. for which a spatial kernel and a range kernel are combined and the output at each pixel relies both on the spatial distance and intensity differences

Bilateral Filter

As a nonlinear, edge-preserving image filtering technique, BLF treats the intensity price at every component as a weighted average of its close pixels' intensity values). BLF is capable of fixing the matter of Gaussian blurs in ancient Gaussian-convolution primarily based image filtering ways because it combines 2 components: geometer distance and radiometric distinction expressed by the subsequent equations:

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$$D(p) = k_p^{-1} \sum_{q \in R_p} W_s(d_{pq}) W_r(f_{pq}) I(q),$$

$$k_p = \sum_{q \in R_p} W_s(d_{pq}) W_r(f_{pq}),$$

Where D and kp denote the image intensities of component within the output image and component within the input image, severally. Represents a collection of components neighboring to pixel. The special kernel and vary kernel, that the weights square measure computed from the geometer distance f and also the measuring distinction between pixels and, severally. The latter is typically measured by image options similar to intensity or texture]. Could be a standardization term computed and each take a worth inverse to the corresponding input and square measure expressed generally as a Gaussian perform. As an example is calculated by

$$W_s(d_{pq}) = \exp\left(-\frac{d_{pq}^2}{2\sigma_s^2}\right).$$

In ( ), is a scale parameter determining the weight distribution pattern of the kernel. A large means that the range Gaussian widens and flattens.

BLF outperforms several different image bilateral filtering algorithms thanks to its ability to attain sensible filtering behavior whereas conserving crisp edges. it's obtained by combining the abstraction kernel and also the vary kernel. In sleek regions, BLF performs as a Gaussian low-pass filter by averaging away the little, feeble correlative variations between picture element values caused by noise, due to the abstraction kernel. For a pointy boundary shaped by a dark region and a bright one, BLF replaces the dark pixels by a median of the dark pixels in its neighborhood whereas ignoring bright pixels and the other way around, due to the vary kernel.

However, it's not trivial for BLF to differentiate between skinny metal and noise once applying it to depict pictures. This can be caused by many characteristics of the particular structure of skinny metal compared with a typical image edge that is made by dark and bright regions. First, the pixels of the skinny metal occupy a smaller portion of the pixels in its native window, inflicting the metal depict pixels to be averaged away by the abstraction kernel. Second, image intensities of skinny metal half area unit probably to be getting ready to the background thanks to the restricted resolution of metal image analysis. Third, the abstraction distribution of metal pixels is considerably completely different from freelance, isolated image noise; however BLF lacks functions to completely capture the connected specific properties.

TEXTURE CLASSFICATION

The texture analysis can be divided into various stages which are explained as follows. In the texture analysis, the image acquisition is the first process and preprocesses the image and feature extraction process can be done for the image and finally classify the images.

At the preprocessing stage, images could be segmented into contiguous regions based on texture properties. Texture features could provide cues for classifying patterns or identifying objects.

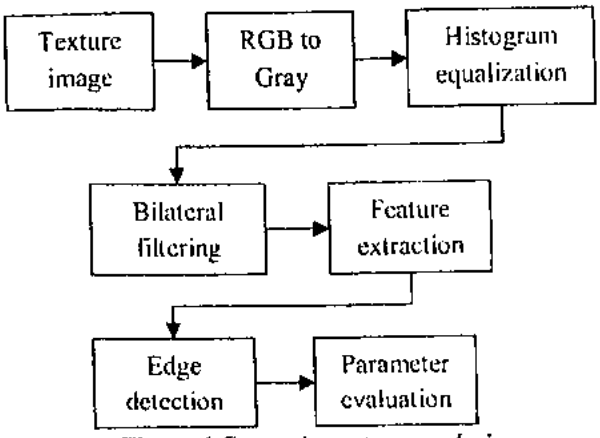

Figure 1 Stages in texture analysis

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Texture classification involves two phases: the training phase and the recognition phase. Within the learning section, the target is to create a model for the feel content of every texture category gift within the coaching knowledge that usually contains of pictures with known category labels. The feel content of the coaching pictures is captured with the chosen texture analysis technique that yields a group of textural options for every image. These options, which may be scalar numbers or distinct histograms or empirical distributions, characterize given textural properties of the photographs, akin to abstraction structure, contrast, roughness, orientation, etc. within the recognition section the feel content of the unknown sample is initial delineate with a similar texture analysis technique. Then the textural options of the sample square measure compared to those of the coaching pictures with a classification algorithmic program, and therefore the sample is appointed to the class with the simplest match.

In training phase, the classifier will be trained by labeling the input image to a specific texture class. On the other hand, the classifier will test and classify the input image into the correct texture class in testing phase, based on the available trained data. In this project, a set of collected dataset will be divided into two portions for each training and testing phase. Lastly, the output results produced by the classifier will be evaluated.

LAMINATION AND PITTING DEFECTS

A lamination defect is also called a de-lamination defect, lamination flaw, lamination fault, laminar, or simply lamination. As , it happens as a result of a flaw in the planchet, whether an incomplete mixing the metal in the alloy or a foreign substance such as dirt or gas trapped in the alloy, causing a layer of the coin's surface to peel or flake away before, during, or after striking, leaving a smaller or larger depression in the coin.

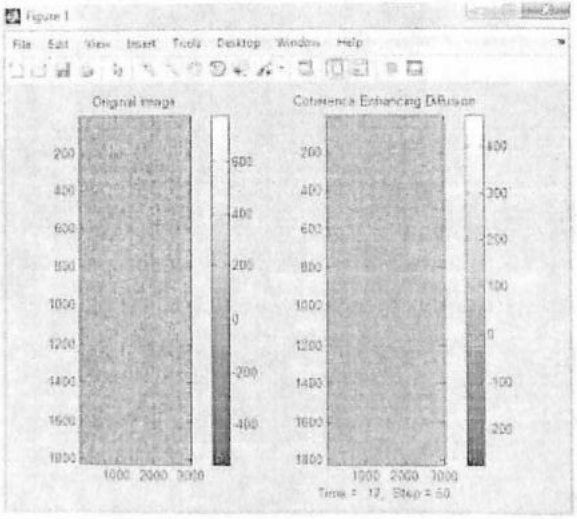

Figure 2 (a) Original Image (b) Enhanced image

In laminated materials, repeated cyclic stresses, impact, and so on can cause layers to separate, forming mica -like structure of separate layers, with significant loss of mechanical toughness. De-lamination also occurs in reinforced concrete structures subject to reinforcement corrosion, in which case the oxidized metal of the reinforcement is greater in volume than the original metal. The oxidized metal therefore requires greater space than the original reinforcing bars, which causes a wedge-like stress on the concrete. This force eventually overcomes the relatively weak tensile strength of concrete, resulting in a separation (or de-lamination) of the concrete above and below the reinforcing bars.

Bonded metal laminations to high accuracy and consistency. The use of a specialized resist provides both insulating properties within the stack as well as bonding capabilities. The etching process provides a burr free finish, ideal to eliminate problems during winding. The full process is available, including post stacking services such as grinding where required.

Metal Laminations:

[1] It can produce and bond stacks of laminations the stack height is completely customizable which incorporates top and bottom resist layers which also acts as an insulated coating and a good bonding agent.

[2] The liquid photosensitive resist that we use on most laminations is the ideal solution for the above.

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[3] In the lamination standards for all applicable mechanical and physical characteristics meet or exceed the recognized industry standards.
[4] A layer of rust inhibiting paper (V.C.I. or equivalent) shall be packed between lamination layers.
[5] In the laminations are made from various grades of electrical steels, silicon steels, nickel-iron alloys, and cold rolled motor lamination steel. To find out more about the metals available.

Major disadvantages in lamination defects are

- Producing poor bonds between layers
- Poor surface finish
- Difficulty in producing hollow parts.

PITTING DEFECTS

The inspection of fine pitch surface-mounted devices by comparison of defect-free and defective packages is a promising area of research. The types of defects considered include missing pins, bent pins, broken pins, and bad solder connections on mounted packages. The feature extraction steps include morphological filtering for thresholding, skeletonization. The diffusion image is used as input for detecting the defects.

In texture classification the goal is to assign an unknown sample image to one of a set of known texture classes. Texture classification is one of the four problem domains in the field of texture analysis. The other three are texture segmentation (partitioning of an image into regions which have homogeneous properties with respect to texture; supervised texture segmentation with a priori knowledge of textures to be separated simplifies to texture classification), texture synthesis (the goal is to build a model of image texture, which can then be used for generating the texture) and shape from texture (a 2D image is considered to be a projection of a 3D scene and apparent texture distortions in the 2D image are used to estimate surface orientations in the 3D scene). In the learning phase, the target is to build a model for the texture content of each texture class present in the training data, which generally comprises of images with known class labels. The texture content of the training images is captured with the chosen texture analysis method, which yields a set of textural features for each image. These features, which can be scalar numbers or discrete histograms or empirical distributions, characterize given textural properties of the images, such as spatial structure, contrast, roughness, orientation, etc. In the recognition phase the texture content of the unknown sample is first described with the same texture analysis method. Then the textural features of the sample are compared to those of the training images with a classification algorithm, and the sample is assigned to the category with the best match.

Using the diffusion techniques image enhanced scaling should be measured. In the texture analysis In the Texture classification process involves two phases: the learning phase and the recognition phase. This domain coincides with the one where the enhancement of the diffusion coefficient versus the tilting force is the most rapid. The necessary and sufficient conditions for the non-monotonic behaviour of the diffusion coefficient as a function of temperature are found. The effect of the acceleration of diffusion by bias and temperature is demonstrated to be very sensitive to the value of the asymmetry parameter of the potential. In the learning phase, the target is to build a model for the texture content of each texture class present in the training data, which generally comprises of images with known class labels in the texture classification images using the fractional wavelet transform image enhanced should be effectively,

RESULT AND DISCUSSION

In this paper, detection of lamination and pitting defects using LDA and Filtering and texture process is performed. LDA is then applied to the collection of the component-based LDA representations yielding a compact description referred to as 'cascaded LDA'. The decomposition of the metal image and its re-combination in the LDA space effectively solves the problem of metal identification.

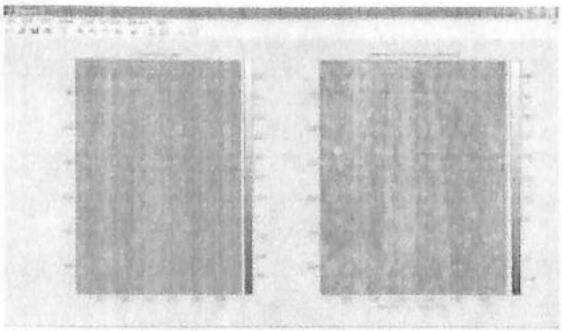

Figure 3 Raw image

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The raw image as shown in Figure 3 is loaded and preprocessing is done. The noise on the borders is quickly eliminated. Diffusion is not inhibited on borders, a rounding effect occurs.

LDA explicitly attempts to model the difference between the classes of data. PCA on the other hand does not take into account any difference in class, and factor analysis builds the feature combinations based on differences rather than similarities.

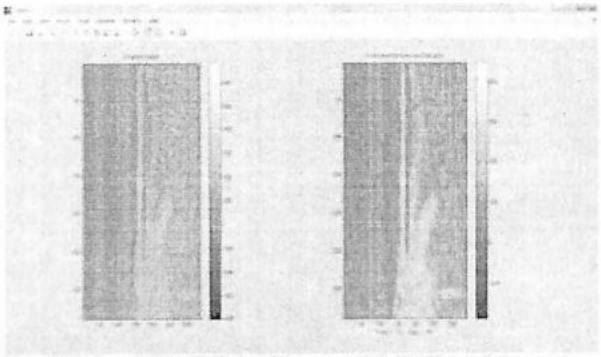

Figure 4 (a) Original image (b) Diffused image

Figure 4(a) indicates an original image and figure 4(b) shows the diffusion. The noise is removed and the defect is identified visually.

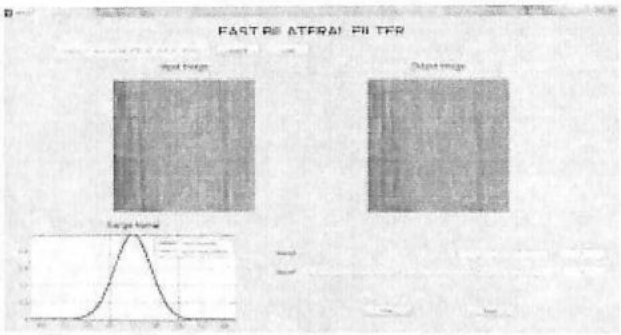

Figure (4c) structure orientation of bilateral filter.

The obtained results clearly state that BLF is better than diffusion techniques and other techniques.

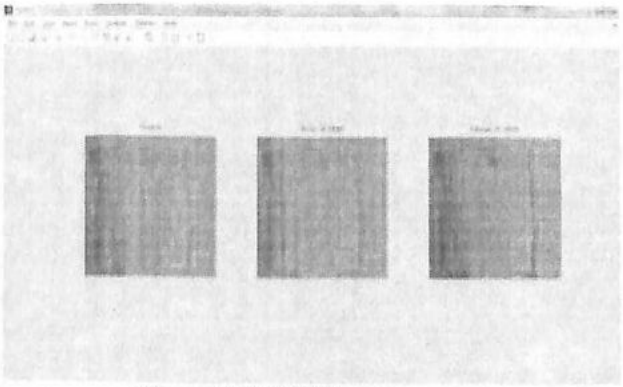

Figure 4(d) PSNR measurement

The analysis and calculation of Peak Signal to Noise Ratio (PSNR) is shown in figure 4(d). The Bilateral technique accurately depicts the metal and eliminates the noise on diffusion and LDA techniques It is predicted that PSNR value is 21.96db from figure 3e. so the greater the value of PSNR the greater the value of metal accuracy. PSNR value for diffusion technique is 10.19db. So, Bilateral filter is more efficient than diffusion techniques.

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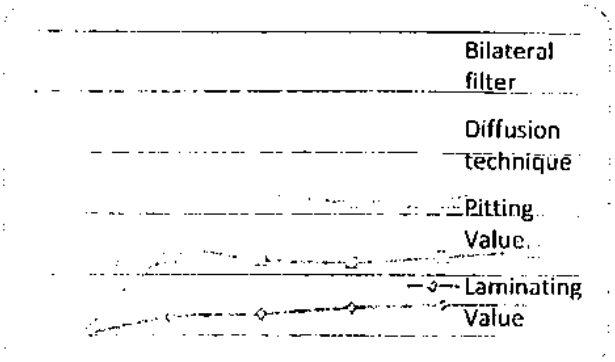
Table 1 Results of pitting

S. No	Image size	Laminating Value (dia/mm)	Pitting Value (dia/mm)	Diffusion technique	Bilateral filter
1	256*256	0.06	0.20	0.25	0.35
2	256*256	0.07	0.18	0.22	0.30
3	256*256	0.09	0.15	0.20	0.28
4	256*256	0.10	0.16	0.19	0.26
5	256*256	0.10	0.18	0.23	0.27

The Bilateral and the pitting defects are shown graphically.



Graph 1Comparision of BLF with existing techniques

The above graph reveals that results obtained for the bilateral defect is more efficient than the laminating defect. The noise is removed more efficiently using BLF technique in pitting and laminating defects.

CONCLUSION

The Bilateral Filter is used in various types of images and detecting the accuracy of spot defect which is greater than scratch defects. The speed of detection is increased as well as accuracy is maintained by using proposed approach. BLF is isotropic across the whole image and we find that adjusting the kernel according to the local image structure can significantly improve the performance of image denoising. These properties can be represented by an LSF that spreads as a Gaussian function. Therefore, we propose to determine the spatial kernel of BLF by a particular LSF, which can be obtained by using the Gaussian-like kernel of MF. The proposed BLF performs significantly better in preserving thin metal in metal images while denoising the image. In the proposed method it is predicted that the original BLF is benefited in crack image structure preservation. The result is accurate for pitting defect than laminating by using Fast Bilateral Filter.

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FEATURES OF GOODS AND SERVICE TAX IN INDIA

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Abstract

This paper is an analysis of what the impact of GST (goods and services tax) will be on Indian tax scenario. Here stated with a brief description of the historical scenario of Indian taxation and its tax structure. Then the need arose for the change in tax structure from traditional to GST model. GST has be detailed discuss in this paper as the background, silent features and the impact of GST in the present tax scenario in India. The goods and services tax (GST) is a value added tax to be implemented in India, the decision on which is pending. GST is the only indirect tax that directly affects all sectors and sections of our economy. Ignorance of law is no excuse but is liable to panel provisions, hence why not start learning GST and avoid the cost of ignorance. Therefore, we all need to learn it whether willingly or as compulsion. The goods and services tax (GST) is aimed at creating a single, unified market that will benefit both corporate and the economy. The changed indirect tax system GST-goods and service tax is planned to execute in India. Several countries implemented this tax system followed by France, the first country introduced GST. Goods and service tax is a new story of vat which gives a widespread setoff for input tax credit and subsuming many indirect taxes from state and national level.

Key words: GST, Features, CGST, SGST, and VAT

Introduction

The GST implementation is not yet declared by government and the drafting of GST law is still under process and a clear picture will be available only after announcement of implementation. India is a centralized democratic and therefore the GST will be implemented parallel by the central and state governments as CGST and SGST respectively. The objective will be to maintain a commonality between the basic structure and design of the CGST, SGST and SGST between states .in this article, I have started with the introduction, in general of GST and have tried to highlight the objectives the proposed GST is trying to achieve. Introduction of the value added tax (VAT) at the central and the state level has been considered to be a major step – an important step forward – in the globe of indirect tax reforms in India. If the vat is a major improvement over the pre-existing central excise duty at the national level and the sales tax system at the state level, then the goods and

services tax (GST) will indeed be an additional important perfection – the next logical step – towards a widespread indirect tax reforms in the country. Initially, it was conceptualized that there would be a national level goods and services tax, however, with the release of first discussion paper by the empowered committee of the state finance ministers on 10.11.2009, it has been made clear that there would be a "dual GST" in India, taxation power – both by the centre and the state to levy the taxes on the goods and services. Almost 150 countries have introduced GST in some form. While countries such as Singapore and new Zealand tax virtually everything at a single rate, Indonesia has five positive rates, a zero rate and over 30 categories of exemptions. In china, GST applies only to goods and the provision of repairs, replacement and processing services. GST rates of some countries are given below. Country Australia France Canada Germany Japan Singapore Sweden Newzealand rate of GST 10% 19.6% 5% 19% 5% 7% 25% 15% world over in almost 150 countries there is GST or vat, which means tax on goods and services. Under the GST scheme, no distinction is made between goods and services for levying of tax. In other words, goods and services attract the same rate of tax. GST is a multi-tier tax where ultimate burden of tax fall on the consumer of goods/ services. It is called as value added tax because at every stage, tax is being paid on the value addition. Under the GST scheme, a person who was liable to pay tax on his output, whether for provision of service or sale of goods, is entitled to get input tax credit (ITC) on the tax paid on its inputs.

Statement of the problem

The ongoing economic down turn and slowdown of economy across the world has, however, given India a golden opportunity to stake claim and get a cushioned berth in the world order. To achieve this, the country nevertheless needs to increase its GDP to at least twice that of the present level. The direct taxation regime has been by and large undergoing annual fine tuning and as a result the revenue receipt in this account has considerably increased. However, reform on such scale in indirect taxes has not been done so far. Indirect taxes are therefore urgently required to be rationalized and unified. If the GST is introduced in letter and spirit, it would certainly increase the volume of tax collection. This will provide a great stimulus to our gently moving economy, which has, of late, arrived at a level playing field vis-a-vis many major economies of the world.

Need for GST

There is a saying in kautilaya'sarthshastra, the first book on economics in the world, that the best taxation regime is the one which is ""liberal in assessment and ruthless in collection"". The present system allows for multiplicity of taxes being collected through an

inefficient and non transparent system, the introduction of GST is likely to rationalize it and thereby plug the loop holes in this system. This will enable the government to stop pilferage and rationalize the overall taxation regime.Introduction of an integrated goods and services tax (GST) to replace the existing multiple tax structures of centre and state taxes is not only desirable but imperative in the emerging economic environment. Increasingly, services are used or consumed in production and distribution of goods and vice versa. Separate taxation of goods and services often requires splitting of transactions value into value of goods and services for taxation, which leads to greater complexities, administration and compliances costs.

There is need to have a nation-wide simple and transparent system of taxation to enable the Indian industry to compete not only internationally, but also in the domestic market. Integration of various central and state taxes into a GST system would make it possible to give full credit for inputs taxes collected. GST being a destination-based consumption tax based on vat principle, would also greatly help in removing economic distortions caused by present complex tax structure and will help in development of a common national marked. The benefits of GST legislation will be uniformity of laws across the board, greater transparency, neutrality in tax rates on various products; credit availability on interstate purchases and reduction in compliance requirements. If GST is implemented in the true spirit, it will have many positives for the stakeholders and will lead to a better tax environment.

Objectives

One of the main objectives of GST would be to eliminate the cascading impact of taxes on production and distribution cost of goods and services. The exclusion of cascading effects i.e. Tax on tax will significantly improve the competitiveness of original goods and services which leads to beneficial impact to the GDP growth. It is felt that the GST would serve a superior reason to achieve the objective of streamlining indirect tax regime in India which can remove cascading effects in supply chain till the level of final consumers only when all such above mentioned indirect taxes are completely included in GST. It is understood that alcohol, tobacco and petroleum products will not be enclosed by GST as alcohol and tobacco are considered as sin goods, and governments do not like to allow free trade on these property.

Review of literature

Rao (2004) tried to examine the extent of gain or loss to the states from the introduction of value added tax, having features of uniform design, tax credit for inputs, extension of tax base to transactions beyond the first-point sale and zero-rating of interstate trade and international exports. She stated that exclusion of services from the base would not eliminate the problem of cascading from the tax system. As manufacturing sector output was the major basis of sales tax, the estimation of impact of vat was limited to registered manufacturing sector only. If the entire cost of tax was passed on as higher prices of output, then the result would be reduction in value of output. The effects of introduction of vat were classified into four parts, i.e., loss from providing input tax credit, loss from reduced value of output, loss from removal of cst, and gains from taxing second and subsequent sales within the state. With certain assumptions, she estimated the losses, gains and net impact on different states for the year 1997-98. With 15 per cent rate of vat, the impact (loss) varied from Rs. 932 crore for U.P. to Rs. 1054 crore for Maharashtra. The author concluded that on the basis of assumptions, some states seemed to gain consistently from introduction of vat, while the others were expected to lose. The losses could be avoided by changing the vat rates and structure but this could be a hindrance in the formation of a common internal market. She cautioned that central government's assurance for compensation in case of losses in revenue from introduction of vat could invite negative response from states in terms of slackness of efforts in collection of VAT.

Empowered committee (2005) laid down the roadmap of state-level vat in India in the white paper, which consisted of three parts. In part-i, justification of vat and background were discussed. Problems of double taxation and multiplicity of taxes were cited as the major drawbacks of sales tax structure. The merits of vat were reported to be input tax credit, abolition of other than vat taxes, rationalization of overall tax burden, and self- 45 assessment by dealers, transparency and higher growth in revenue. To harmonize the vat design in the states, common points of convergence with certain flexibility were reported to be the basis, which were elaborated in part-ii. These points included: input tax credit, its coverage and carrying over; treatment of opening stock; compulsory issue of tax invoice, cash memo or bill; registration; small dealers and composition scheme; tax payer's identification number; return; procedure of self-assessment of vat liability; audit; declaration form; incentives; other taxes; penal provisions; coverage of goods under vat; vat rates and classification of commodities.

Nour and Pramanik (2005) stated that vat is a multi-point turnover tax imposed at each stage of production and distribution on sales minus cost incurred. They discussed different variants of vat, i.e., gross product type, income type, 46 consumption type and the wages type. They also discussed the three methods of computing vat, i.e., addition method, subtraction method and credit (invoice) method. From the methods of computing, they brought out that vat helped in reducing tax evasion, whereas sales tax had considerable scope for evasion. They suggested that for better administration of vat, each taxpayer be allotted a master file and tax identification number (tin). They concluded that vat would help in improving allocative efficiency, growth and balance of payments; avoiding cascading effect; providing less scope for vertical integration; and facilitating accuracy of tax refunds on exports.

Bezborah and Singh (2005) pointed out the weaknesses of sales tax structure which included lack of uniformity in tax rates, multiplicity of rates, cascading nature, pyramiding effect and revenue loss due to incentives. While reporting essentials of good sales tax structure, they opined that vat was a good alternative for sales tax. However, vat also has some black spots. Further, they brought out implementation problems of vat in India. They also discussed the issues of uniformity of rates, removal of cst, making service taxable, unification of taxes, threshold limit and refund mechanism; and concluded that implementation of vat in India should not be delayed further.

Misra (2005) opined that value added tax was a measure to broad-base the tax net and countries all over the world have adopted this miracle tax. He pointed out that the superiority of vat lay in the fact that it prevented cascading effect of taxation 47 and reduced tax evasion. Cross verification of accounts of all the enterprises has been made possible with the help of computers under vat and as such accounts could not be manipulated. Vat could lead to capital formation in the country when depreciation is made deductible from tax base and tax on capital goods is offset against vat liability. Vat could also improve balance of payments of the country as exports are zero-rated. However, vat might not be suitable for a large country with a strong federal system. The author stated that for introduction of vat, existing tax rates be rationalized, tax credit system be introduced in place of incentives and steps be taken to abolish GST.

Sthanumoorthy (2005) reported that states in India carried out a path-breaking tax reform by replacing defective sales tax with value added tax (vat). The author pointed out that sales tax system suffered from many structural weaknesses, including multiplicity of sales tax rates and commodity categories in each state; wide differences in rates within and between

states; cascading effect due to its imposition on a large number of inputs; tax competition among states; tax exportation; large number of exemptions; application of surcharge and additional levies; additional sales tax and turnover tax; entry tax and octroi; complicated and wide variety of tax rules and widespread tax evasion. Even when policy-makers were advocating replacement of sales tax with vat, the attempts were initiated in early 1990s. The process was delayed due to several implementation problems and finally central government persuaded majority of the states to switch over to vat with effect from 1.4.2005. The author discussed important issues and 48 challenges in implementation of vat and in this context experience of some of the Indian states and countries operating vat system was reported.

Salient features of the GST

1) The GST shall have two components: one levied by the centre (referred to as central GST), and the other levied by the states (referred to as state GST). Rates for central GST and state GST would be approved appropriately, reflecting revenue considerations and acceptability.
2) The central GST and the state GST would be applicable to all transactions of goods and services made for a consideration except the exempted goods and services.
3) The central GST and state GST are to be paid to the accounts of the centre and the states individually.
4) Since the central GST and state GST are to be treated individually, taxes paid against the central GST shall be allowed to be taken as input tax credit (itc) for the central GST and could be utilized only against the payment of central GST.
5) Cross utilization of ITC between the central GST and the state GST would not be permitted except in the case of inter-state supply of goods and services.
6) Ideally, the problem related to credit accumulation on account of refund of GST should be avoided by both the centre and the states except in the cases such as exports, purchase of capital goods, input tax at higher rate than output tax etc.
7) To the extent feasible, uniform procedure for collection of both central GST and state GST would be prescribed\ in the respective legislation for central GST and state GST.
8) The states are also of the view that composition/compounding scheme for the purpose of GST should have an upper ceiling on gross annual turnover and a floor tax rate with respect to gross annual turnover.
9) The taxpayer would need to submit periodical returns, in common format as far as possible, to both the central GST authority and to the concerned state GST authorities.

10) Each taxpayer would be allotted a pan-linked taxpayer identification number with a total of 14/15 digits. This would bring the GST pan-linked system in line with the prevailing pan-based system for income tax, facilitating data exchange and taxpayer compliance.

The introduction of the GST brings about a macroeconomic dividend as it reduces the overall incidence of indirect taxation and therefore the overall tax burden by removing the many distortionary features of the present sales tax system. There are four important macroeconomic channels through which this happens:

1) First, the failure to tax all goods and services distorts consumption decisions; it weakens the signaling power of relative prices. GST reduces these distortions and enables all economic agents to respond more effectively to price signals.
2) Second, the unrefined taxation of capital goods discourages savings and investment and retards productivity growth. This is perhaps the most important gain through introduction of GST in an emerging economy like India.
3) Third, for a given constellation of exchange rates and price levels, violation of the destination principle places local producers at a competitive disadvantage, relative to producers in other jurisdictions.
4) Fourth, differences in tax bases of different states and the central government greatly increase costs of doing business. The GST based tax reform provides a real policy opportunity to do something about this problem without waiting for prior and sweeping political economy changes.

Conclusion:-

GST is the most logical steps towards the comprehensive indirect tax reform in our country since independence. GST is leviable on all supply of goods and provision of services as well combination thereof. All sectors of economy whether the industry, business including govt. Departments and service sector shall have to bear impact of GST. All sections of economy viz., big, medium, small scale units, intermediaries, importers, exporters, traders, professionals and consumers shall be directly affected by GST... One of the biggest taxation reforms in India -- the goods and service tax (GST) -- is all set to integrate state economies and boost overall growth. GST will create a single, unified Indian market to make the economy stronger. Experts say that GST is likely to improve tax collections and boost India's economic development by breaking tax barriers between states and integrating India through

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IMPACT OF GST ON TEXTILE INDUSTRY IN INDIA – AN OVERVIEW

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Abstract

Textile industry plays a major role in the Indian economy. It contributes 14 per cent to industrial production and 4 per cent to GDP, with over 45 million people. the industry is one of the largest sources of employment generation in the country. The industry accounts for nearly 15 per cent of total exports. It has been enjoying various tax exemptions. benefits and concessions under indirect taxes. Introduction toGoods and Services Tax(GST) could have a considerable impact on the Indian textile industry. GST would affect the cotton value chain of the textile industry, including all garments for men and women like shirts. trousers. saree, apparels, shoes and any more clothing materials, which is chosen by most small medium enterprises as it currently attracts zero central excise duty. Textile industry products are likely to become more expensive, with the government fixing a higher rate on them under the GST, than the rates at which they are currently taxed. Textile industry has differential treatment for cotton and synthetic fibre on GST rate is an opportunity lost for a uniform rate for the textile manufacturing sector. The handloom sector, powerloom sector and the textile sector as a whole, "about 70 lakh workers are employed in the powerloom sector. They are worried about the excessive slabs of the Goods and Services Tax (GST), it is hampering their livelihood. In this paper, an effort has been made to examine the impact of GST on the Indian Textile Industry.

Keywords: GST, Textile Sector, GST rate, Impact, and Input credit

Introduction

Textile industry plays a major role in the Indian economy. It contributes 14 per cent to industrial production and 4 per cent to GDP, with over 45 million people, the industry is one of the largest sources of employment generation in the country. The industry accounts for nearly 15 per cent of total exports and this value is likely to increase under Goods and Services Tax. Known as one of the oldest manufacturing industry in the country and the second largest, after agriculture, the textile industry employs both skilled and unskilled people. The textile industry has two segments, organised and unorganised. The

unorganisedtextile sector includes handicraft, handloom, small and medium scale mills whereas an organised sector consists of spinning, garment and apparel which uses modern machinery and techniques. Under the GST purview, the rate structure for textile is decided at 5% for cotton fibre and 18% for manmade synthetic fibre while totally exempting silk and jute from the same. The rate of GST on apparels is also decided based on the category, as the apparels whose cost is below Rs. 1000 will attract 5% GST and apparels above this mark will attract 12% GST. Goods and Services Tax would affect the cotton value chain of the textile industry including all garments for men and women like shirts, trousers, saree, apparels, shoes and any more clothing materials which is chosen by most small medium enterprises as it currently attracts zero central excise duty.

Concepts *GST*

The Goods and Services Tax (GST) Council announced rates for the textile and other pending categories on June 3, 2017, moving one step closer to the proposed implementation of the new tax regime with effect from July 1, 2017. While rates for most commodities were announced on May 19, 2017, the announcement for the textile sector came with a lag owing to the complexities involved in the textile value chain, given the multiple layers and considerations as well as its far-reaching implications on the country's output and employment.

GST Rate for the Textile Sector

With the exception of man-made fibres, the GST rates for all input categories viz. cotton, silk, jute, wool as well as other natural fibres have been kept in the Nil/lowest tax slab of 5% up to the fabric-making stage. In the downstream segment of end-product manufacturing, multiple rates have been introduced varying across product categories as well as across price-points. Further, the rates announced for the MMF based products follow an inverted duty structure wherein the raw materials have been subjected to taxation at higher rates

Review of Literature

Mahender (2017)has studied "GST Effect on Manufacturing Industry – India" and concluded that manufacturing industry is playing a significant role in Indian business scenario hence manufacturing sector is economic growth of nation. In his research paper he states that Textile and garment industry maybe negatively impacted with the introduction of GST.

Lourdunathan and Xavier (2017) have studied that "A study on implementation of goods and services tax (GST) in India: Prospectus and challenges". The concluded that GST will bring One Nation and One Tax market. Efficient formulation of GST will lead to resource and revenue gain for both Centre and States majorly through widening of tax base and improvement in tax compliance.**Sankar R, (2017)** has observed that the tax rate of this industry under the regime of GST it is expected at the rates of 15% which will be having a moderate impact on the industry. This moderate impact may either be neutral or slightly negative when compared to the other present system of taxation. But they will be benefited through the reduction of cost in transportation, savings etc.,

Objectives

1) To study about the concepts of Goods and Services Tax.
2) To study about the impact of GST on Textile industry in India.
3) To provide suggestions and recommendations regarding GST.

Methodology

This study is descriptive in nature and it used the exploratory technique. The study is completely based on the secondary data. The secondary data has been collected from the Ministry of Textile, Books, and Journals and so on.

Impact of GST on textile industry

Goods and Services Tax or GST is a reality as business operations have been taking place across the states and around the world under new taxation policy in India. There are certainly expectations that this tax reform will boost the Indian economy; however, there are doubts as well that it will have both positive and negative impacts on industries. So, what is the impact of GST on various sectors in India? Let's get the answer of it by putting some light on impact of GST on various sectors such as textile, iron & steel, pharma& healthcare, cement and telecom.

It is expected that the tax rate under GST would be higher than the current tax rate for the textile industry. Natural fibers (cotton, wool) which are currently exempt from tax, would be taxed under Goods and Services Tax.

Impact up to the Fabric-Manufacturing Stage

The effective tax incidence on cotton and MMF/ blended textiles (up to fabric stage) under the existing tax regime is in the range of 5-7% and 11-14% respectively. Besides excise

duty, this captures the impact of other multiple levies such as Value Added Tax (VAT), Central Sales Tax (CST) and Entry Tax/ Octroi. Considering that the GST rates announced for these textile categories are more or less in line with the existing effective tax rates, ICRA does not envisage any impact on these product categories. However, the rates announced are expected to be positive for wool/ silk-based textiles which will be taxed at a lower rate of 5% vis-à-vis their prevailing tax incidence of 8-10%

Impact on Apparel Manufacturers

Though the impact is unlikely to be substantial up to the fabric stage, differential rates for the apparels based on pricing points is likely to create some impact on the apparel-manufacturers. While the impact is likely to be positive for apparels priced at less than Rs. 1,000/ piece in terms of reduced tax liability, the impact is likely to be marginally negative to negative for costlier apparels priced at more than Rs. 1,000 per piece.

Break in input credit chain

A significant portion of the textile industry in India operates under the unorganized sector or composition scheme, thus creating a gap in flow of input tax credit. Input tax credit is not allowed if the registered taxpayers procure the inputs from composition scheme taxpayers or the unorganized sector. GST would enable a smoother input credit system, which would shift the balance towards the organized sector.

Reduction in manufacturing costs

GST is also likely to subsume the various fringe taxes like Octroi, entry tax, luxury tax etc. which would help reduce costs for manufacturers in the textile industry.

Input credit allowed on capital goods

Currently, the import cost of procuring the latest technology for manufacturing textile goods is expensive as the excise duty paid is not allowed as input tax credit. Whereas under GST, there will be input tax credit available for the tax paid on capital goods.

Revenue Neutral rate proposed to be higher under GST:

Currently, the State VAT is 4-5% on apparels and with 1.2% effective central excise duty on branded garments with MRP of more than Rs 1000, the overall tax incidence on the finished goods, i.e. apparels is lower than 12%, which is the lowest rate being proposed in GST. This would be in spite of credit not being available for all tax/ duties paid in the past.

An important determinant of the tax incidence under GST will be the GST rate Applicable to the textile segments. While the final GST rates are yet to be announced, even at the 12% lower rate recommended by the Dr. Arvind Subramanian Committee, The textile

sector is likely to be negatively impacted. The cotton value chain is likely to be the worst affected as it is currently attracting zero central excise duty and tax in Inputs may not be more than 2-4%.Further the apparel retailers will not have sufficient input credits (such as service tax on rent of showrooms) to offset the increased tax liability if the GST is not levied on upstream sectors like yarn and fabrics and will be negative for retailers.

Conclusion

It is concluded that introduction of GST will usher in a plethora of changes in the textile business of India with an overall positive impact on the sector. GST implementation is expected to produce impetus to various reforms and policy measures envisaged by the Government for the ease of doing business and to usher India into a simple, transparent and tax friendly regime.GST would affect the cotton value chain of the textile industry, including all garments for men and women like shirts, trousers, saree, apparels, shoes and any more clothing materials, which is chosen by most small medium enterprises as it currently attracts zero central excise duty. Textile industry products are likely to become more expensive, with the government fixing a higher rate on them under the GST, than the rates at which they are currently taxed. But it is safe to say that GST will help this industry in the long run by getting more registered taxpayers under a well-regulated system. It can also be hoped that GST will help the textile industry to get more competitive in both the global and domestic markets and create opportunities for sustainable, long-term growth.

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Farmers Perspective of Agricultural Economics in Tamilnadu

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Abstract

Agricultural sector is the primary sector whose growth will act as a catalyst to the growth of other sectors. Theorists have propounded the growth stages in that an economy's growth is transited from agriculture through industry to the service sector. So far as the state economy is concerned there is virtually no growth in the agricultural sector and in the manufacturing sector. The growth of the economy is mostly contributed by the service sector. However, one cannot neglect the primary sector if one seeks long run sustainable growth of the economy. The performance of the agricultural sector, especially in developing countries often depends on environments outside the reach of policy-makers. The weather, world prices (depending on how much the world demands of agricultural products and how much the rest of the world delivers), external trade barriers, terms of trade and global market access all play pivotal role in influencing agricultural outcomes. The present study is descriptive by nature. The sample was selected based on the convenience sampling or purposive sampling. The sample size is confined as 100 farmers who are having account in the co-operative banks. These farmers are selected from all in the Tanjavore district. Farmers must shift their cultivation pattern from traditional crop to commercial crop, so that they can earn more income from their cultivation. And also use natural seeds and fertilizers for their cultivation.

KEYWORDS: *agricultural finance, changes in technology, agricultural productivity*

Introduction

Agriculture is the back-bone of Indian economy, it offers direct employment to 2/3rd of our population and it is a provider of food, clothing, fodder and other basic necessities of life for the entire population. The role of agricultural finance in the agricultural development of a country cannot be overemphasized. One of the reasons for the decline in the contributions of agriculture to the economy is lack of a formal National Credit Policy and paucity of credit institutions, which can assist farmers.

The development dynamics of the regional economy of Tamilnadu are formulated by the interaction of a variety of unique historical, geographical, cultural and economic environment. The importance of agriculture in the economic development of a country is undebtable. Agriculture is the oldest industry in the World and the largest even today. The major part of the population of the World is dependent upon it for a living. And its contribution to economic development of a country is significant.

Economic development may be defined as transformation of an economy which is predominantly agricultural and traditional; into one of largely industrial and modern. In the former, agricultural and non-agricultural sectors remain separate presenting economic dualism, while in the latter they get integrated.

Agricultural sector is the primary sector whose growth will act as a catalyst to the growth of other sectors. Theorists have propounded the growth stages in that an economy‟s growth is transited from agriculture through industry to the service sector. So far as the state economy is concerned there is virtually no growth in the agricultural sector and in the manufacturing sector. The growth of the economy is mostly contributed by the service sector. However, one cannot neglect the primary sector if one seeks long run sustainable growth of the economy. The performance of the agricultural sector, especially in developing countries often depends on environments outside the reach of policy-makers. The weather, world prices (depending on how much the world demands of agricultural products and how much the rest of the world delivers), external trade barriers, terms of trade and global market access all play pivotal role in influencing agricultural outcomes.

Technological change in agriculture is reflected directly on the productivity of crops. It enhances the productivity of land and improves the capability of agricultural labour. Technical change in agriculture ranges from the use of high yielding varieties of seeds, irrigation, fertiliser and machines such as pump sets, mechanical devises for tilling the soil, sowing and harvesting for raising per hectare output. Therefore, the

study of productivity, both partial and total productivity of crops is also a study of the technological change in the crop sector.

Importance of the study

India is basically a rural economy and rural India virtually includes the cultivators, the village craftsmen and agricultural laborers. One of the serious and unrelenting problems faced by the Indian farmers‟ households has been the indebtedness. Despite substantial improvement in agricultural output and distribution of credit, still a majority of the farmers are suffering from this major economic malaise called indebtedness along with lack of timely and adequate farm credit. It is a symptom of a deep rooted malady arising from inadequate public investment and insufficient public action in recent years. It is essential that a sound system of credit should be built up so as to fulfill the credit needs of the farmers and to ensure that agricultural credit serves the national economy in a dynamic way. Various criteria for a good credit system have been laid down by various experts and institutions.

Financing for agriculture has been a gigantic task for banks in India. Ensuring timeliness and adequacy of credit to farmers have posed the most serious challenge for banks while financing the agricultural sector. The success of agriculture in our country depends not only on the use of new technology in the shape of application of high yielding varieties to more and more areas, use of better seeds, fertilizers and plant protection methods, development of water resources and improvement in the soil conservation practices, but also in the provision of adequate credit at the right time.

Review of literature

According to Bhalla, of the three sectors of economy in India, the tertiary sector has diversified the fastest, the secondary sector the second fastest, while the primary sector, taken as whole, has scarcely diversified at all. Since agriculture continues to be a tradable sector, this economic liberalization and reform policy has far reaching effects on (I) agricultural exports and imports, (ii) investment in new technologies and on rural infrastructure (iii) patterns of agricultural growth, (iv) agriculture income and employment, (v) agricultural prices and (vi) food security.

Lena Roussenova and Dimiter Nenkov (2007) in their study on “Agricultural Finance and Institutional Reforms in Bulgaria” revealed that agriculture has traditionally played a significant role in the Bulgarian economy. Since 1997, the government has made rapid progress in implementing a wide-ranging reform program in agriculture, the financial sector and in the economy in general. Most of these programs are continuously undergoing changes, consistent with the developments in the agricultural and banking sectors. With continuing recovery of public trust in banks, and with more than 70 per cent of banks‟ assets owned or controlled by foreign private banks, the sector is expected to overcome conservative lending.

Dr. Jason L. Johnson (2009) in his study “The Financial Condition and Sources of Financial Risk for Agriculture in 2009” divulged that agricultural stakeholders throughout the U.S. and within Texas indicated a high probability that the volatility of input prices, commodity prices, and profit margins in agriculture will likely to lead increased levels of financial stress in the coming years. The resulting business climate will place even more emphasis on superior financial management skills and documentation to secure external funding for operations. All agricultural producers should begin (or continue) their process of examining the many risk factors that threaten their future profitability and survival. If necessary, new or expanded risk management skills and strategies should be developed by farm and ranch managers to ensure that they are able to remain viable through this period.

C. Mahadeva Murthy B. H. Suresh and K. P. Veena (2009) in their article “Dimensions of Institutional Finance for Agricultural Activities: An Analysis” pointed out that agriculture is a way of life, a tradition, which for centuries has shaped the thought, the outlook, the culture and the economic life of the people of India. Nearly 61 per cent of the workforce depends upon agriculture for livelihood. Credit is a vital factor of the production function, more so in Indian agriculture. The paper concludes that institutional credit has played a vital role in supporting cultural production in India and the amount of institutional credit for agriculture and allied activities has increased over the years.

S. Gandhimathi and S. Vanitha (2010) in their study “Determinants of Borrowing Behaviour of Farmers – A Comparative Study of Commercial and Cooperative Banks”, analyzed that the preference of farmers between commercial and cooperative banks for borrowing has been studied with the objectives of finding distribution of institutional credit across various categories of farmers and to assess the coverage and quantum of credit and socio-economic factors which tell on the borrowing behavior of farmers towards commercial and cooperative banks. In the study, based on 100 farmer borrowers, the discriminant analysis has been carried out. The study has offered some suggestions also for a better access of farmers to institutional credit.

Statement of the problem:

The signs of continuous sluggishness have been reflecting upon the performance of agricultural sector, particularly crops sector of Tamilnadu. Several factors have been identified as agents for improving agricultural production. Both institutional and technological factors work behind a thriving agricultural sector. Land reform measures are one of the important institutional changes that invigorate agricultural development. Tamilnadu is one of the regions where state directly intervened in the redistribution of land by legislative measures and made land available to the „tillers‟ of the soil. The other institutional mechanism is related to the provision of credit. Tamilnadu is considered to be one of the best in regard to provision of credit in the country. Thus land reform measures and institutional credit system may be reckoned as favorable factors for the growth of Tamilnadu"s agriculture. Other crucial factors that govern the growth of agricultural sector are a vibrant market for agricultural labour and the technological change. Tamilnadu has well-organized and spirited agricultural labour market that is controlled by labour unions that were able to raise agricultural wages. Many research studies in the remote and recent past on the crops sector as a whole and on specific crops in particular concluded that the prime factor behind the diffidence of agricultural sector was the absence of productivity growth and stagnant technology in the sector. Now it is a known and established empirical fact that agriculture in the state has been sinking. And almost all studies in the Tamilnadu context have recorded that the productivity of agriculture in the state has been falling. There are some relevant questions that arise in this context. What were the dynamic factors that historically contributed to low productivity, particularly land productivity? Is low productivity common to all crops or limited only to certain crops? What has been the contribution of productivity growth to total output growth of the agriculture? What have been the sources of total factor productivity growth in the crop sector of the state? The present study focuses on these questions.

Objectives of the study

The following objectives were framed for the present study

To know the factors influencing agricultural productivity fallen in the Tamilnadu

To study perception of farmers about reduction agricultural production

To give suitable suggestion to improve agricultural productivity in Tamilnadu

Methodology

Sources of the study

The data required for the study have been collected from both the primary and secondary sources. The primary data have been collected directly from Farmers by using Interview schedule. The secondary data have been collected from the published journal, books, magazines and websites.

Sampling

The present study is descriptive by nature. The sample was selected based on the convenience sampling or purposive sampling. The sample size is confined as 100 farmers who are having account in the co-operative banks. These farmers are selected from all in the Tanjavore district. Because Tamilnadu major agricultural cultivation from Tanjavore. So that researcher is selected respondents from Tanjavore district.

Analysis and interpretation

S. No	Educational qualification	No. of Respondents	Percentage
1.	Illiterate	06	6%
2.	Primary school	21	21%
3.	Higher secondary school	28	28%
4.	UG	32	32%
5.	others	13	13%
	Total	100	100%

The above table shows that maximum of 32% of the respondents are having UG level educational qualification. 28% of the respondents are having higher secondary school level educational qualification. 21% of the respondents are having primary school level educational qualification.

Number of years in Agricultural work

S. No	Number of years	No. of Respondents	Percentage
1.	Up to 5 years	29	29%
2.	6-10 years	24	24%
3.	11- 15 years	30	30%
4.	Above 15 years	17	17%
	Total	100	100%

The above table shows that maximum of 30% of the respondents are doing agricultural work in 11-15 years. 29% of the respondents are doing agricultural work in up to 5 years. 24% of the respondents are doing agricultural work in 6-10 years.

Suggestions

The agricultural finance should be provided for fairly long period and it should be commensurate with the operations for which it is designed to facilitate and it should be provided at lower rate of interest.

Crop loan should be given under the bank‟s lending programme and almost all needy farmers especially small and marginal farmers should be given crop finance for raising crops with recommended package of practices for higher returns. Farmers should be provided guidance for improved farming techniques, balanced fertilization, use of water saving devices and proper plant protection measures.

Farmers must motivate the women family members to take up in agriculture cultivation in this area, also encourage the youngsters to participate in agriculture activities for enhancing the production.

Farmers must shift their cultivation pattern from traditional crop to commercial crop, so that they can earn more income from their cultivation. And also use natural seeds and fertilizers for their cultivation.

Government must motivate the farmers to cultivate the flower and vegetables plants which give more income throughout the year. Cultivation of medicinal plants should be encouraged in dry farming areas.

Conclusion

Agriculture plays an important role in the economic development of India. Agriculture is the source of livelihood of more than 65 per cent of the population in India and contributes less than 20 per cent to GDP, with a sizable share of exports. To meet the requirement of the growing population and rapid developing economy, agriculture has to grow fast and get modernized. This requires the use of high pay off inputs, adoption of high yielding varieties, fertilizers, plant protection chemicals, modernized equipments and machineries which need huge investment. The agricultural sector of the Indian economy is labour intensive, land poor and capital scarce. So it would be very difficult to get the benefits of modernization of agriculture without adequate finance to the farmers at reasonable interest. The farmers are the most hapless victims of the private money lenders who are free to recover their loans by high handedness and attachment of the crop of the poor farmers as well as their personal belongings, land and living quarters. Available resource base and the capacity to generate sufficient levels of financial resource within the rural sector particularly in agricultural sector are, however limited at present. Institutional financing is viewed from this angle as a principal resource of external finance to support in a planned manner. Institutional finance enables the farmer to procure the necessary wherewithal of production and creates conducive climate for enhanced output. Since institutional finance exerts a “push effect and has a catalytic role in development process, provision of adequate, timely and liberal finance to the farmer becoming an integral part of the agricultural development policy in India. As a result, agricultural finance in the country is provided through three main channels, viz., commercial banks including private sector banks in the recent years, regional rural banks and cooperatives.

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IMPACT OF GST ON TOURISM SECTOR

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Abstract

Tourism sector holds great strategic importance in the Indian economy providing several socio-economic benefits. Tourism represents world's third largest export avenue in terms of global earnings after fuel and chemicals. Modern tourism is closely linked to socio-economic development. Tourism is responsible for one out of 11 jobs and 10% of the world's economic output. Tourism development is pressing forward at a swift pace, oriented to maximizing profit and with the evident exclusion of most of the local population. It is argued that locals must be better integrated into the tourism process in order to reverse the spiral of its adverse effects and promote integrated and sustainable development in harmony with the local economy.

Key words: GST. Impacts, Tourism industry, Review, Price and Market

Introduction

Tourism represents world's third largest export avenue in terms of global earnings after fuel and chemicals. Modern tourism is closely linked to socio- economic development. Tourism is responsible for one out of 11 jobs and 10% of the world's economic output. Apart from providing employment, income and foreign exchange for the country, the trade in the tourism sector has an economically positive impact on other associated industries such as food manufacturing, services, construction, agriculture, handicrafts etc.

Tourism Industry in India

The travel and tourism sector holds great strategic importance in the Indian economy providing several socio-economic benefits. Apart from providing employment, income and foreign exchange for the country, the trade in the tourism sector has an economically positive impact on other associated industries such as food manufacturing, services, construction, agriculture, handicrafts etc. In addition, investments in infrastructural facilities such as transportation, accommodation and other tourism related services lead to an overall development of infrastructure in the economy. Despite that the Tourism Sector, including Inbound Tourism pay a plethora of taxes and do not get any significant benefits as compared

to other Export sectors. There are multiple taxes charged on the same Service/ Product offering by the Central as well as State Governments. It is an understanding that the Taxes levied on Inbound Tourism is amongst the highest in the country, and this is one of the major reasons for India losing Foreign Tourists to competing South East Asian Countries. Tourism sector in some of the key competing destinations in South Asian countries attract much lesser taxes thereby making the products more competitive.

Review of literature

Sanjay K Nepal (2003) "Measuring Tourism Impacts: Interdisciplinary Perspectives from the Nepalese Himalaya", summarize the main findings of a large research project on tourism, environment and society in Nepal's Annapurna and Everest Regions by concluding that despite of some problems, overall trends in tourism indicate a positive impact on livelihood conditions of local communities. Tourism has been considered as conservation tool, as a social catalyst and as an income and employment generator 60 Abdoukhadrediagene (2004) "Tourism Development and its Impacts in the Senegalese Petite Cote: A Geographical Case Study in Centre–Periphery Relations". This paper reveals that tourism has modified the traditional structure of the small rated societies of Senegalese by disrupting local tradition and breaking Islamic moral codes, and has spawned previously unknown social ills, such as prostitution and mugging. It has transformed many villages in the small rated into satellites for cheap labour, where locals, who have abandoned agriculture, are employed as menial laborers. The environment of traditional villages, formerly unpolluted, is now subject to an array of pollutant factors as tourist accommodation proliferates. In summary, tourism development in the small rated surrounding of Senegalese is pressing forward at a swift pace, oriented to maximizing profit and with the evident exclusion of most of the local population. Such development, and its related 'mis-developmental' impacts, can be usefully viewed as a concrete example of centre–periphery relations embodied in a concrete central touristic 'enclave' expanding on the local periphery; indeed, a laboratory for, and microcosm of, such asymmetrical relations. It is argued that locals must be better integrated into the tourism process in order to reverse the spiral of its adverse effects and promote integrated and sustainable development in harmony with the local economy.

Kitnuntaviwat and Tang (2008) show cased a structural model that explored residents' attitudes towards tourism developments and to what extent residents interface with

destination sustainability strategies. Factors influencing these attitudes were examined using a model consisting of six latent constructs and eight path hypotheses. Findings from 432 resident-respondents from Bangkok, Thailand were analysed using LISREL (linear structural equations), a confirmatory factor analysis and structural equation modeling procedure on the collected data. Results indicated that the residents' support was strongly affected by most constructs, except by the relationship between "sustainability attitudes" and "perceived negative tourism impacts".

Milan Ambro (2008) "Attitudes of local residents towards the development of tourism in Slovenia: The case of the Primorska, Dolenjska, Gorenjska and Ljubljana regions" focused on the attitudes of local residents toward tourism development. It was observed that long-term residents were generally less favourable to tourism development. In contrast, perceived positive tourism impacts, cultural tourism, quality of tourism and leisure structure and quality of natural environment positively influenced local residents' perceptions of tourism development. The economic reasons for tourism development revealed by the attitudes of local residents were evident. Local residents were deeply concerned about the quality of their life and environment. Managers and planners should be aware that tourism development activities could evoke strong emotional responses of some groups of local residents. To avoid conflicts, local residents should be actively involved in the decision making process of tourism development.

AzizanMarzuki (2009) observed that tourism is always regarded as an important means to benefit local communities. The success of the developed countries in expanding tourism industry has inspired many developing countries including Malaysia to give a due recognition to the industry as the main driver in the nation's 64 economic development. Based on a case study conducted in Langkawi Island, attempt has been made to track the progress of tourism development of the island from 1986 to 2004. The Government and private sector had invested a lot of money in providing public infrastructure and facilities to boost the tourism industry in the island. Despite the massive amount of money spent on tourism development, no study had been conducted to relate tourism spending with the impact of these developments towards the local economy and socio-culture. The case study conducted from March to July 2004 explored and identified economic, environmental and socio-cultural impacts of tourism development in Langkawi Island. Forty semi-structured interviews with local stakeholders involving hotel managers, government and non-government organizations representatives, resort and tourism developers and community

leaders were conducted and analysed using Ritchie and Spencer's 'framework method'. Two key issues viz.(1) the benefits of tourism development; (2) the costs of tourism development were identified and discussed. The analysis also found that despite the limitation and development issues, the benefits of tourism development in Langkawi far outweighed the costs accrued to the local populace.

Nawaz Ahmed (2013) pointed out that sustainable tourism can be taken in four different interpretations that include economic sustainability of tourism, the ecologically sustainable tourism, and sustainable development tourism with both focus for environment as well as long term feasibility of the industry and finally tourism as a part of strategy for sustainable development. In this paper integrated approach and establishment of new plans for the sustainable development of tourism in Uttarakhand have been adopted to synthesise all the findings and give feasible suggestions and recommendations for further development of tourism in the region.

GST impacts

Tourism sector shall be impacted both positively and negatively under the GST regime.

Positive

1. Uniformity in Taxes

The multiple taxes would be replaced by one single tax, the rate of which is likely to be between 16%-18%. The sector may benefit in the form of lower tax rates which should help in attracting more tourists in India.

2. Increased Revenue for State Government

Under GST the place of supply is shifted to the place where immovable property is situated in case of Hotels, Restaurant & Monuments for sightseeing. This will increase the revenue of such states where immovable property is located. Currently, on such income, States charges local Luxury Tax on hotel stay and VAT on food supplied. While Union Government gets revenue from Service Tax on such services. Because of GST, the States having maximum tourist places, hotels or restaurants for tourist shall earn the maximum revenue by way of SGST which will be equivalent to CGST.

In the case of Passenger traveling, the state with the maximum outbound journey shall earn the highest revenue so the station or the port having highest outbound flights, train journey or local cab journey shall earn substantial revenue.

3. Saving in Food and Beverage operations

Companies specializing in food and beverages operations could be the biggest beneficiaries of GST within the hospitality sector. Food and beverages bills have multiple components which inflate the bills by 30- 35%. It is expected that GST to result in savings of 10-15% on the overall bill.

Negative

1. Multiple Registration

Service providers having centralized registration will have to get registered in each state from where they provide services. Although Government has been claiming "One Nation One Tax", practically it is not going to be so. Service providers will have an option to take different registration for separate business verticals which need to be examined on a case by case basis. Every state has been constitutionally granted right to collect GST on services.

2. Increased Compliance Burden

The procedure for all the invoices/receipts towards inward and outward supplies will become cumbersome as each one of them will have to be uploaded in the system. The concept of credit matching under GST would be very difficult to handle and would lead to increase in working capital requirements.

The frequency and number of returns to be filed will go up. In place of a half yearly service tax return, under GST law, one will be required to file state wise monthly three GST returns along with an annual return will also be required to be filed.

3. No Credit on Work Contract Services

The hotel industry spends a lot of money on construction and renovation. The money paid as taxes on the works contract services when supplied for construction of an immovable property is not allowed for this sector when such services are not used for the further supply of works contract service. This would have a negative cascading effect despite strong promises being made by the government in this regard.

Any proposal to make supplier of goods or services liable to pay tax under reverse charge when receiving supply from an unregistered supplier can increase burden in case of B2B transactions on registered assessee.

4. Liquor not included

Liquor should have been included in GST to ensure the seamless credit for the tourism industry. Exclusion of liquor from GST regime defeats the very purpose of bringing in a uniform tax structure across the nation.

Impact on Consumers

In Pre GST era, there was a composite levy of both Service tax i.e 6%, as well as, Value Added Tax i.e 14.5% (Vary from State to State) on food and beverages served by hotels and restaurants which finally put the burden of 20.5% in the pocket of ultimate consumers. However, some relief was provided for Non-AC Restaurants supplying food and beverages as no service tax was levied on these restaurants. Post GST, the scenario shall be completely different. As discussed above that supply of food and drinks in a restaurant shall be treated as a supply of services. Hence, only GST shall be levied on such services @ 18% which saves around 3% as compared to the previous regime.

Erstwhile, Non AC Restaurants were exempt from levy of Service Tax. But State vat was charged at 12%. In Present System, Restaurant not having the facility of air-conditioning or central heating at any time during the year and not having a licence to serve liquor is liable to tax at GST Rate of 12%. Overall things shall continue to remain status quo as far as pricing goes.Further, staying in a good hotel is going to be very costlier as the rate of tax has been doubled from 9% to 18%. Even Luxury Hotels of 5 stars or above-rated charging room rent Rs. 7,500/- or above will attract 28% tax.

Conclusion

GST is going to be an efficient and harmonized destination-based tax system and will remove the problems faced by the sector leading to cost optimization and a free flow of transactions. GST is a glimmer of hope for the Hotel and Tourism Industry if we can keep the GST rate between 10 to 15%. GST might herald with its uniformity of tax rates, a better utilization of input credit which in turn benefits the end user in terms of affordability.

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An Economic Pros and Cons of Goods and Service Tax (GST) In India

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Abstract

World over in almost 150 countries there is GST or VAT, which means tax on goods and services. Under the GST scheme, no distinction is made between goods and services for levying of tax. This means that goods and services attract the same rate of tax. GST is a multi-tier tax where ultimate burden of tax fall on the consumer of goods/services. It is called as value added tax because at every stage, tax is being paid on the value addition. Under the GST scheme, a person who was liable to pay tax on output, whether for provision of service or sale of goods, is entitled to get input tax credit (ITC) on the tax paid on its inputs. The major reasons for implementation of VAT are to have control over the taxation under single ambit and have single tax base throughout the country and major revision required in the present VAT are uniform tax base in all States Single registration and identification for assessing both under Central and State GST to have a upgraded and expanded IT structure to reconcile and cross check GST with declared income returns, fostering greater levels of tax compliance

Introduction

One of the biggest taxation reforms in India -- the Goods and Service Tax (GST) is all set to integrate State economies and boost overall growth. GST will create a single, unified Indian market to make the economy stronger. The implementation of GST will lead to the abolition of other taxes such as octroi, Central Sales Tax (CST), State-level sales tax / Value Added Tax, entry tax, stamp duty, telecom license fees, turnover tax, tax on consumption or sale of electricity, taxes on transportation of goods and services, et cetera. Thus avoiding multiple layers of taxation that currently exist in India, GST is a comprehensive tax levy on manufacture, sale and consumption of goods and services at a national level. Through a tax credit mechanism, this tax is collected on value-addition on goods and services at each stage of sale or purchase in the supply chain. The system allows the set-off of GST paid on the procurement of goods and services against the GST which is payable on the supply of goods or services. However, the end consumer bears this tax as he/she is the last person in the supply chain.

Experts say that GST is likely to improve tax collections and boost India's economic development by breaking tax barriers between States and integrating India through a uniform tax
rate. Under GST, the burden of tax collection will be divided equitably between manufacturing and services, through a lower tax rate by increasing the tax base and minimizing exemptions.

It is expected to help build a transparent and corruption-free tax administration. Final impact of total GST will be only at the destination point, presently it is at various points (from manufacturing to retail outlets) i.e. a manufacturer needs to pay tax when a finished product moves out from a factory, and it is again taxed at the retail outlet when sold. At present excise duty paid on the raw material consumed is being allowed as input credit only on manufactured goods. For other taxes and duties paid for post-manufacturing expenses, there is no mechanism for input credit under the Central Excise Duty Act. GST will divide the tax burden equitably between manufacturing and services. It will be replacement of Excise Duty and other taxes.

Objective of GST in India

GST aims to remove barriers among states and unify the country into a common national market. Presently credit for service tax paid is being allowed as input service tax to manufacturer/ service provider to a limited extent. In order to give the credit of service tax paid in respect of services consumed, it is necessary that there should be a comprehensive system under which both the goods and services are covered. A major defect under the State VAT is that the State is charging VAT on the excise duty paid to the Central Government, which goes against the principle of not levying tax on taxes. In the present State level VAT scheme, input vat is allowed on the goods remains included in the value of goods to be taxed which is a cascading effect on account of vat element. Presently CST is being levied on inter-state transfer of goods, as there is no provision for taking input tax credit (ITC) on such CST, this leads to additional burden on the dealers. The existing CST will be discontinued. Instead, a new statute known as IGST will come into place. It will empower the Central Government to levy and

collect the tax on the inter-state transfer of the Goods and Services. Many of the States are still continuing with various types of indirect taxes, such as luxury tax, entertainment tax, etc.

In India a dual GST system is being implemented. Under dual GST, a Central Goods and Services Tax (CGST) and a State Goods and Services Tax (SGST) is being levied on the taxable value of a transaction. All goods and services, barring a few exceptions, are to be brought into the GST base. As a measure of support for the states, petroleum products, alcohol for human consumption and tobacco have been kept out of the purview of the GST. There is no distinction between goods and services. In the GST system, both Central and State taxes are to be collected at the point of sale. Both components (the Central and State GST) are to be charged on the manufacturing cost or value of services rendered. This will benefit individuals as prices are likely to come down. Lower prices will lead to more consumption, thereby helping companies. The prices are expected to fall in the long run as dealers might pass on the benefits of the reduced tax to consumers.

The inter-State seller will pay IGST on value addition after adjusting available credit of IGST, CGST and SGST on their purchases. The Exporting State will transfer to the Centre the credit of SGST used in payment of IGST. However, only the Centre may levy and collect GST on supplies in the course of inter-state trade or commerce. The tax collected would be divided between the Centre and the states in a manner to be provided by parliament, on the recommendations of the GST Council. Cross utilization of ITC between the CGST and the SGST would not be allowed except in the case of inter-State supply of goods & Services.

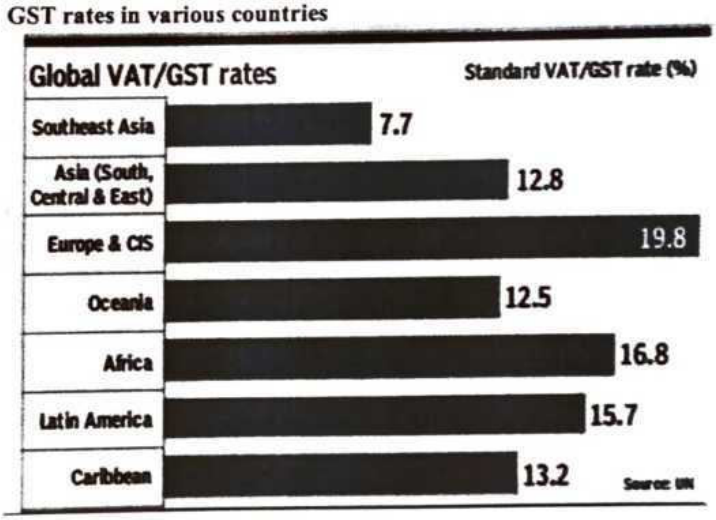
The scope of IGST Model is that Centre would levy IGST which would be CGST plus SGST on all inter-State transactions of taxable goods and services with appropriate provision for consignment or stock transfer of goods and services.

The inter-State seller will pay IGST on value addition after adjusting available credit of IGST, CGST, and SGST on his purchases. The Exporting State will transfer to the Centre the credit of SGST used in payment of IGST. The Importing dealer will claim credit of IGST while discharging his output tax liability in his own State. The Centre will transfer to the importing State the credit of IGST used in payment of SGST. The relevant information will also be submitted to the Central Agency which will act as a clearing house mechanism, verify the claims and inform the respective governments to transfer the funds thereby it will maintain uninterrupted ITC chain on inter-State transactions.

As all inter-State dealers will be e-registered and correspondence with them will be by software-generated automated e-mail, the compliance level will improve substantially. Model can take 'Business to Business' as well as 'Business to Consumer' transactions into account. GST will not be an additional tax. CGST will include central excise duty (CENVAT), service tax, and additional duties of customs at the central level; and value-added tax, central sales tax, entertainment tax, luxury tax, octroi, lottery taxes, electricity duty, state surcharges related to supply of goods and services and purchase tax at the State level.

The Centre and the States would have concurrent jurisdiction for the entire value chain and for all taxpayers on the basis of thresholds for goods and services prescribed for the States and the Centre While greatly accelerating the pace of all their tax legislation, the world's governments have relied most heavily on indirect taxes for extra revenue. As a result, there is increased risk that taxpayers will be caught unprepared, making a current, detailed guide like the *Worldwide VAT, GST and Sales Tax Guide* all the more valuable.

GST rates in various countries



World over in almost 150 countries there is GST or VAT, which means tax on goods and services. Under the GST scheme, no distinction is made between goods and services for levying of tax. This means that goods and services attract the same rate of tax. GST is a multi-tier tax where ultimate burden of tax fall on the consumer of goods/services. It is called as value added tax because at every stage, tax is being paid on the value addition. Under the GST scheme, a person who was liable to pay tax on output, whether for provision of service or sale of goods, is entitled to get input tax credit (ITC) on the tax paid on its inputs.

Since VAT was beneficial for the taxation system but with certain shortcomings which are expected to be overcome by the Goods and Service Tax. Thus, it would definitely a positive reform for the Indirect tax system in India.

Impact of goods and service tax:-

Section 2, GST has a positive impact on the economy and on various sectors which are as follows.

Fast moving consumer goods sector:-

With the implementation of Goods and Service Tax, FMCG sector would really change. FMCG sector consist 50% Food and Beverage sector and 30% is Household and Personal care. FMCG sector is the major taxation contributor both direct and indirect in the economy. The multiplicity of the taxation influences the company's decision on manufacturing location and distribution of Goods. FMCG companies set their manufacturing units and warehouses where they can avail tax benefits. To transfer the stock from the warehouses among the states they have to pay taxes. So, GST would surely impact on FMCG sector as taxes affect the cost to the company.

Food Industry:-

Since food constitutes a large portion of the consumer expense of lower income households, any tax on food would be regressive in nature. Therefore, extending GST to food processing sector will also cause difficulty in view of the fact that production and distribution of food is largely unorganized in India. On global front, most of the countries tax food at a lower rate keeping in view the considerations of fairness and equity. Even in countries such as Canada, UK and Australia where food constitute a relatively small portion of the consumer basket, food is taxed at zero rates. While in some countries, food is taxed at a standard rate which is as low as 3% in Singapore and Japan at the inception of the GST. Even in international jurisdictions, no distinction is drawn on the degree of processing of food. Hence, the benefit of lower or zero tax rates should also be extended to all food items in India regardless to degree of processing.

Information Technology enabled services:-

The proposed GST rate under the IT industry is not yet decided. While the discussed combined rate of GST for the product is 27%. According to proposed GST if the software is transferred through electronic form it would be regarded as service (intellectual property).and if it is transferred through media or any other tangible property then it should be treated as goods. Implementation of GST will help in uniform simplified and single point taxation and thereby reduced price.

Infrastructure sector:-

The Indian infrastructure sector largely comprises power, road, port, railways and mining. And the indirect tax levy is different and unique for each of them, and this is complex in nature. Although this sector enjoys different exemptions and concessions as it is important on national front. With the implication of GST the multiplicity of taxes will be removed and it would increase the tax base with continuation of exemptions and concessions for national interest and growth

Impact on small enterprises:-

In the small scale enterprises there are three categories:-

- Those below threshold need not to register for the GST
- Those between the threshold and composition turnovers will have the option to pay a turnover based tax or opt to join the GST regime
- Those above threshold limit will need to be within framework of GST.

In respect of the central GST the situation is slightly complex.GST is expected to encourage compliance and which is also expected to widen tax base adding up to 2% to GDP. Manufacturers, traders will have to pay less tax with the implication of GST.

Objectives of Goods and service tax:-

GST is proposed to fulfill the following objectives:

- GST would help to eliminate the cascading effects of production and distribution cost of goods and services. This would help to increase GDP and then to economic condition of the country.
- GST would eliminate the multiplicity of indirect taxation and streamline all the indirect taxes which would be beneficial for manufacture and ultimate consumer.
- GST would be able to cover all the shortcomings of existing VAT system and hopefully serve the economy health.
- Incidence of tax falls on domestic consumption
- The efficiency and equity of system is optimized
- There should be no export of taxes across taxing jurisdiction
- The Indian market should be integrated into single common market
- It enhances the cause of co-operative federalism.

Present Indirect Tax structure in India is very complicated and complex in nature. It consists of cascading effects of tax. These add to cost of goods and services through "tax on tax" which the final consumer have to bear.

Suggestions

- It is necessary to insist on invoice while making any transactions. The precautionary measure taken by authorities is to control tax-evasion which really works well.

- The major reasons for implementation of VAT are to have control over the taxation under single ambit and have single tax base throughout the country and major revision required in the present VAT are uniform tax base in all States Single registration and identification for assessing both under Central and State GST to have a upgraded and expanded IT structure to reconcile and cross check GST with declared income returns, fostering greater levels of tax compliance.
- The mostly taken disciplinary action against traders by tax authorities is levying 'interest' followed by 'fine'. An efficient tax administration yields maximum revenue with a minimum cost. This depends on the quality of machines for tax administration, which includes the manpower devoted to tax collection and assessment, the mindset of the people to understand the tax system and its benefits to the economic development. There is a need to embark on business enumeration in each State with a view to have data base on business. Fast disposition of tax cases will have better administration. It may be advisable to have a magistrate courts in each zone to specifically handle State revenue matters.
- More than 150 countries in the world experience the GST system and practice three major system of Taxation. The experts view that the best method of proposed GST is dual method out of the three methods.

Conclusion

VAT has really showed a progress in many States and the Centre has rightly compensated to many States. The success story would continue by the implementation of GST in India. There were hurdles and agitation for implementation of VAT in India. Tamilnadu was the last but before/State to implement VAT. GST is an extension of VAT which includes services also. Initial losses of revenue to States would be compensated by the Centre. When GST is implemented in good spirit the revenue of both Central Government and State Government shall be increasing in the long run. The main lag behind the implementation of GST is due to differences amongst the Centre and States on the RNR (Revenue Neutral Rate), compensation package and its Constitutional amendment which is required to be passed with two-third majority in both the Houses of Parliament and ratification by a simple majority by at least half of State assemblies.

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MARGARET LAURENCE'S "A BIRD IN THE HOUSE": A REVIEW ON INDIAN SOCIETY

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ABSTRACT
Margaret Laurence a well-known Canadian writer known for her famous novel *The Stone Angel*. Laurence's contribution to Canadian feminist modernism is highly commentable. An ideal feminist who studied and projected the psyche of women through her fictional female characters. She stands unique in creating women of boldness who have realized their powers and liberate themselves. One among the Manawaka series is a collection of short stories.

A Bird in the House is found similar with the society of India and taken for discussion to see it in different feminist perception. Vaneesa Mac Leod *is* a narrator of the story and she has recorded her observation on the treatment of women from her childhood. She could understand the patriarchal domination of her grandfather, and how it has stolen the freedom of women of her family finally she escapes from the clutches through her education. This paper aims to spell out the similar situation prevails in Indian families, its causes and solution through the writing of Margaret Laurence.

Key Words: Feminism, patriarchal society, freedom, power, education.

INTRODUCTION

Feminism has been a topic of discussion on many literary works, dissertations and seminars as women of our society have been enduring the problem. There is no answer to the question how long they have to endure? But there is an answer for the question how long they have been enduring? The knowledge of feminism enters when an individual gets affected by the problem or observed the problem. Indian women have been a victim of patriarchal society nearly 3000 years. The problems have been changing from age to age but women remains as victim. Female authors come out with varied perceptions. But overall contributions made by women writers are less and so they have been invisible and their voice become unheard. Thus the empowerment of women becomes the recurring subject in order to create an identity for them in this patriarchal society. The modern women though educated or employed are divided between domestic duties or professional forays and inevitably most of the women undergo a psychological tension and that has become a part of their life. Helene Cixous in "Sorties: Out and Out: Attacked Ways Out/ Forays" writes of the dilemma for women who look for, but do not recognize themselves in the world: "What is my place if I am a woman? I look

for myself throughout the centuries and don't see myself anywhere" (574). Being a nation of multiculture Canada and its literature are similar to India in some aspects. A women writer of Canadians literature projects the plights of women. It was found Canadian modernism paves the way for writers to project themselves and being recognized and they have become the voice of the voiceless.

Laurence and Feminism

Among the women writers of 20th century Canada, Margaret Laurence is discovered as a literary fore mother known for her projection of female characters with different perspectives.Her works are blaring the feminist modernism which has been omitted during the emergence of modernism. Her novels aim to make women to realize and manipulate the techniques of individual and communal enablement. A woman has been taken as a powerful tool to represent her nation and women in general. The part contributed by Laurence in empowering women, nation and literature through her highly crafted universal personalities are commendable. Thus she is considered a suitable example to represent feminism.

Vaneesa and her family

A Bird in the House is a collection of short stories comes under Manawaka series and published in the year1970. It was narrated by the female character Vaneesa Mac Leod started from her childhood to the present age of forty. She narrates what she has observed from her surrounding, listen to others' words and sometimes eavesdrops. Who considered herself as a bird in the cage maintained by her grandfather Timothy connor. Vaneesa sometimes called her grandfather the great bear who used to wear a thick fur coat. His exposition of disapproval of things can be seen even in the way he walks. He is very punctual, strict, and conservative and short- tempered. No one could tolerate his words and especially Vaneesa but everyone didn't want to reveal as it may hurt Grandmother Agnes. During the course of the stories she slowly learns about all the tragedies concerning the people surrounding her and she ventures out more and learns about what goes on outside the safety of her home and people related to her. After few years there came a situation Vaneesa has to stay with her grandfather connor as she has lost her father who passed away by pneumonia. Similar to her mother and aunt felt she is also liked to escape from Manawaka and from the brick house. Women of the first brick house of Manawaka called it as 'Confounding dungeon' and want to get out it and search their identity Aunt Edna did so as she has decided to marry Wes Grigg who is also insulted by Timothy Connor decided to leave the house but Beth in another hand wishes to vanish herself from the place but unable to do as she is a widow depended her father but having a hope of sending their children's out of this cage.Finally Vaneesa was sent to the University of Winnipeg.

A Great Bear

Timothy connor is a grandfather of the protagonist and early settlers of Manawaka is referred as 'A great bear' because "The name had many association other than his coat and surliness. It was the way he would stalk around the Brick House as though it were a cage."(63) He has earned by shoeing horses after some years become a blacksmith later saved enough money and set a hardware store for him and always talk to her about his past which made her to feel bore. Timothy connor played a vital role in the collection of stories. He is very punctual, strict, conservative and short- tempered and can be called an example of patriarchal society. Terence stated " He could never show any of his own. All he could ever come out with in was anger.Well everybody to his own shield in this family"(85) Grandmother Agnes is known for her manners and she never pushes her belief over others not even hurt others through her words though she didn't like one's activities. She was praised as angel by Timothy after her death but never during her life time once. The character of grandmother resembles more to the woman of Indian society. Beth, mother of Vanessa ,a widow would like to free herself from clutches of the society but couldn't do even from her father. She wishes to fulfill her dream through her daughter. Beth said "Your grandfather didn't believe in education for women"(187) He has not allowed her for her higher studies. She likes to send her daughter for higher education. Vanessa ultimately liberates herself through her education. Aunt Edna's friend Jimmy Lorimer wished to marry her. Edna had fear to inform it to her father so her mother asked his permission and further she requested him to be nice to the guest for her sake but as they have feared grandfather talked ill of his profession and made him left the place

immediately. Edna who said unable to endure his father like her mother and comes to know later her boyfriend got married with some other girl. When Aunt Edna gets a second chance she no more wants to be submissive. She has decided to marry Wes Grigg who is also insulted by Timothy Connor decided to marry him and left the house. Vaneesa who was exceptionally intolerable to her grandfather and started to hate him never before and had a frantic state to get away from Manawaka.

Conclusion

Grandmother and mother Beth are similar in their attitude of submissiveness and considered that as their fate. This is the attitude most of the Indian women used to have. They have considered it as fate and become ignored and invisible inside their family. They have inherited this quality from their mothers as Beth did so from her mother. But Aunt Edna and Vaneesa liberates themselves from the clutches by their boldness, there was an urge in them to create an identity for themselves. Freedom takes place when they realize their power and by changing their attitude. Thus Laurence offers a hint to the society of women that change must took place within the women not on the outsiders. Timothy lived and died as same who never changed himself for others.

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"UNKNOWN AUTOBIOGRAPHY OF A WELL KNOWN ENGINEER"

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Abstract

Sir. M Visveswaraya is an internationally reputed engineer, whose birthday is celebrated all over India as Engineers' day, on 15th September. His engineering marvels stay strong and functional in several parts of the country even today. However, not many people know that he has written an autobiography of about 175 pages, in English. This paper introduces Sir MV as an Indian writer in English. The paper makes a stylistic analysis of tone and tenor of his chaste English comparing it with other autobiographies of his period. Sir MV's work seems to be influenced by Nehru's Autobiography which was published much before 'Memoirs of My Working Days' as MV also has preferred to make an account only of his professional ventures and hardly anything about his private life and childhood. The paper argues that Sir. MV must be given the status of an Indian writer in English for his 'Memoirs of My Working Days', taking into account the chastity of language and his contribution to the country. While the works of politicians and philosophers are considered as literature, this autobiography of an engineer may also be treated as mainstream literature of Indian Writing in English.

A full autobiography coversone's life from his or her birth until today. Turninng backin time, it digs deep and tracks down all the things that made the person who he is. It finds out the meaning of his life. A biography lets everyone know his real self. It givesthe readers inside information.

A memoir revolves around a specific time, place or relationship. More limited than the autobiography, it focuses on an important part of one's life. It can be a coming-of-age memoir, focusing on one'schildhood years that made him who he is now. It can be a memoir of place, focusing on one's hometown or a place one loved and where onespent a significant part of his or her life. It can be a historical memoir and focus on his or her life's facts given in the form of reportage, or it can be a portrait and revolve around a relationship that shaped him as a person, inspired him or changed him.

In this sense, Sir M Visvesvaraya's memoir is typical of its genre. Sir MV wrote his memoirs in the year 1951. By then J.Nehru had written his autobiography in the year 1936, and Mahatma Gandhi's experiments were published in 1927.

Sir MV's work seems to be influenced by Nehru's Autobiography which was published much before *'Memoirs of My Working Days'* as MV also has preferred to make an account only of his professional ventures and hardly anything about his private life and childhood. The paper argues that Sir. MV must be given the status of an Indian writer in English for his 'Memoirs of My Working Days', taking into account the chastity of language and his contribution to the country. While the works of politicians and philosophers are considered as literature, this autobiography of an engineer may also be treated as mainstream literature of Indian Writing in English.

M.V was aware of the changes that were taking place in science and technology, and he was also aware of the rapidly increasing population in the country. He was alarmed

about the mouths to be fed and the low working power of our country despite growing population. So, He stressed on educating the people and adapting advanced science to save the country from economic crisis. He had concern for the development of the country to be at par with the first world countries. He had visualized that a sound practical knowledge of world affairs was the need of the hour.

The Memoir begins with the record of his first entry into government service and the further chapters account for the various challenging tasks he undertakes and accomplishes with an overwhelming success. At the end of his memoirs, Sir MV has added three chapters which is an unusual feature for a work of this nature. They deal with the national problems and are not directly related with the main purport of the book. But MV justifies that those chapters suggest some of the lessons which he has learnt through experience and observation for the application to the national life of the country.

While the political writings of Nehru may be recognized as Indian non-fiction writing in English, or while the religious and philosophical writings of Swami Vivekananda Tagore or Arobindo, may be considered as representative Indian writing in English, Sir M V's memoirs may also be certainly brought into the main-stream of Indian writing in English. The content and form of his writing, the chastity of the language is at par with any contemporary Indian writer in English.

It is not necessarily needed for an author to write voraciously. Writers like Harper Le, Anna sewell, and Emile Bronte, have proved their superiority as writers with their solitary contributions. It is a great disgrace to India and more so to Sir MV, because let alone bringing his memoirs into the main stream of Indian writing in English, not many of the educated Indians know that this BharathRatna has written his memoirs.

The fact that the contents of autobiographies are from real life, that is, actual happenings which have not changed by their authors, does not make the writing of autobiography any less artistic than that of novel or the poem, for instance. Indeed, the actual arrangement of the story, what events to record and in what order, what details to expunge – all require even more challenging levels of artistic imagination from the writer and these are of significant interest to stylistics.

Sir. M V's writing is not ornamental with figures of speech or studded with unusual length and thundering words. It has the clarity and dignity of a journalistic style. His writing has the precision and accuracy of a scientist. Never in his memoirs, is MV's writing emotional or ambiguous.

Even in instances where he has been wronged, M V retains the dignity of a scholar and remains composed in his narration.

Lucid and explicit mode of writing of MV makes the memoirs readable. The sentence structures are hardly ever involved and misleading. They are journalistically crisp and short. This consistency is maintained all through his work. The language is treated very formally. The generous use of the passive voices has helped him to maintain the impersonal narrative style and also it has helped him to avoid the mentioning of certain names in several occasions.

The major domain of the text is referential as he has deliberately avoided either being too personal or too emotional. The best part of MV's writing is, despite his technical background, he has wisely avoided met linguistic language. Even in instances 2awwq where he had to use technical jargons he has restrained from it. He knew his target readers were laymen and so he has employed the simplest of the language to explain the most complicated concepts.

The last three chapters have a different tenor which has a conative function in persuading Indian masses into an awakened society. These chapters have suggestions for the nation about the problems concerning the

future of India. As early as 1950's he had visualized the threat of rapid growth of population and the fall in the food grain production. He suggested 'grow more food' campaigns. In order to grow more crops without depending on the rains, he suggested to have reservoirs. He also suggests rural industrialization. MV suggests planned parenthood association. In all his suggestions for a healthy and sound growth of India his tenor gets conative with a persuading motive. The language is very effectively and gently used. With all these merits of language chastity, charity of presentation and interesting incidents and projects all along the career, this memoirs could be taken to the mainstream and be included academically for study in the syllabus or a few excerpts may be included in the text books. This work has the status of being considered one of the great Indian writings in English.

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A PYSCHOLOGICAL INSIGHT IN PAUL CHELO *ALCHEMIST* AND JONATHAN LIVINSTON *SEA GULL*

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Abstract

Brazilian literature and American literature have come a long way from being viewed patronizingly by the United States to making occasional forays into the literary scene and being acknowledged as a popular genre of modern English Literature. Both writers have contributed to quality and gave a distinctive touch to those who have not breathed the air of this land and lived in the midst of its people and can hardly aspire to appreciate. The present study aims at describing the inescapable postmodern condition prevalent in the moral, social and personal spheres and sheds light on postmodern features such as alienation, paranoia, patriarchy, amorphous identity, the free-floating, ephemeral, fragmented, fractured self, disintegration of life, and multiple spectrums of sexuality. It presents how characters experience the inevitability of isolation and fragmentation and distance themselves from one another, and proves how this diminution of social contact is a quintessential feature of post modernity.

Introduction

Paulo Chelo is an exceptional novelist who stands apart from the rest of the novelist who has taken up the themes based on human predicament in almost all his novel. Most of his novels concentrate on direction and meaning in one's life. Jonathan Livingston novels are based on literary tradition beginning as linked to the broader tradition of English literature.

Brazilian literature is a collection of work in literature written in the Portuguese language by Brazilian works written prior to the country's independence in 1822 till now. A Brazilian's most significant literarcy award is the cameos prize which share with the entire Portuguese. American literature is the literature written or produced in the area of the United States and its former colonies.

Psychology is the science of the mind and behaviour. The word psychology comes from the Greek word psyche means breath, sprit, soul and Greek word 'logia' meaning the study of something. The mind is highly complex and enigmatic. Developmental psychology also looks and compares innate mental structures against learning through experience.

The *Alchemist* follows the journey of an Andalusia shepherd boy named Santiago. Believing in his recurring dream to be prophetic, he decides to travel to a romantic fortune teller in a nearby town to discover its meaning.

The *Seagull* is a story about a seagull named Jonathan who is a story about a seagull named Jonathan who is an outcast quite. He knew that there was meaning and he found that Jonathan carries on these teaching and goes back to earth. He believes in freedom and that all the gulls are free things from the chains of life not just flight.

Whoever you are, or whatever it is that you do , when you really want something ,its because that desire originated in the soul of the universe. It's your mission on earth. [AC- 7]

Santiago wants to search something in the universe because that desire comes from soul of the Universe. He has the dream every time and sleeps under a sycamore tree that grows out of the ruins of a church. Santiago enjoys his life as a shepherd not only because it allows him to travel but also because he loves his sheep. Here he is psychologically affected on is his way through his own direction. He rejects a sort of suffering.

One day Jonathan Livingston seagull you shall learn that irresponsibility does not pay. Life is the unknown and the unknowable except that we are put into this world to eat, to stay alive as long as we possibly can[SG-24]

Jonathan Livingston's Seagull learns that irresponsibility does not pay for him. He tells that life is an unknown and unknowable to one. The seagull wants to fly in the world but other seagulls wanted to eat and stay alive. He wants freedom to fly and who learns more from the universe. He always thinks about his achievement something in the world. He sees a two brilliant seagulls

and he learns from them. He is not having a bone and feather but a perfect idea of freedom and flight. Jung developed the notion of an individual's life long process in which the center of psychological life shifts from the ego to the self. Erikson described human development throughout the life span in the theory of psychological development. "Everything on the face of the earth is constantly being transformed because the earth is alive and has a soul".[AC -1]

Everything on the earth is related to the world. This world and everything in it including inanimate objects has a soul, and that soul is connected to the soul of the world. Santiago's ability to communicate with the forces of nature is itself both an act of communication across perceived divides and an act of transformation which is not living, cannot communicate while the earth engages in conversation and is thus a living being just like Santiago. Know thyself and be free this is the perennial wisdom; teaching wisdom which rings the eternal message of the ageless quest of all creation bound fields of self awareness. His notion of repressed memories though based on false assumption has become part of western mainstream thinking.

We choose our next world through what we learn in this one. Learn nothing, and the next world is the same as this one, all the Same limitation lead weight overcome.(SG 45).

He has learned the lesson of life that it is not just to get through but to seek their own perfection in some way. Most of the gulls have to go through a thousand lives before they realize this. Jonathan Livingston knows that the gull sees farthest who flies highest. If pondering big charges in the life the books allegory borrows and blends diverse religious beliefs. The personal dimension of self realization refers to being awake on the level to arrive at the state of pure subjectivity within the consciousness. According to Laving R.D(1990) observes, Self realization that begins from universal and descends into the personal, but the evolution actually ascends from the personal to the universal, while individual self realization is bridging the two In both directions.(Laving31)

While the object of maturity and age is dissolution of the individual and a re-entry into the universal unity of life from which the individual emerged, the object of people is the formation of a unique personality, separate and distinct from the cosmic unity of all life. "Love never keeps a man from pursuing his personal legend. If he abandons that pursuit its because it was it was not True love". (AC 32)

The Alchemist utters these words to Santiago in reference to the romance with Fatima. This passage thus signals a major turning point in the novel the moment at which Santiago must choose between the short term pleasure of his romance and his stay in the oasis and the lingering quest to achieve his personal legend .Alchemist suggests that true love will never stands in the way. The philosopher Reuben Abel in his view that man in order to make life worth living in the world and says, "when Socrates also felt desire and felt that source of his searching. "I am done with the way i was , i am done with everything i learned I am seagull like every other seagull and i will fly like one".(SG 11).

He thinks that he is going to achieve his objective whatever he left of his past experiments on the flights. He thinks that he finishes his aim and learns everything in the work. He says, "I am seagull like every other seagull" He has interest in flying in the sky. The only exception to a normal seagull is to achieve individuality and perfection in his flying. He is practicing in the night time also because he thinks only of his goal. He puts a hard work of his life time. Jonathan Livingston seagull joined the flock on the beach. He thinks and finds one himself as a full fillment of becoming a creature and of excellence.

Edward Paul (1970) observes in the encyclopaedia of philosophy of the self. The individual knows simultaneously the actual self and the ideal self. The individual has outside himself as the image in whose likeness; he is to form himself and which on the other hand he has within himself, since it is he himself.

Conclusion

Both novels represent their own destiny. Their personal legend or destiny is their reason for being alive. Everyone is entrusted to metamorphosis into something, whether it be becoming great or finding a treasure. Jonathan Livingston found a life exceedingly meaningless and so he achieves his personal legend. It gave his life and gives a meaning of it. In the Alchemist, Santiago is able to overcome his fear and find true happiness in his life. Alchemist and Seagull's protagonist are affected in a psychological way and travel to find the happiness through their life journey. Both novels are

existential as it is about an individual's loneliness and feelings of anguish emanating from his estrangement from environment tradition and the search for the inner-self. Paulo Chelo and Livingston have clearly handled the existential themes of rootlessness, detachment and the quest for the self. Both of the protagonists behave in a more confident way with the expansion of their vision. The barriers of detachment gradually melt away with the flow of humanism and comparison.

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SOCIAL ECOLOGY IN AMISH TRIPATHI'S SHIVA TRILOGY

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Abstract

The term "Eco criticism" was first coined by Cheryll Glotfelty's. It meant the study of the relationship between literature and the physical environment. The term "Social Ecology" is not much familiar to the reader. Social Ecology is a critical theory founded by American anarchist and libertarian socialist author Murray Book chin. They focus on the complexity of relationship between people and nature. But the basic insight of social ecology is defined are mixed together. In order to understand today's critical issues we need to consider as human society and the trans-human world of nature. Social Ecology's component comes from its potion that nearly all of the world's ecological problems stem from social problems. And these social problems in turn arising from structures and relationships of dominating hierarchy. Apart from natural dilates ones problem came economic, enrich cultural and gender courtiers. The consideration of society and the natural world social ecology emphasizes about the ideal of the freedom of all human beings to pursue their natural fulfillment. This freedom is not chaotic but self-organizing. Human beings are essentially members of communities, and so individual fulfillment can only take place within the human and natural communities which we are part of it. This paper intends to show that Amish Tripathi's debut novels Shiva trilogy-(The Immortals of Meluha, The Secret of Nagas and The oath of Vayuputras)- a thrilling experience.Lord Brahma and Shiva's effort to keep Ganga safe, pure and the ban on the production of Somaras are relevant. Amish have touched every character and place in the series with a humanistic and eco-critical approach. In his recreation of the story Amish is proved contemporary. The paper throws light on the realistic presentation of technology, medicine, the production of Somras, the civilized lifestyle, convincing relations and the journey of a man from a Tibetan tribe towards becoming Lord Shiva

The study of literature has long been preoccupied with historical approaches. However, in recent years critics are increasingly aware of the relation between literature and geography, and drawing insights from the mutual study of these two fields. Nature and literature have always shared a close relationship as is evidenced in the works of poets and other writers down the ages in almost all cultures of the world. Today the intimate relationship between the natural and social world is being analyzed and emphasized in all departments of knowledge and development. "The study of literary texts with reference to the interaction between human activity and the vast range of natural' or non-human phenomena which bears upon human experience (Childs 55). The literary critic tries to study how this close relationship between nature and society has been textualized by the writers in their works. In this context two terms have become very important today 'ecology' and 'ecocriticism'. The two components of nature, organisms and their environment are not only much complex and dynamic but also interdependent, mutually reactive and interrelated.

Amish Tripathi was born in Mumbai, in Indian who brought up near Rourkela, Odisha. Amish was an Indian familiar novelist who depicted social categories such as culture, polity, social structure and economy through his writings. He used only simple language so that reader understands easily. Generally Amish wants to become a historian, later he became as a novelist. He was a MBA graduate and the thirst in him, made him as an author. He is the author of the series *Shiva Trilogy* which has contains three novels such as *The Immortal of Meluha, The Secret of Nagas* and *The Oath of Vayuputras*.

He wrote four novels among them The Immortals of Meluha is very popular to the readers. All the three books are based on the tales of Shiva, Sati, and Daksha. Shiva is a protagonist of the novel. Daksha is the powerful emperor of Meluha. He is regarded as the greatest king that ever been lived in India. Meluha is a near perfect empire created many centuries earlier by Lord Ram. Meluha lies beyond the great mountains. It is considered to be as Heaven. It is the richest and most powerful empire in India. Indeed the richest and strongest city not only in India but also the whole world. The government of Meluha provides special rights for immigrants' people. As Amish Tripathi's says: People do what their society rewards them for doing. It the society rewards trust, people will beg trusting (P.4)

Sati is the princess of Meluha. She is the beautiful daughter of the emperor of Daksha. At first sight, shiva falls

in love with Sati but he could not marry her. Because of a law that considers her to be a Vikarma, an untouchable girl. Vikarmas are people who bears misfortunes in this life due to sins which is committed by them in their past births. During her childhood, she is a skilled sword woman and is very courageous girl. During the course of novel, she married Shiva and bears his child.

Shiva is a Tibetan immigrant to Meluha. Also Shiva is the chief of the Guna, his uncle tribes. Somras was prepared by Saraswathi river water which pollutes the entire city and it also affects other river too. Meluhans believe that the drink which increase the life span of the people. But whereas, it would affected the born children too. But inform child with deformity are separated by others from the city of Meluha. This deformation is done through the low temperature in the region where people lives. It affects both physically and mentally. As Oedipus Anti in his *Capitalism and Schizophrenia* he describes:

No distinction between man and nature: the human essence of nature and the natural Essence of man become one within nature in the form of production or industry.

Man and nature are not like two opposite terms confronting each other. Not even in the sense of bipolar opposites within a relationship of causation, Ideation or expression. Rather they are one and the same essential reality, the Producer-product. (Anti-Oedipus 4-5)

However, the once proud empire and it Suryavanshi rulers face severe crisis as it primary river, the river, the revered Saraswathi is slowly drying to extinction. They also face devastating terrorist attacks from the east, the land of the Chandravanshis who have joined forces with the Nagas, a cursed race with physical deformities. The present king of Meluha, Daksha, sends his emissaries to North India in Tibet, to invite the tribes to live there in Meluha. One of those invited are the Gunas, whose chief Shiva accepts the proposal and moves to Meluha with his tribe. They reach the city of Srinagar and they are received by Ayurvati, the chief doctor of the Meluhans. Shiva and his tribe are impressed with the Meluhan way of life. On their first night of stay at Srinagar the Gunas wake up amid high fever and sweating, the Meluhans, under Ayurvati order carry on the healing process. However, Ayurvati finds out that Shiva is the only one devoid of these symptoms and that his throat has turned blue. The Meluhan announce Shiva as the Neelkanth, their fabled saviour.

Then Shiva is taken to Devagiri, the capital city of Meluha, where he meets, king Daksha. While staying there, Shiva and his comrades, Nandi and Veerbhadra, encounter a beautiful and mysterious woman who has a look of penance on her face. They later come to know that she is princess Sati, the daughter of Daksha and is a Vikrama, an untouchable in this life due to sins committed in her previous births. Shiva tries to court her, but she rejects his advance. Intimately Shiva wins her leant and they decide to get married, even though the Vikarma rule prohibits them from doing so. Enraged by the so-called obsolete law, Shiva declares himself as the Neelkanth and swears to dissolve the vikarma law. Daksha allows Sati to get married to Shiva, amid much joy and happiness.

During his stay is Devagiri, Shiva comes to know of the treacherous was that the Chandravanshis are carrying on the Meluhas. He also meets Brahaspati, the chief inventor of the Meluhas. Brahaspati invites Shiva and the royal family on expedition to Mount Mandar, where the legendary Somras is manufactured using the waters of the saraswathi river. Shiva learns that the potion which made his throat turn blue was actually undiluted somras, which can be lethal when taken in its pure form. However, Shiva was unaffected which was the first sign that he was the Neellanth. He also learns that somras was the reason why the Meluhans lived for so many years. Brahaspati and Shiva develop a close friendship and the royal family return to Devagiri. One morning, the whole of Meluha wakes up to loud noises coming from Mount Mandar. Shiva and his troops reach the hill to find out that a large part of Mandar has been blasted off and many of the inventors killed. There is no sign of Brahaspati, but Shiva finds the insignia of the Nagas, confirming their involvement in the treacherous wars of the Chandravanshis.

Enraged by this, Shiva declares war on the Chandravanshis. With consultation from the Devagiri chief minister kanakhala and the Head of Meluhan Army, parvateshwar, Shiva advances towards swadweep, the land of the chandravanshis. A fierce battle is fought between the Meluhans and the swadweepans in which the Meluhans prevail. The Chandravanshi king is captured but becomes enraged upon seeing the Neelkanth. The Chandravanshi princess Anandmayi explains that they too had a similar legend that the Neelkanth will come forward to save their land by launching an assent against the "evil" Suryavanshis. Hearing this Shiva is dumbfounded and utterly distressed. With Sati he visits the famous Ram temple Ayodhya, the capital of Swadweep. There he meets a priest from whom he comes to know about his Karma fate and his choices in life which would guide him in future.

As priest says

Towards the "new" earth from the Christian perspective, towards the "fullness" (Purnam) the Hunter perspective, towards "nothingness" (sunya) in the Buddhist perspective, towards the paradise-like abode of justice and mercy in the Islamic perspective Towards the abode of belongingness of God world and man from the perspective of the original inhabitants of the world (D'sa 26).

As Shiva comes out of the temple, he notices Sati standing out of the temple waiting for him and Naga standing near a tree. The first book ends with Shiva charging to save Sati:

According to Amish, throughout the world there is still a great diversity of cultures and over six thousand languages, as there has been millennia. These should be respected locally and internationally, as should human rights social justice and ecological responsibility. In ecology, man's tragic flaw is his anthropocentric (as opposed to biocentric) vision and his compulsion to conquer, humanize, domesticate, violate, and exploit every natural thing (Rueckert 113). In the face of this great diversity and complexity of cultures and ecological communities, we became, humble and realize our responsibility to be nonviolent in our communication at every level, including verbal. In various ways, social ecology is an approach than can broaden the developing field of Eco criticism.

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PALAEO 3

Ostracod biodiversity from shelf to slope oceanic conditions, off central Bay of Bengal, India

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ABSTRACT

Thirty seven surface sediment samples collected through a multi-corer in seven transects of ORV Sagar Kanya, SK 308 Leg-1 from off central Bay of Bengal (shelf to slope environment) were analysed for living and dead Ostracoda. The samples, which ranged in water depth from −29 m to 2540 m, yielded a total of 46 species belonging to 32 genera. The ostracod fauna of the Bay of Bengal exhibit a depth-related distribution that is controlled by substrate and hydrographic conditions. Sandy substrates of shallow water depth (~28 m) are characterized by *Propontocypris* sp. and *Cytherelloidea malaccaensis*. These species are replaced by *Neonesidea cracenticlavula* and *Bairdoppilata paraalcyonicola* in high population, which shows positive linear correlation with salinity, temperature and Total Calcium Carbonate (TCC) in the outer shelf ~55–73 m. *Paijenborchella* sp. dominates at ~763 m in the bathypelagic zone, giving way to *Parakrithella* sp. at greater depths of ~2540 m on soft-bottom substrates. The fauna represents an interesting mixture of displaced species and others known from bathyal and abyssal depths in the Bay of Bengal, including some pandemic deep sea species. The ostracod faunal diversity is higher in shallower water than in the deeper water, which may be due to the optimum temperature, pH, salinity and substrate. The fauna are comprised of three associations (Shelf/Upper Slope; Slope; Lower Slope/Abyss). A marked faunal turnover occurs at the outer-shelf. Factor Analysis was performed to determine the correlation of water and sediment parameters with the ostracod species. This study provides a detailed account of bathymetry and ostracod biodiversity recorded in the study area.

1. Introduction

The ostracods from the deep marine environment of the Bay of Bengal are incompletely known because of a lack of sampling and study. This study is the first to report species from a wide depth range of material, often well preserved, in the Bay of Bengal. Changes seen in the ostracod assemblages with depth, between 29 m and 2540 m, and their relationship to environmental parameters are the focus of this contribution. Some scarce species belonging to *Callistocythere*, *Loxoconcha*, *Neocytherideis* and *Cytheridea* are also reported. Noteworthy, several taxa can be considered as stenothermic and rather ecologically restricted to cold waters independent of depth. This is the case for *Cytheropteron testudo*, and probably for *Bythocypris obtusata*, *Macropyxis adriatica* and *Echinocythereis echinata* (Breman, 1975; Sciuto, 2009). Previous studies of ostracods from the North Atlantic and other climate-sensitive areas have shown their utility for paleoceanographic reconstructions because their species distribution is linked to particular deep-water masses (Dingle and Lord, 1990; Ayress et al., 1997; Cronin and Raymo, 1997; Didie and Bauch, 2000; Alvarez Zarikian, 2009; Yasuhara et al., 2009, 2012). The lower diversity of the Indian Ocean fauna compared to the Pacific may possibly be a reflection of sampling frequency and water depth. Therefore, there is a distinct variation in diversity from the Atlantic to the Indian Ocean as well as from the Indian to the Pacific Ocean. This is not a phenomenon unique to the deep sea Quaternary Ostracoda. Many environmental factors, including temperature and organic carbon flux, a primary determinant of food availability for benthic organisms, can change with depth or latitude. Sea ice is known to influence polar marine benthic communities, but little is known about its impact on species diversity (Gradinger, 1995; Gutt, 2001; Piepenburg, 2005; Tamelander et al., 2006; Hoste et al., 2007; Soltwedel et al., 2009). Deep-water and sediment characteristics (e.g., temperature, oxygen, sediment flux) and food supply (i.e., surface primary productivity, almost the only food resource in deep ocean floor, except hydrothermal vents) are important factors controlling deep-sea ostracod distribution and abundance (Cronin et al., 2002; Didie et al., 2002). Bay of Bengal is traditionally considered

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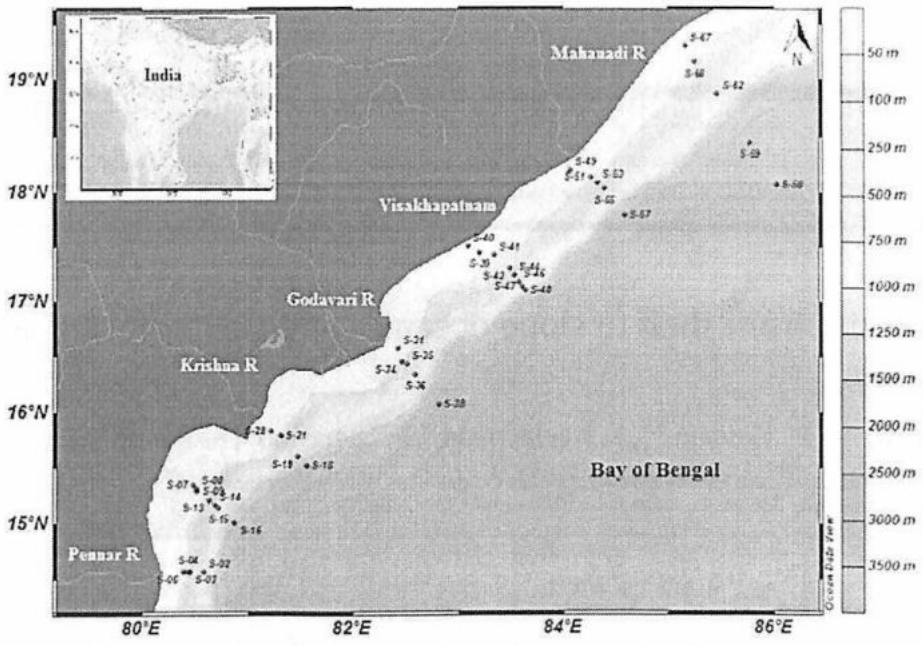

Fig. 1. Bathymetry of the central Bay of Bengal, showing shelf, slope, abyssal and sampling stations.

to have poorer biological productivity compared to its western counterpart, the Arabian Sea. Although the riverine flux may bring in nutrients, they are thought to be lost to the deep sea because of its narrow shelf (Qasim, 1977; Sen Gupta et al., 1977; Radhakrishna et al., 1978). Low species richness might occur in sediments with low to moderate Total Organic Carbon (TOC) for such reasons as insufficient amounts of

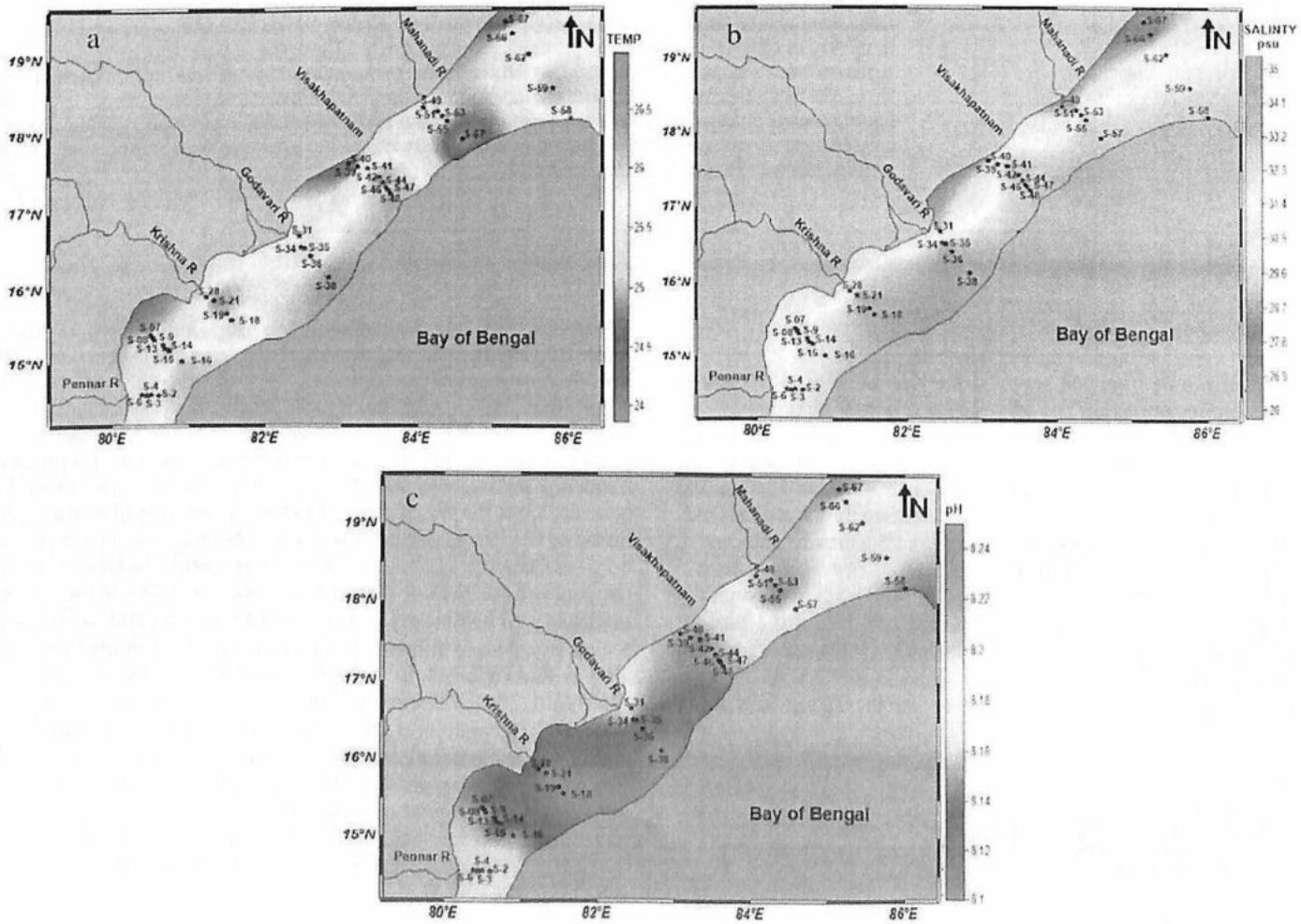

Fig. 2. Spatial distribution of hydrological and sediment parameters: a) temperature (°C), b) salinity (psu) and c) pH in the inner shelf to upper abyssal region of central Bay of Bengal.

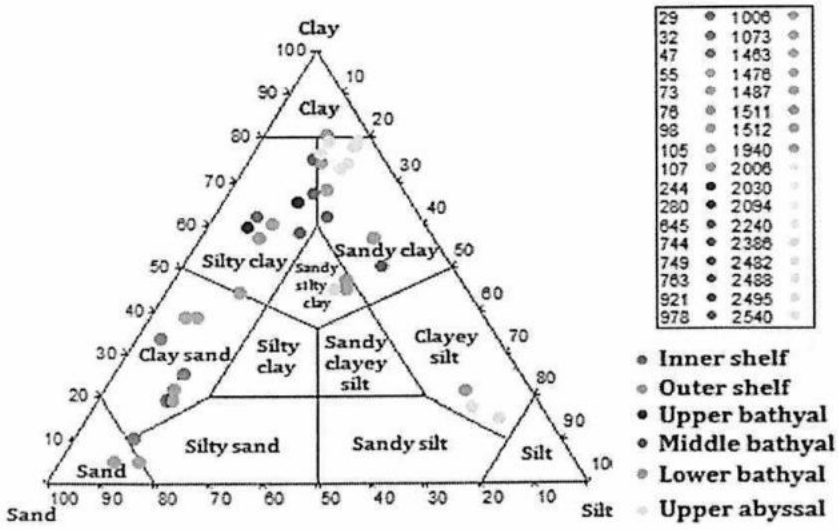

Fig. 3. Trilinear plot of sand, silt, clay in the inner-shelf to upper-abyssal region of the central Bay of Bengal.

organic matter with nutrient rich components that can be utilized as food, natural influence of salinity or grain size, geochemical, physical, and hydrodynamic factors restricting recruitment of larvae, natural physical disturbances or biological interactions (e.g., competition, predation, trophic-group amensalism) (Gray, 1974, 1981; Coull, 1977; Lopez and Levinton, 1987; Lopez et al., 1989).

2. Geographical setting of the study area

Bathymetric sections off Krishna, Godavari and Mahanadi River mouths indicate that the shelf is very narrow off Krishna and Godavari Rivers whereas it is wide off Mahanadi River. The shelf break off Krishna and Godavari Rivers occurs at a depth of nearly 130 m and the

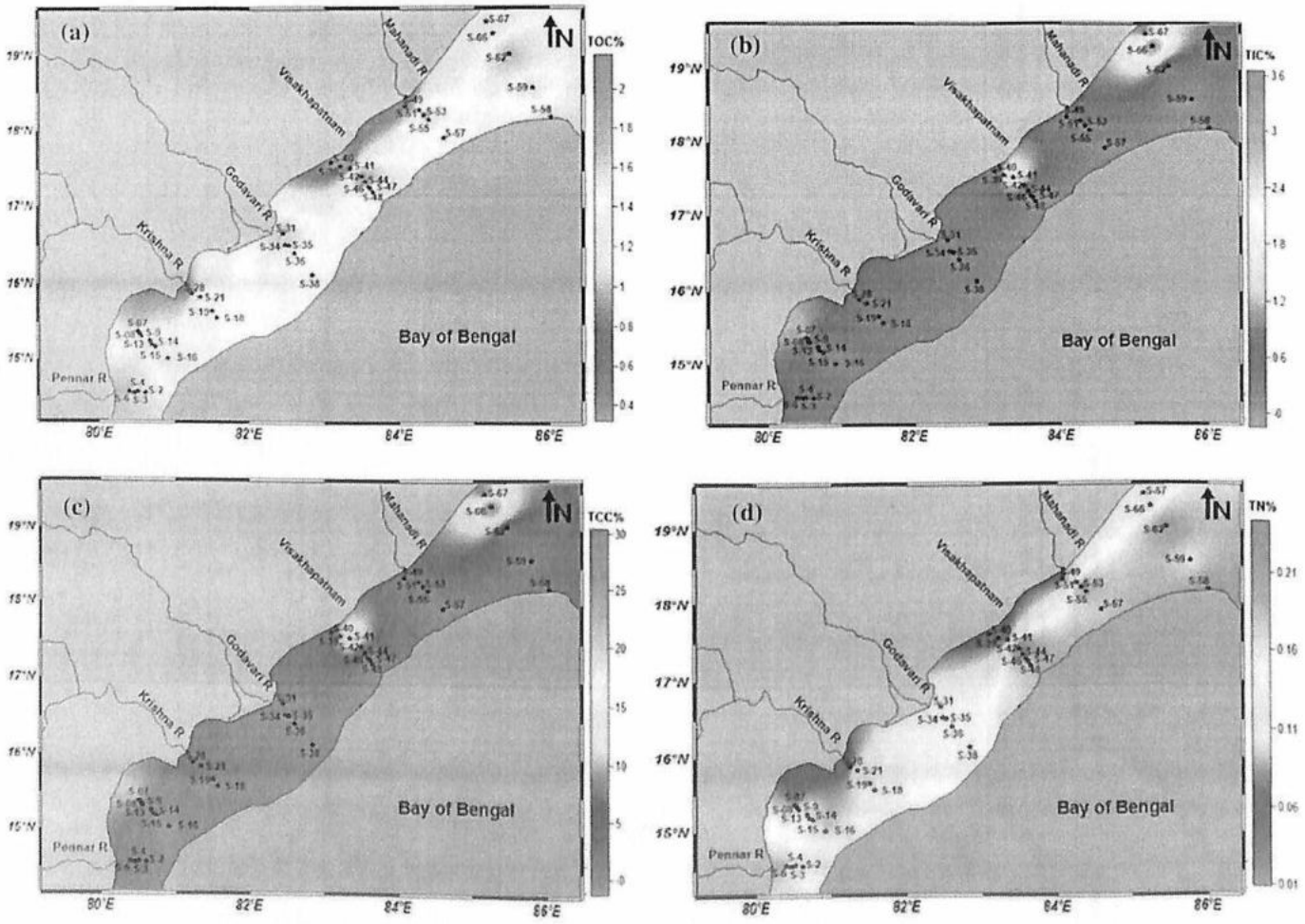

Fig. 4. Spatial distribution of organic geochemistry: a) TOC (wt%), b) TIC (wt%), c) TCC (wt%) and d) TN (wt%) in the continental shelf to slope region of Bay of Bengal.

Table 1
Depthwise distribution of Ostracoda species of the central Bay of Bengal.

Water depth (m)	S. no.	Species															
		Cytherella semitalis	*Cytherella inzohata*	*Cytherella* sp.	*Keijcyaidea* sp.	*Cytherelloidea inolaccaensis*	*Neocytheropteron vandijki*	*Cytheropteron higashikawai*	*Cytheropteron rhombiformis*	*Cytheropteron* sp. 1	*Cytheropteron* sp. 2	*Cytheropteron* sp. 3	*Cyprideis* sp.	*Paijenborchella malaiensis*	*Paijenborchella* sp. 1	*Paijenborchella* sp. 2
2094	2											×				
1476	3													×		
978	4															
244	6															
47	7															
76	8												×			
98	9				×			×			×					
921	13							×							×	
1172	14															
1940	15		×					×								
2482	16														×	
2006	18							×			×					
1463	19							×	×		×				×	
749	21															
32	28															
107	31								×							
744	34															
1006	35													×	×	
1511	36													×		
2495	38														×	
55	39					×										
29	40		×						×							
73	41		×												×	×
280	42					×	×	×	×	×						
763	44															
2030	47													×	×	
2540	48															
29	49		×	×		×					×					
73	51															
645	53							×	×							
1487	55								×							
2488	57															
2386	58										×					
2240	59															
1073	62															
105	66															
55	67								×							

(continued on next page)

Table 1 (continued)

Water depth (m)	Species														
	Spinocornutina spinosa	*Bythoceratina pauciornata*	*Actinocythereis scutigera*	*Abnocythereis guangdongensis*	*Henryhowella kenutapangensis*	*Hemikirithe orientalis*	*Keijella karwarensis*	*Keijella reticulata*	*Lankacythere multiformi*	*Lankacythere corallaides*	*Lankacythere* sp.	*Neocytheromorpha* sp. cf. *N. reticulata*	*Mutilus splendideornatus*	*Echinocytheretis* sp.	*Bonsecythere paucipunctata*
2094															
1476															
978										×					
244		×				×	×	×							
47	×		×								×				
76		×	×					×	×						
98															
921															
1172															
1940															
2482															
2006															
1463													×		
749		×													
32						×									
107															
744															
1005															
1511															
2495									×		×	×			
55	×	×	×	×					×		×	×			
29				×											
73	×	×	×	×	×					×	×	×			
280															
763												×			
2030															
2540						×									
29															
73	×					×									×
645	×	×		×	×										
1487															
2488															
2386														×	
2240															
1073															×
105		×	×							×	×				
55		×													

Table 1 (*continued*)

Water depth (m)	Species															
	Neohornibrookella sp.	*Hemicytheridea reticulata*	*Bradleya* cf. *B. japonica*	*Bradleya andamanae*	*Krithe* sp.	*Parakrithella* sp.	*Neomonoceratina iniqua*	*Loxoconcha lilljeborgii*	*Ilyocypris bradyi*	*Paracypris bradyi*	*Propontocypris* aff. *P. bengalensis*	*Peripontocypris* sp.	*Argilloecia* sp.	*Bairdoppilata parvalcyonicola*	*Neonesidea crocenticlavula*	*Paracatacythere scabra*
2094					×											
1476					×								×			
978						×										
244																
47				×				×			×					
76		×		×							×		×	×	×	
98																
921					×						×					
1172					×					×	×					
1940																
2482																
2006					×											
1463											×					×
749					×	×										
32							×					×	×			
107			×				×									
744						×					×					
1006			×													
1511																
2495			×													
55		×		×				×		×	×	×	×	×	×	
29		×		×							×	×	×			
73		×		×				×			×		×	×	×	
280																
763					×											
2030					×											
2540																
29		×					×				×	×	×			
73		×					×				×	×		×	×	
645		×		×				×		×	×			×	×	
1487												×				
2488	×				×											
2386									×							
2240																
1073																
105								×						×	×	
55				×										×	×	

topography of the shelf is irregular at some places, particularly off Krishna River. Bay of Bengal receives a large freshwater influx of $1.6 * 10^{12}$ m^3 yr^{-1} compared to $0.3 * 10^{12}$ m^3 yr^{-1} for the Arabian Sea (Subramanian, 1993) from the rivers draining the subcontinent. Sediments of the western Bay of Bengal are supplied mainly by the major rivers draining the Himalayas (e.g., the Brahamaputra and the Ganga Rivers) and peninsular India (e.g., the Godavari, Krishna and the Mahanadi Rivers). Presently, these rivers together supply about 1350 million tons of sediments per year to the Bay of Bengal, which accounts for ~8% of the total riverine supply to the oceans (Milliman and Syvitski, 1992; Milliman, 2001). The continental slope is very steep and a marginal rise is recorded at the foot of the slope along almost all the traverses at depth varying from 1000 to 1200 m. The relief of this rise varies from 50 to 250 m. Off Mahanadi River, the shelf width is nearly 70 km and the shelf-break occurs around 200 m. The continental slope is highly rugged and is associated with several valleys and rises. Marginal rise (MR) is recorded in all the profiles at depths varying from 800 to 1500 m (Murthy, 1990). The extent of the Bengal Fan is limited to the west by the continental shelf and slope of Peninsular India, which formed as a passive margin during the break-up of Gondwana (Powell et al., 1988; Ramana et al., 2001; Radhakrishna et al., 2012). The depo center of the Bengal Fan has received continental sediments from the modern Mahanadi, Krishna, Godavari, and Kaveri Rivers and predecessor rivers on the eastern margin of Peninsular India, near the mouth of the Krishna and Godavari Rivers and south of the Mahanadi River discharge, respectively (Flores et al., 2014). Within the Andaman Sea, terrigenous sediments from the Irrawaddy River are deposited on the shelf and slope, north of the Andaman back arc spreading center (Ramaswamy et al., 2008). Transportation of fine-grained sediments from the modern Irrawaddy River is restricted to the nearshore region by monsoonal surface currents (Rodolfo, 1975; Babu et al., 2010; Tripathy et al., 2011). The winter and summer monsoons result in drastic changes in surface water salinity, river discharges, surface currents and eddies, and Mixed Layer Depths and stratification. Changes in the monsoon intensity from decadal to million year time scales have been documented through paleoenvironmental and paleoceanographic proxies applied to many records, including marine sediments (Clift et al., 2001; Emeis et al., 1995; Oppo and Sun, 2005; Prell et al., 1980; Prell and Kutzbach, 1992, 1997).

3. Materials and methods

This study is based on prepared ostracod assemblages. In the present study, the original material was obtained using 37 multi-core samples collected during Sagar Kanya-308 Leg-I cruise from Chennai to Paradip (Fig. 1). The collected cores are short and vary from 30 to 40 cm in length. However, in the present study only the surface samples have been taken for micropaleontological studies. The sampling locations have been plotted on the study area bathymetry map using the geographic coordinates and water depth at which samples were collected (Fig. 1). The hydrographical parameters of viz. pH and salinity were measured onboard. The sediment samples were collected mainly at major river discharges into the Bay of Bengal especially, Pennar, Krishna, Godavari and Mahanadi Rivers. The samples range from 29 to 2540 m of water depth along seven transects in the central east coast toward the Bay of Bengal, India.

Samples were originally washed through a 63 μm sieve; the specimens were observed under a stereo-binocular microscope and were collected in faunal slides. The specimens were then sorted at species level to determine adult/juvenile assemblages. All the specimens have been identified to species level for this report. A detailed study on ostracod species was carried out from the samples collected in water depth from 29 m to 2540 m (Table 2) and discussed in the following content.

4. Results

4.1. Hydrographical and sediment parameters

Water mass characterizing a narrow water temperature range of 23.9 °C at 2488 m to 27 °C at 763 m is recorded from the combined sample stations. Sea salinities range from 27.64 psu at 55 m to 33.45–33.78 psu between 73 m and 1511 m. pH values are in range from 8.1 to 8.24, the lower values are recorded in the Krishna River and Godavari River discharging areas and the higher values are recorded from the Mahanadi River discharge area. (Fig. 2a, b, c)

Table 2 and Fig. 3 show the nature of substrate of the multicore samples. Sediment textural analysis shows sand clay is the dominant substrate present in the study area, which is followed by silty clay and

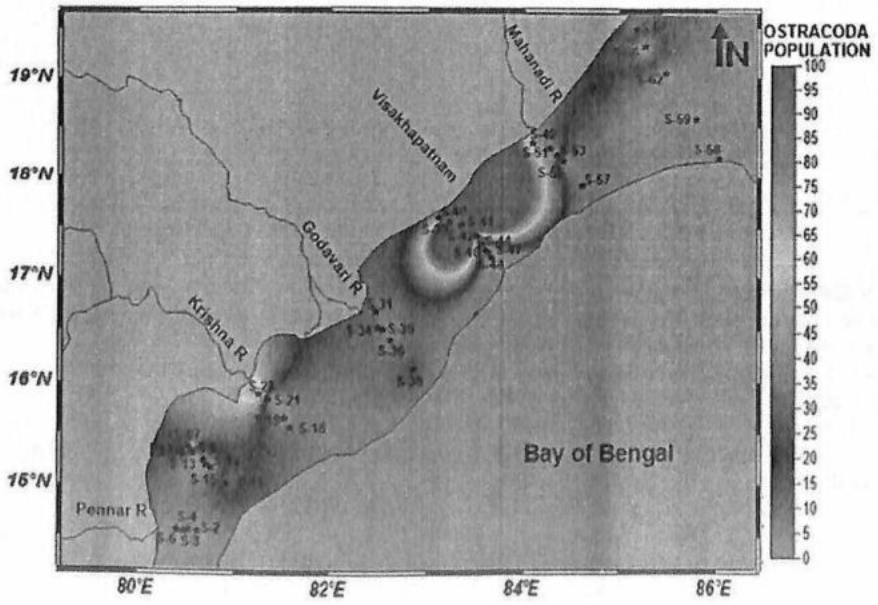

Fig. 5. Spatial bathymetry assemblage of Ostracoda in the central Bay of Bengal.

Table 2
Bathymetry and characteristic Ostracoda assemblage of the central Bay of Bengal.

S. no	Depth (m)	TN (wt%)	TC (wt%)	TIC (wt%)	TOC (wt%)	TCC (wt%)	Salinity (psu)	Temp (°C)	pH	Substrate	Ostracoda population	Ostracoda total population	General bathymetric zonation	Species
S-40	29	0.04	0.58	0.23	0.36	1.87	28.94	24.3	8.15	Silty sand	45	181	Inner-shelf	*Hemikrithe orientalis, Bradleya andamanae, Keijella reticulata, Cyprideis* sp., *Spinoceratina spinosa, Actinocythereis scutigera, Neomonoceratina iniqua, Propontocypris* aff. *P. bengalensi, Cytheropteron rhombiformis*
S-49	29	0.06	0.84	0.24	0.60	2.03	28.58	25.3	8.2	Clayey sand	45			
S-28	32	0.05	1.30	0.52	0.79	4.30	30.66	25.1	8.13	Silty clay	71			
S-7	47	0.08	2.14	1.20	0.95	9.96	31.74	24.9	8.14	Clayey sand	20			
S-39	55	0.04	1.65	1.17	0.48	9.75	30.47	24.88	8.15	Clayey sand	288	1526	Outer-shelf	*Neonesidea cracenticlavula., Bairdoppilata paraalcyonicola, Cytherelloidea malaccaensis, Cytherella incohata, Propontocypris* aff. *P. bengalensis, Argilloecia* sp., *Cytheropteron rhombiformis, Actinocythereis scutigera, Bradleya* cf. *B. japonica, Bradleya andamanae, Neocytheromorpha* sp. cf. *N. reticulata, Abrocythereis guangdongensis, Lankacythere* sp., *Lankacythere coralloides, Hemicytheridea reticulata, Henryhowella kuutapangensis, Keijella reticulata, Loxoconcha lilljeborgii, Bythoceratina pauciornata, Cytherella semitalis, Borneocythere paucipunctata*
S-67	55	0.12	2.09	0.90	1.19	7.49	27.64	24.4	8.25	Sand	8			
S-41	73	0.07	2.91	2.27	0.64	18.94	33.45	25.8	8.14	Clayey sand	1067			
S-51	73	0.14	2.05	0.91	1.13	7.60	28.85	25	8.21	Clayey sand	36			
S-8	76	0.09	1.89	0.81	1.08	6.74	31.8	25.7	8.15	Clayey sand	68			
S-9	98	0.14	2.19	0.64	1.55	5.36	31.71	25.7	8.16	Sandy clay	2			
S-66	105	0.12	4.89	3.69	1.19	30.77	27.81	25.5	8.17	Sand	51			
S-31	107	0.14	1.99	0.24	1.75	2.03	29.17	25.6	8.16	Sandy clay	6			
S-6	244	0.19	2.51	0.66	1.86	5.46	31.13	25.2	8.16	Sandy clay	3	5	Upper-bathyal	*Bythoceratina pauciornata, Borneocythere paucipunctata*
S-42	280	0.24	3.14	0.96	2.19	7.97	32.86	26.2	8.15	Sandy clay	2			
S-53	645	0.23	2.10	0.28	1.81	2.35	32.37	25.3	8.23	Silty sand	44	85	Middle-bathyal	*Neonesidea cracenticlavula, Bairdoppilata paraalcyonicola, Cytherelloidea malaccaensis, Propontocypris* aff. *P. bengalensis, Hemikrithe orientalis, Paracypris bradyi, Bythoceratina pauciornata, Cytheropteron rhombiformis, Borneocythere paucipunctata, Bradleya andamanae, Hemicytheridea reticulata, Keijella reticulata, Loxoconcha lilljeborgii., Parakrithella* sp., *Krithe* sp., *Argilloecia* sp., *Krithe* sp., *Bradleya* cf. *B. japonica Paijenborchella malaiensis, Cytherella incohata, Cytheropteron* sp. 2, *Propontocypris* aff. *P. bengalensis, Paijenborchella* sp. 1
S-34	744	0.16	1.91	0.30	1.61	2.46	32.58	25.5	8.15	Sandy clay	14			
S-21	749	0.15	2.03	0.43	1.60	3.61	33.24	26.8	8.1	Silty clay	4			
S-44	763	0.22	2.73	0.65	2.09	5.38	32.49	27	8.15	Sandy clay	15			
S-13	921	0.14	1.97	0.48	1.49	4.04	31.95	25.3	8.13	Sandy clay	3			
S-4	978	0.11	1.81	0.54	1.28	4.47	31.58	24.8	8.14	Silty clay	5			
S-35	1006	0.14	1.97	0.34	1.63	2.86	33.14	25.3	8.13	Silty clay	1	23	Lower-bathyal	
S-62	1073	0.23	2.06	0.26	1.80	2.19	31.29	25.4	8.17	Clayey silt	3			
S-19	1463	0.10	1.51	0.35	1.16	2.88	33.44	26.2	8.11	Silty clay	2			
S-3	1476	0.17	2.21	0.42	1.79	3.49	31.71	25.2	8.19	Silty clay	8			
S-55	1487	0.19	1.96	0.36	1.59	3.02	32.69	25.1	8.25	Silty clay	1			
S-36	1511	0.15	1.62	0.17	1.45	1.42	33.78	25.2	8.13	Sandy silty clay	2			
S-14	1512	0.17	1.99	0.33	1.67	2.71	31.99	25.2	8.12	Sandy clay	4			
S-15	1940	0.10	1.46	0.33	1.13	2.78	31.6	24.6	8.12	Silty clay	2			
S-18	2006	0.12	1.70	0.35	1.35	2.87	33.3	25.2	8.1	Silty clay	7	66	Upper-abyssal	*Krithe* sp., *Cytheropteron* sp. 2, *Bradleya* cf. *B. japonica Cytheropteron higashikawai, Neocytheromorpha* sp. cf. *N. reticulata, Echinocythereis* sp., *Cytheropteron rhombiformis*
S-47	2030	0.15	1.47	0.11	1.36	0.95	32.67	25.8	8.14	Silty clay	2			
S-2	2094	0.14	1.98	0.43	1.55	3.62	31.91	25.9	8.18	Silty clay	2			
S-59	2240	0.16	1.30	0.07	1.22	0.62	32.22	26.3	8.17	Silty clay	2			
S-58	2386	0.21	1.89	0.29	1.60	2.43	33.09	25.7	8.14	Clayey silt	2			
S-16	2482	0.09	1.31	0.17	1.14	1.43	31.96	26.1	8.15	Silty clay	27			
S-57	2488	0.17	1.46	0.08	1.38	0.67	32.45	23.9	8.18	Sandy clay	5			
S-38	2495	0.14	1.53	0.14	1.39	1.19	33.3	26.6	8.1	Sandy silty clay	14			
S-48	2540	0.18	1.52	0.11	1.41	0.91	32.9	26.4	8.15	Silty clay	5			

clayey sand. In addition to the substrates mentioned above, sandy silty clay, clay silt, silty sand and clay are also observed. Sandy substrate was noticed particularly in the stations 66 and 67 at water depths of 55 and 105 m, respectively, in the Mahanadi River discharge transect. The sandy sediments are deposited under medium to high energy environmental condition in this area. The species viz., *Actinocythereis scutigera, Neonesidea cracenticlavula, Bairdoppilata paraalcyonicola, Bradleya andamanae, Lankacythere* sp., *Lankacythere coralloides, Loxoconcha lilljeborgii, Borneocythere paucipunctata* are able to sustain these energy conditions and could thrive. Whereas, silty clay and clay substrate show the sediments are deposited under low energy conditions, in Pennar River discharge and off Visakhapatnam transects and accordingly the related ostracod species exist such as *Cytherelloidea malaccaensis, Hemikrithe orientalis, Paracypris bradyi, Spinoceratina spinosa, Propontocypris* aff. *P. bengalensis, Neomonoceratina iniqua.*

4.2. Organic geochemistry

This study includes, Total Organic Carbon (TOC), Total Inorganic Carbon (TIC), Total Calcium Carbonate (TCC) and Total Nitrogen (TN) content in the collected sediment samples. The TOC profile content shows six trends. Relatively constant TOC values in the inner-shelf approximately range from 0.36 to 0.95 wt%, outer-shelf range from 0.48 to 1.75 wt%, slightly higher as compared to inner-shelf. Upper-bathyal and middle-bathyal ranges are very high between 1.86 to 2.19 and 1.28 to 2.09 wt%, respectively lower-bathyal and upper-abyssal

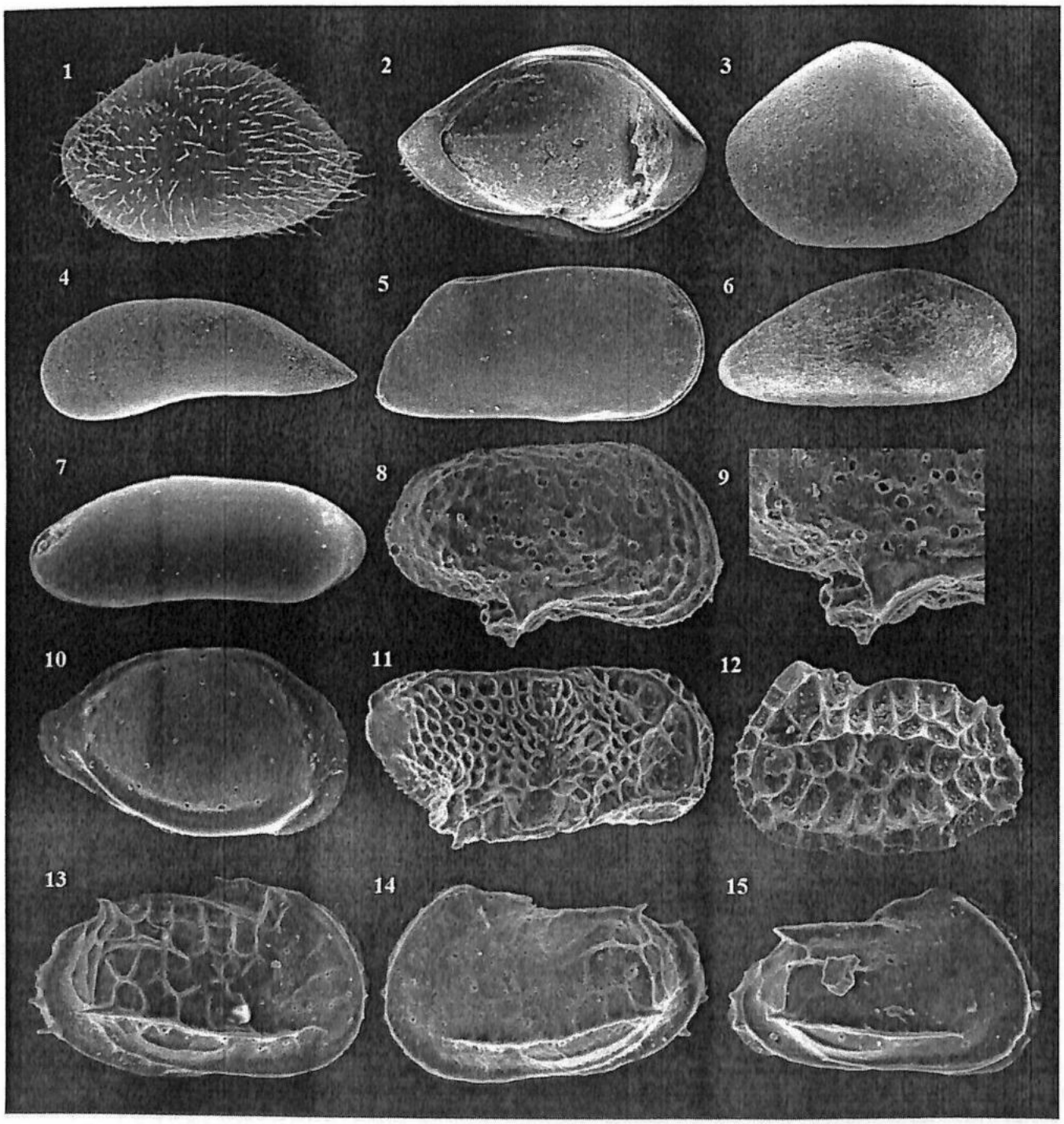

Plate I. Images 1, 2 *Neonesidea cracenticlavula* (Size: L 0.84 mm, H 0.52 mm), (Size: L 0.79 mm, H 0.44 mm), 1 LV external view, 2 LV internal view. Image 3 *Bairdoppilata paraalcyonicola* (Size: L 0.87 mm, H 0.46 mm), LV external view. Image 4 *Paracypris bradyi* (L 0.76 mm, H 0.48 mm), LV external view. Image 5 *Krithe* sp. (L 0.78 mm, H 0.32 mm), RV external view. Image 6 *Propontocypris* aff. *P. bengalensis* (L 0.47 mm, H 0.32 mm), RV external view. Image 7 *Argilloecia* sp. (L 0.67 mm, H 0.52 mm), RV external view. Image 8, 9 *Neocytheromorpha* sp. cf. *N. reticulata*. Image 8 RV external view. Image 9 the 'protuberance' is on the ventral side of *Neocytheromorpha* sp. cf. *N. reticulata* (L 0.54 mm, H 0.28 mm), a piece of biogenic carbonate. Image 10 *Cytheropteron* sp. (L 0.42 mm, H 0.31 mm), RV external view. Image 11 *Bythoceratina reticulata* (L 042 mm, H 0.37 mm), RV external view. Image 12 *Bradleya andamanae* (L 0.79 mm, H 0.53 mm), LV external view. Images 13, 14, 15 *Bradleya* cf. *B. japonica*. Image 13 (L 0.73 mm, H 0.57 mm). Image 15 (L 0.67 mm, H 0.53 mm), RV external view. Image 14 LV external view (L 0.69 mm, H 0.55 mm), (RV – Right valve; LV – Left valve). (The actual size of the hypotypes are given. L: length, H: height).

between 1.13 to 1.80 wt% and 1.14 to 1.60 wt%, respectively ranges are average compared to the inner-shelf and upper-middle bathyal. TIC content values in the inner-shelf are range from 0.23 to 1.20 wt%, outer-shelf 0.64 to 3.69 wt%, upper-bathyal 0.66 to 0.96 wt%, middle-bathyal 0.28 to 0.65 wt%, lower-bathyal 0.15 to 0.42 wt% and upper-abyssal 0.07 to 0.43 wt%. The TCC profile content shows six trends. Relatively constant values are seen in inner-shelf (1.87 to 9.96 wt%), high values from 2.03 to 30.77 wt% in the outer-shelf, upper-bathyal and middle-bathyal between 5.46 to 7.97and 2.35 to 5.38 wt%, respectively lower-bathyal and upper-abyssal 1.28 to 3.49 wt% and 0.62 to 3.62 wt%, respectively. TN content varies approximately in inner-shelf from 0.04 to 0.08 wt%, outer-shelf ranges from 0.04 to 0.14 wt%, higher than the inner-shelf, upper-bathyal 0.19 to 0.24 wt%, lower-bathyal 0.11 to 0.23 wt%. TN values are gradually increasing from shelf to slope (Table 2, Fig. 4).

4.3. Bathymetric distribution of the Ostracoda

It may be seen from Table 1 and Fig. 5 that the ostracod fauna recorded from the central Bay of Bengal includes shallow-marine to deep-sea taxa, together with a few (e.g., *Argilloecia* sp.) showing a wide bathymetric distribution. The observed ostracod assemblage composition occurring within each water masses appears to be significantly distinct. In the inner shelf region, ostracods of typical shallow marine species include *Hemikrithe orientalis*, *Neomonoceratina iniqua* and *Keijella reticulata*. The outer-shelf region at a depth of 73 m contains the dominant species *Neonesidea cracenticlavula*, *Bairdoppilata paraalcyonicola* and *Cytherelloidea malaccaensis*, an assemblage significantly different from upper-bathyal assemblage (244–280 m) composed of *Bythoceratina pauciornata* and *Borneocythere paucipunctata*. The depth of around 244 m marks a distinct change in the nature of the ostracod fauna. This faunal change is possibly the most pronounced of the entire ostracod depth zonation recorded here. In the samples of middle-bathyal depth 645–978 m, transition from a characteristically shallow to deep-sea fauna is seen, characterized most notably by the assemblage of species at 645m indicating Mixed Layer Depth (MLD). *Neonesidea* and *Bairdoppilata* belonging to the shallow water region occurred in MLD along with deep water forms. The displacement of the above mentioned genera from shallow water to deep water may be due to currents in that area. With increasing depth beyond 744 m, the upper limits of various deep-sea (psychrospheric) species *Parakrithella* sp., *Krithe* sp. are gradually encountered. The lower-bathyal at around 1006 to 1940 m appears to be characterized by *Paijenborchella* sp. and *Krithe* sp. In the upper abyssal of the Bay of Bengal, a dramatic increase in the diversity of the deep-sea dominant *Krithe* sp. is seen at about 2006 m. In addition to *Krithe*, *Echinocythereis* sp. and *Neocytheromorpha* sp. cf. *N. reticulata* are also abundant in the water depth of 2006 to 2540 m (Tables 1, 2). The shell *Neocytheromorpha* sp. cf. *N. reticulata* is affected by dissolution as seen on the surface of the specimen (Plate I, Images 8 and 9), which indicates high amount of organic matter and microcubes of pyrite and when these crystals oxidize, they become acidic and can cause partial dissolution. Plate I, Images 13–15 represent *Bradleya* cf. *B. japonica*. It is a shallow water species recorded in shallow and intermediate water in station no. 31 (107 m deep) and is displaced to deeper water due to current activity, at station 35 (1006 m deep), Image 13 represents in-situ fauna at a water depth of 2495 m, such specimens are identified by their earthy colour, dull luster and abraded or polished surfaces due to its movement and dispersal (Plate I, Images 14, 15) in the study area. This is the only dominant species with moderate to high ornamental features (Table 2), off Visakhapatnam and Godavari River discharge transects.

4.4. Diversity

The samples, which range in water depth from −29 m to 2540 m, yielded a total of 46 species belonging to 32 genera. The ostracod fauna of the Bay of Bengal exhibit a depth-related distribution that is

Table 3
Spatial distribution of 12 Ostracoda in the central Bay of Bengal (A = absolute abundance; R = relative abundance).

Station	2		3		7		8		13		14		16		18		29		39		40		41		49		51		53		66		67	
Ostracoda species	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R
Neonesidea cracenticlavula	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	43.0	0.2	0.0	0.0	284.0	0.4	0.0	0.0	6.0	0.2	8.0	0.3	10.0	0.3	1.0	0.2
Bairdoppilata paraalcyonicola	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	74.0	0.4	0.0	0.0	327.0	0.4	0.0	0.0	16.0	0.6	10.0	0.4	15.0	0.5	2.0	0.4
Cytherelloidea malaccaensis	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	20.0	0.1	8.0	0.4	43.0	0.1	10.0	0.3	2.0	0.1	2.0	0.1	0.0	0.0	0.0	0.0
Propantocypris aff. *P. bengalensis*	0.0	0.0	0.0	0.0	0.0	0.0	9.0	0.3	2.0	0.7	1.0	0.3	0.0	0.0	0.0	0.0	4.0	0.5	7.0	0.0	9.0	0.4	16.0	0.0	12.0	0.4	2.0	0.1	2.0	0.1	0.0	0.0	0.0	0.0
Argilloecia sp.	0.0	0.0	2.0	0.3	0.0	0.0	2.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.3	7.0	0.0	6.0	0.3	16.0	0.0	8.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Krithe sp.	1.0	0.5	4.0	0.7	0.0	0.0	0.0	0.0	1.0	0.3	1.0	0.3	0.0	0.0	1.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cytheropteron higashikawai	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.1	0.0	0.0	1.0	0.3	1.0	0.0	1.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	5.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bythoceratina pauciornata	0.0	0.0	0.0	0.0	0.0	0.0	4.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	13.0	0.1	0.0	0.0	17.0	0.0	0.0	0.0	0.0	0.0	2.0	0.1	4.0	0.1	1.0	0.2
Cytheropteron sp. 2	1.0	0.5	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	26.0	1.0	3.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Paijenborchella sp. 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.2	2.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bradleya andamanae	0.0	0.0	0.0	0.0	0.0	0.0	9.0	0.2	9.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	13.0	0.1	0.0	0.0	70.0	0.1	0.0	0.0	0.0	0.0	4.0	0.1	2.0	0.1	0.0	0.0
Lankacythere sp.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	36.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.2
Total	2	1	6	1	42	1	29	1	3	1	3	1	27	1	6	1	8	1	179	1	23	1	815	1	30	1	27	1	28	1	31	1	5	1
Species diversity	0.69		0.64		0.86		1.67		0.64		1.1		0.16		1.24		1.04		1.64		1.09		1.51		1.09		1.15		1.57		1.16		1.33	

controlled by substrate and hydrographic conditions. Ostracod population is low due to low productivity prevailing in the study area. Spatial distribution of Ostracoda (adult and juvenile) in terms of absolute and relative numbers is given in Table 3. At selected stations species diversity varies from 0 to 1.67; stations 8 and 39 show have the highest diversity. The most dominant species in the sub-order Bairdiocopina are *Neonesidea cracenticlavula* and *Bairdoppilata paraalcyonicola* in stations 39 to 41 and 51 to 66. The distribution of species shows that *Krithe* sp. and *Argilloecia* sp. are present at several stations. The remaining taxa represented by sub-orders Platycopa (*Cytherelloidea*) and Podocopa (*Cytheropteron, Propontocypris, Paljenborchella*) show sporadic occurrence at stations 7–67, of these only 12 species were dominant in several stations (Table 3). The faunal carapaces are fresh, shiny, and not pyritised. The ornamentation on the carapaces changes gradually from coarse to fine towards the deeper water (Plate I). Of the total Ostracoda population, 90% are open valves and the rest are carapaces in the area studied, which indicates a relatively slow rate of sedimentation from shelf to slope region in the central Bay of Bengal. During a slow rate of sedimentation, the carapaces disarticulate. While a faster sedimentation rate will cause the carapaces be buried immediately and preserved (Oertli, 1971; Hussain et al., 2007; Mohammed Nishath et al., 2015).

4.5. Dominant species

Neonesidea and *Bairdoppilata* are typical genera that are associated with coral reef environments (Maddocks, 1969). *Neonesidea* is a cosmopolitan genus occurring in shallow sub-littoral and reefal environments with more than 100 named species (living and fossil) (Maddocks, 1969, 1995; Titterton and Whatley, 1988; Weissleader et al., 1989) each reported 8 co-occurring species of *Neonesidea* (some in open nomenclature). This level of diversity appears to be reasonable for larger atolls and well-sampled lagoons and platforms (contrary to Eager, 1999). In the present study, *Bairdoppilata paraalcyonicola*, *Neonesidea cracenticlavula* and *Bradleya andamanae* are the dominant species present in most of the shallow water stations. The bathymetric distribution of *B. paraalcyonicola* and *N. cracenticlavula* in the off Visakhapatnam transect of the Bay of Bengal is given in Fig. 6, which shows the highest living population of these species were recorded in the water depth of 73 m and the population is decreasing towards the deeper water level.

4.6. Factor analysis

4.6.1. Component and correlation matrix

Bivariate Pearson correlation matrix was carried out to assess the relationship between Ostracoda species with other parameters like organic geochemistry, sedimentological and hydrological characteristics of the surface sediments. Component matrix extracted factor loadings of the studied parameters show three distinct factors in which depth, clay and salinity fall under factor 1, other parameters such as TN and TOC fall under factor 2 and finally factor 3 includes TCC, TIC, sand and Ostracoda population (Tables 4 and 5, Fig. 7). A significant strong correlation (0.05 levels) was observed between TCC, TIC and sand for Ostracoda. TCC strongly correlated with Ostracoda population. Negative correlation between TOC and TN was noticed. TOC shows a strongly negative correlation with Ostracoda population.

Table 4
Component matrix of water and sediment parameter with Ostracoda species of central Bay of Bengal.

Component matrix			
	Component		
	Factor1	Factor 2	Factor 3
Depth	0.763	−0.067	0.189
TN	0.654	0.573	−0.331
TC	−0.310	0.922	−0.016
TIC	−0.747	0.601	0.145
TOC	0.673	0.583	−0.255
TCC	−0.747	0.601	0.145
Salinity	0.676	0.109	0.588
Temp	0.365	0.422	0.469
pH	−0.187	0.094	−0.779
Sand	−0.875	−0.320	0.022
Silt	0.077	0.374	−0.134
Clay	0.735	0.007	0.082
Ostracoda	−0.525	0.107	0.552

5. Conclusions

A total of 46 benthic species belonging to 32 genera have been found from the collected multi-core surface samples ranging in water depth from 29 to 2540 m from the central portion of Bay of Bengal, India. Two species namely *Neonesidea cracenticlavula* and *Bairdoppilata paraalcyonicola* are dominantly present in the shallow water region while the species *Krithe* sp. and *Argilloecia* sp. are present in the deeper water region. Depth plays an important role in controlling the ostracod distribution. Depth results in a decrease of the ostracod population. Living species with a preference for shallow water as well as deep water species occurred both at a depth of 645 m, which indicates the Mixed Layer Depth (MLD). Ostracod population is low wherever higher amount of TOC is recorded. Similarly, TN is negatively correlated with ostracod population. TOC increases toward the deeper depth and also

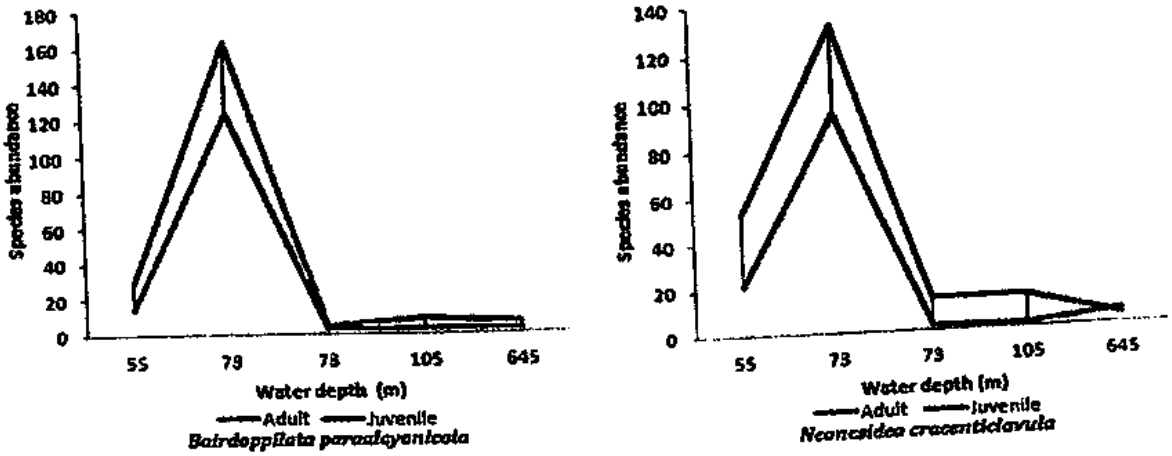

Fig. 6. Histogram shows the distribution of two species in the study area, adult/juvenile forms.

Table 5
Correlation matrix of water and sediment parameter with Ostracoda species of central Bay of Bengal.

	Depth	TN (wt%)	TC (wt%)	TIC (wt%)	TOC (wt%)	TCC (wt%)	Salinity (psu)	Temp (°C)	pH	Sand (wt%)	Silt (wt%)	Clay (wt%)	Ostracoda population
Depth	1												
TN (wt%)	0.321*	1											
TC (wt%)	−0.332*	0.308	1										
TIC (wt%)	−0.503**	−0.243	0.815**	1									
TOC (wt%)	0.244	0.901**	0.373*	−0.234	1								
TCC (wt%)	−0.501**	−0.242	0.815**	1.000**	−0.234	1							
Salinity (psu)	0.573**	0.376*	−0.124	−0.370*	0.384*	−0.370*	1						
Temp (°C)	0.228	0.311	0.192	−0.029	0.368*	−0.028	0.440**	1					
pH	−0.220	0.213	0.116	0.083	0.054	0.084	−0.488**	−0.334*	1				
Sand (wt%)	−0.790**	−0.677**	−0.025	0.407*	−0.689**	0.406*	−0.580**	−0.353*	0.089	1			
Silt (wt%)	0.279	0.271	0.169	0.095	0.127	0.097	0.014	0.166	0.035	−0.296	1		
Clay (wt%)	0.503**	0.409*	−0.105	−0.441**	0.530**	−0.441**	0.516**	0.196	−0.107	−0.682**	−0.497**	1	
Ostracoda population	−0.272	−0.344*	0.211	0.485**	−0.423**	0.486**	0.088	0.027	−0.056	0.435**	−0.123	−0.300	1

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

the ostracods are exposed to increasing amounts of physiological stress from oxygen depletion due to higher Biological Oxygen Demand (BOD). Dissolution of ostracod shells is noticed in *Neocytheromorpha* sp. cf. *N. reticulata*. The distribution of *Bradleya* cf. *B. japonica* in deeper as well as shallower water regions is also noticed, which may be due to tsunami-like events and current action. Higher ostracod biodiversity is seen in the shallower water region compared to the deeper water environment. A gradual and slow rate of sedimentation is inferred from the carapace/valve ratio from the shelf to slope region of Bay of Bengal, which is due to less transportation of terrigenous material by the rivers from shallow to deep marine regions.

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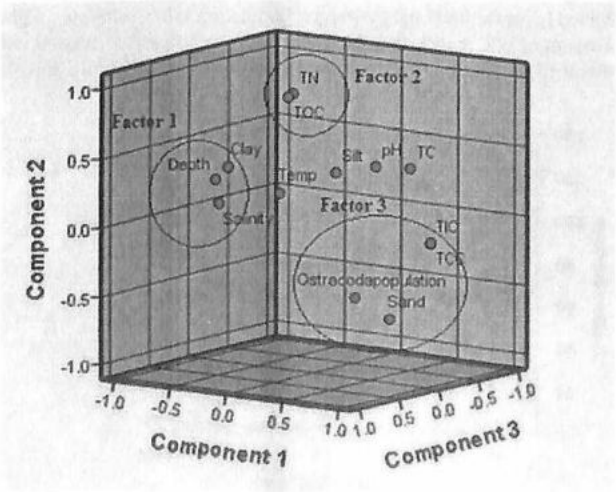

Fig. 7. Component matrix shows three factors in the surface sediment samples of central Bay of Bengal.

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Special Issue

Total Chromatic Number of Star and BistarGraphs

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Abstract

A total coloring of a graph G is an assignment of colors to both the vertices and edges of G, such that no two adjacent or incident vertices and edges of G are assigned the same colors. In this paper, we have discussed the total coloring of $M(K_{1,n})$, $T(K_{1,n})$, $L(K_{1,n})$ and $B_{n,n}^2$and we obtained the total chromatic number of $M(K_{1,n})$, $T(K_{1,n})$, $L(K_{1,n})$and $B_{n,n}^2$.

AMS Subject Classification: 05C15

Keywords and Phrases: Middle graph, line graph, total graph, star graph, square graph, total coloring and total chromatic number.

Proof:

Let $V(K_{1,n}) = \{v\} \cup \{v_1, v_2, v_3, \ldots\ldots v_n\}$ and $E(K_{1,n}) = \{e_1, e_2, e_3, \ldots\ldots e_n\}$where $\{e_i = vv_i : 1 \le i \le n\}$. Now we construct the middle graph of star, each edge $\{e_i = vv_i : 1 \le i \le n\}$ in $K_{1,n}$ is subdivided by the vertices $\{v_i' : 1 \le i \le n\}$in $M(K_{1,n})$ and the vertices $\{v, v_1', v_2', v_3', \ldots\ldots, v_n'\}$ induce a clique of order $n+1$. Let it be K_{n+1}. In $M(K_{1,n})$, the vertex set and the edge setis given by $V(M(K_{1,n})) = \{v\} \cup \{v_1, v_2, v_3, \ldots\ldots v_n\} \cup \{v_1', v_2', v_3', \ldots\ldots, v_n'\}$ and $E(M(K_{1,n})) = \{vv_i' : 1 \le i \le n\} \cup \{v_i'v_i : 1 \le i \le n\} \cup \{v_i'v_j' : 1 \le i \le n-1,\ j > i,\ i+1 \le j \le n$Now we define the total coloring f, such that$f: S \to C$ as follows, where$S = V(M(K_{1,n})) \cup E(M(K_{1,n}))$ and $C = \{1, 2, 3, \ldots n+3\}$. The total coloring is obtained by coloring these vertices and edges as follows. We consider the following two cases:

Case(i): when n is odd

$$f(v) = n+2 \qquad f(v_i') = i \quad : \quad 1 \le i \le n.$$

$$f(v_i) = n+1 \quad : 1 \le i \le n$$

$$f(vv_i') = \begin{cases} 2i, & if\ 2i \not\equiv 0\ (mod\ n+2) \\ n+2, & otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(v_i'v_j') = \begin{cases} i+j, & if\ (i+j) \not\equiv 0 (mod\ n+2) \\ n+2, & otherwise \end{cases}$$

$$\text{for } 1 \le i \le n-1,\ j > i,\ i+1 \le j \le n$$

$$f(v_i'v_i) = i-1 \quad : \quad 2 \le i \le n$$

$$f(v_1'v_1) = n+2$$

Based on the above method of totalcoloring, the graph$M(K_{1,n})$ is total colored with $n+2$colors.

Hence the total chromatic number of $M(K_{1,n})$, $\chi''(M(K_{1,n})) = n+2$.

Case (ii): when n is even

$$f(v) = n+3 \qquad f(v_i') = i \quad : \quad 1 \le i \le n.$$

$$f(v_i) = n+1 \quad : 1 \le i \le n$$

$$f(vv_i') = \begin{cases} 2i, & if\ 2i \not\equiv 0\ (mod\ n+3) \\ n+3, & otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(v_i'v_j') = \begin{cases} i+j, & if\ (i+j) \not\equiv 0 (mod\ n+3) \\ n+3, & otherwise \end{cases}$$

$$\text{for } 1 \le i \le n-1,\ j > i,\ i+1 \le j \le n$$

$$f(v_i'v_i) = i-1 \quad : \quad 2 \le i \le n$$

$$f(v_1v_1) = n+2$$

Based on the above ruleof total coloring, the graph $M(K_{1,n})$ is total colored with $n+3$colors.Hence the total chromatic number of$M(K_{1,n})$, $\chi''(M(K_{1,n})) = n+3$.

Illustration 2.3: Consider the middle graph of star

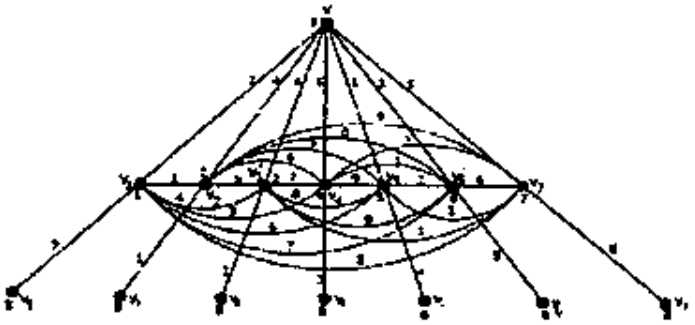

Figure 1: Total Coloring of Middle Graphof Star $M(K_{1,7})$ for n is Odd

Illustration 2.4: Consider the middle graph of star

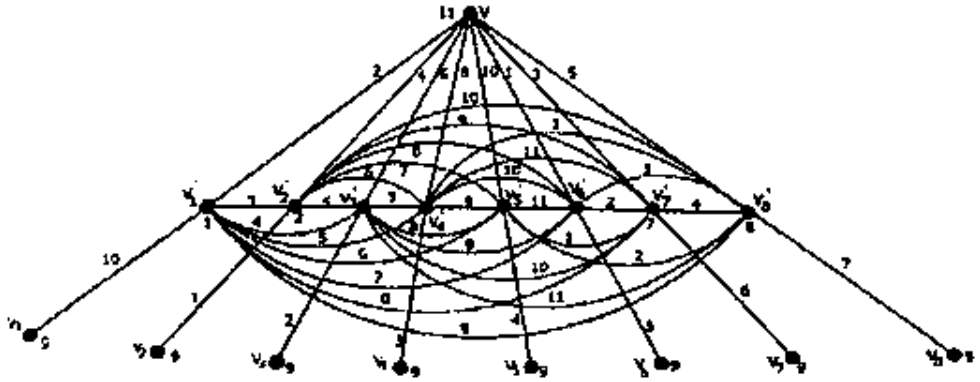

Figure 2: Total Coloring of Middle Graph of Star $M(K_{1,8})$for n is Even

3. Total Chromatic Number of $T(K_{1,n})$

Definition 3.1. The *Total graph* of a graph G, denoted by $T(G)$ is define as, the vertex set of $T(G)$ is $V(G) \cup E(G)$. Two vertices x, y in the vertex set of $T(G)$ are adjacent in $T(G)$ in case one of the following condition holds: (i) x, y are in $V(G)$ and x is adjacent to y in G. (ii) x, y are in $E(G)$ and x, y is adjacent in G. (iii) x is in $V(G)$, y is in $E(G)$and x, y are incident in G.

Theorem 3.2. Let $T(K_{1,n})$be the total graph of star graph. Then

$$\chi''(T(K_{1,n})) = 2n + 1,$$

Proof:

Let$V(K_{1,n}) = \{v\} \cup \{v_1, v_2, v_3, \ldots\ldots v_n\}$ and $E(K_{1,n}) = \{e_1, e_2, e_3, \ldots\ldots e_n\}$where $\{e_i = vv_i : 1 \le i \le n\}$. Now we construct the total graphof star, each edge $\{e_i = vv_i : 1 \le i \le n\}$ in $K_{1,n}$ is subdivided by the vertices $\{v_i' : 1 \le i \le n\}$in $T(K_{1,n})$ and the vertices $\{v, v_1', v_2', v_3', \ldots\ldots, v_n'\}$ induce a clique of order $n + 1$. Let it be K_{n+1}.

Proof:

Let $V(K_{1,n}) = \{v\} \cup \{v_1, v_2, v_3, \ldots\ldots v_n\}$ and $E(K_{1,n}) = \{e_1, e_2, e_3 \ldots\ldots e_n\}$where $\{e_i = vv_i : 1 \le i \le n\}$. Now we construct the middle graph of star, each edge $\{e_i = vv_i : 1 \le i \le n\}$ in $K_{1,n}$ is subdivided by the vertices $\{v_i' : 1 \le i \le n\}$in $M(K_{1,n})$ and the vertices $\{v, v_1', v_2', v_3', \ldots\ldots, v_n'\}$ induce a clique of order $n+1$. Let it be K_{n+1}. In $M(K_{1,n})$, the vertex set and the edge setis given by $V(M(K_{1,n})) = \{v\} \cup \{v_1, v_2, v_3 \ldots\ldots v_n\} \cup \{v_1', v_2', v_3', \ldots\ldots, v_n'\}$ and $E(M(K_{1,n})) = \{vv_i' : 1 \le i \le n\} \cup \{v_i'v_i : 1 \le i \le n\} \cup \{v_i'v_j' : 1 \le i \le n-1,\ j > i,\ i+1 \le j \le n$.Now we define the total coloring f, such that $f: S \to C$ as follows, where $S = V(M(K_{1,n})) \cup E(M(K_{1,n}))$ and $C = \{1, 2, 3, \ldots, n+3\}$. The total coloring is obtained by coloring these vertices and edges as follows. We consider the following two cases:

Case(i): when n is odd

$$f(v) = n+2 \qquad f(v_i') = i \quad : \quad 1 \le i \le n.$$

$$f(v_i) = n+1 \ : \ 1 \le i \le n$$

$$f(vv_i') = \begin{cases} 2i, & if\ 2i \not\equiv 0 \ (mod\ n+2) \\ n+2, & otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(v_i'v_j') = \begin{cases} i+j, & if\ (i+j) \not\equiv 0 (mod\ n+2) \\ n+2, & otherwise \end{cases}$$

$$\text{for } 1 \le i \le n-1,\ j > i,\ i+1 \le j \le n$$

$$f(v_i'v_i) = i-1 \quad : \quad 2 \le i \le n$$

$$f(v_1'v_1) = n+2$$

Based on the above method of totalcoloring, the graph $M(K_{1,n})$ is total colored with $n+2$colors.

Hence the total chromatic number of $M(K_{1,n})$, $\chi''(M(K_{1,n})) = n+2$.

Case (ii): when n is even

$$f(v) = n+3 \qquad f(v_i') = i \quad : \quad 1 \le i \le n.$$

$$f(v_i) = n+1 \ : \ 1 \le i \le n$$

$$f(vv_i') = \begin{cases} 2i, & if\ 2i \not\equiv 0 \ (mod\ n+3) \\ n+3, & otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(v_i'v_j') = \begin{cases} i+j, & if\ (i+j) \not\equiv 0 (mod\ n+3) \\ n+3, & otherwise \end{cases}$$

$$\text{for } 1 \le i \le n-1,\ j > i,\ i+1 \le j \le n$$

$$f(v_i'v_i) = i-1 \quad : \quad 2 \le i \le n$$

$$f(v_1v_1) = n+2$$

Based on the above ruleof total coloring, the graph $M(K_{1,n})$ is total colored with $n+3$colors.Hence the total chromatic number of$M(K_{1,n})$, $\chi''(M(K_{1,n})) = n+3$.

In $T(K_{1,n})$, the vertex set and the edge setis given by $V(T(K_{1,n})) = \{v\} \cup \{v_1, v_2, v_3 \ldots\ldots v_n\} \cup \{v_1', v_2', v_3', \ldots\ldots, v_n'\}$ and $E(T(K_{1,n})) = \{vv_i' : 1 \le i \le n\} \cup \{vv_i : 1 \le i \le n\} \cup \{v_i'v_i : 1 \le i \le n\} \cup \{v_i'v_j' : 1 \le i \le n-1, j > i,\ i+1 \le j \le n$.

Now we define the total coloring f, such that$f: S \to C$ as follows, where $S = V(T(K_{1,n})) \cup E(T(K_{1,n}))$ and $C = \{1, 2, 3, \ldots 2n+1\}$. The total coloring is obtained by coloring these vertices and edges as follows.

$$f(v) = 2n+1 \qquad f(v_i') = i \quad : \quad 1 \le i \le n.$$

$$f(v_i) = 2n \quad : 1 \le i \le n$$

$$f(vv_i') = \begin{cases} 2i, & if\ 2i \not\equiv 0\ (mod\ 2n) \\ 2n, & 0 otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(vv_i) = \begin{cases} 2i-1, & if\ 2i-1 \not\equiv 0\ (mod\ 2n-1) \\ 2n-1, & 0 otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(v_i'v_j') = \begin{cases} i+j, & if\ (i+j) \not\equiv 0 (mod\ 2n+1) \\ 2n+1, & otherwise \end{cases}$$

$$\text{for } 1 \le i \le n-1,\ j > i,\ i+1 \le j \le n$$

$$f(v_i'v_i) = i-1 \quad : \quad 2 \le i \le n$$

$$f(v_1'v_1) = n+2$$

Based on the above rule of total coloring, the graph $T(K_{1,n})$ is total colored with $2n+1$colors. Hence the total chromatic number of the total graph of $T(K_{1,n})$, $\chi''(T(K_{1,n})) = 2n+1$.

Illustration 3.3: Consider the total graph of Star graph

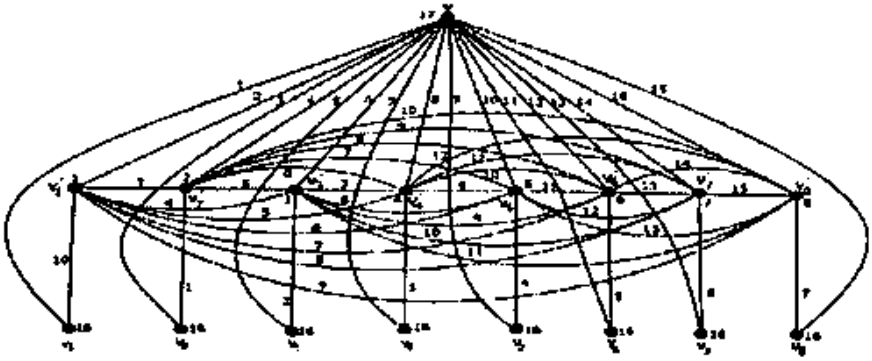

Figure 3: Total Coloring of Total Graph of Star $T(K_{1,8})$

4. Total Chromatic Number of$_{L(B_{n,n})}$

Definition 4.1. *Bistar graph* is the graph obtained by joining the root vertices of two copies of star $K_{1,n}$

Definition 4.2. The *line graph* of graph G, denoted by $L(G)$ is the graph whose vertices are the edges of G, (iii) x is in $V(G)$, y is in $E(G)$and x, y are incident in G.

Theorem4.3. Let $L(B_{n,n})$be the line graph of star graph. Then

$$\chi''(L(B_{n,n})) = 2n + 1.$$

Proof:

Let $V(B_{n,n}) = \{u\} \cup \{v\} \cup \{u_i : 1 \le i \le n\} \cup \{v_i : 1 \le i \le n\}$and $E(B_{n,n}) = \{uu_i : 1 \le i \le n\} \cup \{vv_i : 1 \le i \le n\} \cup \{uv\}$. Let$uu_i$ $(1 \le i \le n)$ be the edge between the vertices u and $u_i (1 \le i \le n)$ (i.e) $uu_i = u_i'$ and v_i' $(1 \le i \le n)$ be the edge between the vertices v and $v_i (1 \le i \le n)$ (i.e) $vv_i = v_i'$ and u' be the edge between the vertices u and v. Here u' is adjacent with both the vertices u_i' $(1 \le i \le n)$ and $v_i (1 \le i \le n)$.Now we construct the line graph of Bistar, the edge set of $B_{n,n}$ corresponding to the vertex set of $L(B_{n,n})$. The vertices u_i' $(1 \le i \le n)$ along with u' forms a complete graph of order $n + 1$ and also the vertices v_i' $(1 \le i \le n)$ along with u' forms a complete graph of order $n + 1$. Let it be K_{n+1}' and K_{n+1}''. In $L(B_{n,n})$, the vertex set and the edge set is given by

$$V\left(L(B_{n,n})\right) = \{u_i' : 1 \le i \le n\} \cup \{v_i' : 1 \le i \le n\} \cup \{u'\} \text{ and}$$

$$E\left(L(B_{n,n})\right) = \{u'u_i' : 1 \le i \le n\} \cup \{u'v_i' : 1 \le i \le n\} \cup \{u_i'u_j' : 1 \le i \le n-1,\ j > i, i+1 \le j \le n\} \cup \{v_i'v_j' : 1 \le i \le n-1, j > i,\ i+1 \le j \le n\}.$$

Now weconstruct the total coloring f, such that$f: S \to C$ as follows, where $S = V\left(L(B_{n,n})\right) \cup E\left(L(B_{n,n})\right)andC = \{1, 2, 3, \ldots .2n + 1\}$. The total coloring is obtained by coloring these vertices and edges as follows.

$$f(u') = 2n + 1$$

$$f(u_i') = \begin{cases} i, & if\ i \not\equiv 0\ (mod\ n) \\ n, & 0 otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(v_i') = \begin{cases} n + i, & if\ n + i \not\equiv 0\ (mod\ 2n) \\ 2n, & 0 otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(u'u_i') = \begin{cases} 2i, & if\ 2i \not\equiv 0\ (mod\ 2n) \\ 2n, & 0 otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(u'v_i') = \begin{cases} 2i - 1, & if\ 2i - 1 \not\equiv 0\ (mod\ 2n - 1) \\ 2n - 1, & 0 otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(u_i'u_j') = \begin{cases} i + j, & if\ (i + j) \not\equiv 0 (mod\ 2n + 1) \\ 2n + 1, & otherwise \end{cases}$$

$$\text{for } 1 \le i \le n - 1,\ j > i,\ i + 1 \le j \le n$$

$$f(v_i'v_j') = \begin{cases} i + j - 1, & if\ (i + j - 1) \not\equiv 0 (mod\ 2n + 1) \\ 2n + 1, & otherwise \end{cases}$$

$$\text{for } 1 \le i \le n - 1,\ j > i,\ i + 1 \le j \le n$$

It is clear that, the above rule of total coloring, the graph$L(B_{n,n})$ is total colored with $2n + 1$colors.

Hence the total chromatic number of $L(B_{n,n})$, $\chi''\left(L(B_{n,n})\right) = 2n + 1$.

Illustration 4.4: Consider the line graph of Bistar graph

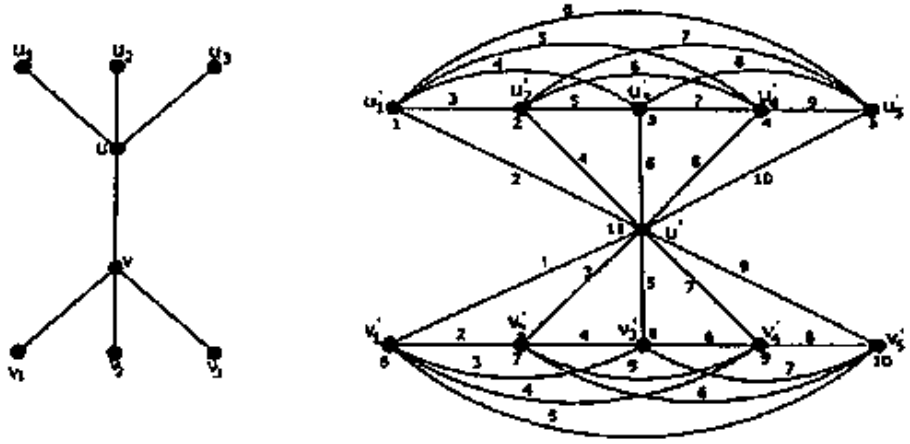

Figure 4: Bistar Graph $B_{3,3}$ and Total Coloring of Line Graph of Bistar $L(B_{5,5})$

5. Total Chromatic Number of $B_{n,n}^2$

Definition 5.1. For a simple connected graph G, the square *graph*G, is the graph G^2 obtained by adding edges to G between any two vertices of G is distance 2.

Theorem 5.2. Let $B_{n,n}^2$ be the square graph of Bistar graph. Then

$$\chi''(B_{n,n}^2) = 2n + 2, \quad n \geq 2.$$

Proof:

Let $V(B_{n,n}) = \{u\} \cup \{v\} \cup \{u_i : 1 \leq i \leq n\} \cup \{v_i : 1 \leq i \leq n\}$ and

$E(B_{n,n}) = \{uu_i : 1 \leq i \leq n\} \cup \{vv_i : 1 \leq i \leq n\} \cup \{uv\}$. Now we construct the square graph of Bistar graph, the new edges in $B_{n,n}^2$ is obtained by adding the edges to $B_{n,n}$ between any two vertices of $B_{n,n}$ of distance two. In $B_{n,n}^2$, the vertex set and the edge set is given by

$$V(B_{n,n}^2) = \{u\} \cup \{v\} \cup \{u_i : 1 \leq i \leq n\} \cup \{v_i : 1 \leq i \leq n\} \text{ and}$$
$$E(B_{n,n}^2) = \{uu_i : 1 \leq i \leq n\} \cup \{uv_i : 1 \leq i \leq n\} \cup \{vu_i : 1 \leq i \leq n\} \cup \{vv_i : 1 \leq i \leq n\}$$

Now we construct the total coloring f, such that $f: S \to C$ as follows, where $S = V(B_{n,n}^2) \cup E(B_{n,n}^2)$ and $C = \{1, 2, 3, \ldots 2n + 2\}$. The total coloring is obtained by coloring these vertices and edges as follows.

$$f(u) = 1 \qquad f(v) = 2n + 1$$
$$f(u_i) = f(v_i) = f(uv) = 2n + 2 \; : \; 1 \leq i \leq n$$

$$f(uu_i) = \begin{cases} 2i, & if\ 2i \not\equiv 0\ (mod\ 2n) \\ 2n, & Otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(uv_i) = \begin{cases} 2i+1, & if\ 2i+1 \not\equiv 0\ (mod\ 2n+1) \\ 2n+1, & Otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(vu_i) = \begin{cases} 2i-1, & if\ 2i-1 \not\equiv 0\ (mod\ 2n-1) \\ 2n-1, & Otherwise \end{cases} \text{ for } 1 \le i \le n$$

$$f(vv_i) = \begin{cases} 2i, & if\ 2i \not\equiv 0\ (mod\ 2n) \\ 2n, & Otherwise \end{cases} \text{ for } 1 \le i \le n$$

It is clear that, the above rule of total coloring, the graph $B^2_{n,n}$ is total colored with $2n + 2$colors. Hence the total chromatic number of$B^2_{n,n}$, $\chi''(B^2_{n,n}) = 2n + 2$.

Illustration 5.3: Consider the square graph of Bistar graph.

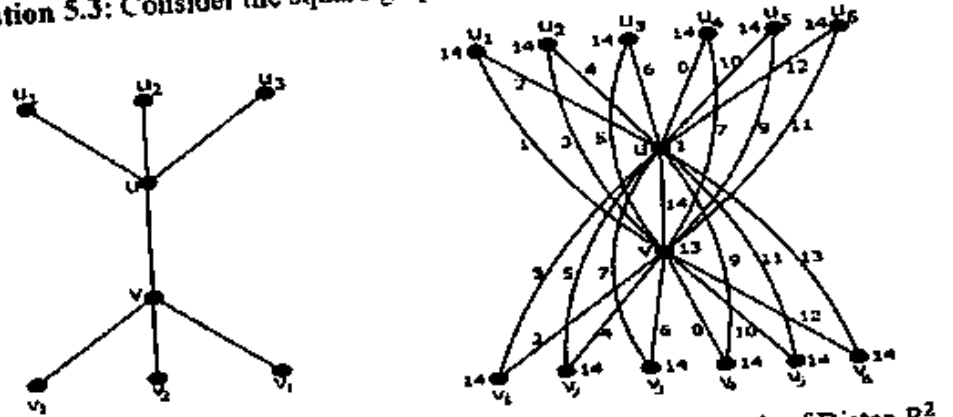

Figure 5: Bistar Graph $B_{3,3}$ and Total Coloring of Square Graph of Bistar $B^2_{6,6}$

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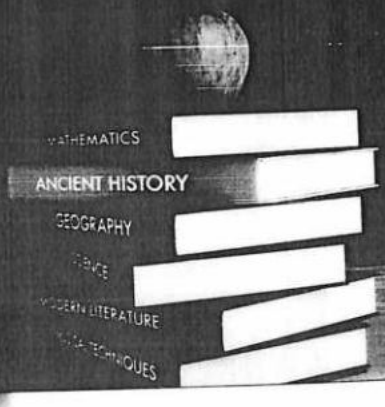
"The study of mathematics, like the Nile, begins in minuteness but ends in magnificence". The aim of this book is to give the reader an opportunity to learn and to know interesting results in the elementary theory of numbers. A reasonably large number of problems on solving systems of equations have been provided to enable the students to deepen their understanding of the subject. This book is aimed at students, researchers and anyone with an interest in numbers and equations. Some aptitude is needed for general readers. It will be particularly useful to students who wish to do research in polynomial Diophantine equations. The author's goal is to illustrate the art of finding integer solutions to systems of Diophantine equations. We hope the students may be motivated to search for integer solutions to systems of multi degree multivariate polynomial Diophantine equations.



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Special Diophantine Problems on Integer Pairs, Triples with Solutions

Dr.M.A.Gopalan is currently Professor of Mathematics at Shrimati Indira Gandhi College, Tiruchirappalli and has taught Mathematics for nearly two decades.He is interested in problem solving in the area of Diophanine equations and Number Patterns.He serves on the editorial boards of IJPMS and IJAR and a life member of Kerala Mathematics Association.

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A

Classification

of

Special Diophantine Problems

on

Integer Pairs and Triples

with

Solutions

By

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A Classification of Special Diophantine Problems on Integer Pairs and Triples with Solutions

Authors Preface

The definition of

A good mathematical problem is the mathematics it generates rather than the problem itself

- Sir Andrew John Wiles

Diophantus, the "*father of algebra*", is best known for his book "*Arithmetica*", a work on the solution of algebraic equations and on the theory of numbers. It is a collection of 150 problems giving approximate solutions to determinate equations up to 3rd degree and also contains equations that deal with indeterminate equations.

For various problems on solving Diophantine equations, the readers may also refer the book entitled "A collection of Diophantine problems with solutions" by James Matteson, Artemas Martin, Washington, 1888. The above two reference books motivated us to search for integer solutions to other choices of systems of multiple equations.

This book reproduces, with minor changes, the notes prepared for a course at Shrimati Indira Gandhi College, Tiruchirappalli, South India, the audience being Post Graduate and research scholars with an interest in and aptitude for mathematics. The presentation is kept as elegant and self-contained as possible because the discussion was carried to introduce the scholars to some areas of current research. A portion of the subject matter of this book has been available to scholars through papers by the authors of this book.

The present book is essentially designed for advance undergraduates, postgraduates and research scholars in mathematical sciences. The prerequisite for this book is a little algebra- nothing more than entrance requirements at most colleges.

We hope the readers-especially those who don't like mathematics will complete the course with greater confidence in their ability to solve system of Diophantine equations. A study of this book will reveal to the readers the remarkable progress in the study of Diophantine equations which has been our main goal.

This book consists of two chapters I and II. Chapter I deal with the system of double, triple Diophantine equations with two unknowns with complete solutions to the considered problems.

Chapter II concerns with the problem of solving three and four equations with three unknowns. Complete integer solutions are given for each problem.

Notations

1. Regular Polygonal Number of rank n with sides m : $t_{m,n} = n[1 + \frac{(n-1)(m-2)}{2}]$
2. Pyramidal Number of rank n with sides m : $p_n^m = \frac{1}{6}[n(n+1)][(m-2)n + (5-m)]$
3. Centered Pyramidal Number of rank n with sides m : $cp_{m,n} = \frac{m(n-1)n(n+1)}{6} + n$
4. Pronic Number of rank n : $pr_n = n(n+1)$
5. Gnomonic Number of rank n : $G_n = 2n-1$
6. Jacobsthal Number of rank n : $J_n = \frac{1}{3}[2^n - (-1)^n]$
7. Jacobsthal Lucas Number of rank n : $j_n = 2^n + (-1)^n$
8. Star Number of rank n : $S_n = 6n(n-1) + 1$
9. Kynea Number of rank n : $Ky_n = (2^n + 1)^2 - 2$
10. Fourth – dimensional figurate number of rank r whose generating polygon has s - sides:
$F_{4,s}^r = \frac{r(r+1)(r+2)(rs-s+4)}{4!}$

$(s = 1 \Rightarrow triangle, s = 2 \Rightarrow square, s = 3 \Rightarrow pentagon \text{ and so on})$

Problem: 1

On The System of Double Diophantine Equations

$$N_1 - N_2 = 2p, N_1 N_2 = \left(k^2+1\right)q^2$$

Solution:

Let N_1 and N_2 be two non-zero distinct integers such that

$$N_1 - N_2 = 2p \tag{1.1}$$

$$N_1 N_2 = \left(k^2+1\right)q^2 \tag{1.2}$$

where $p, q \neq 0$

Eliminating N_2 between (1.1) and (1.2), we get

$$N_1^2 - 2pN_1 - \left(k^2+1\right)q^2 = 0 \tag{1.3}$$

Treating (1.3) as quadratic in N_1 and solving for N_1, we get

$$N_1 = p \pm \sqrt{p^2 + \left(k^2+1\right)q^2} \tag{1.4}$$

Let $Y^2 = \left(k^2+1\right)q^2 + p^2$ (1.5)

This equation is satisfied by

$$q = 2rs,\quad p = (k^2+1)^2 - s^2,\quad Y = (k^2+1)^2 + s^2 \qquad (1.6)$$

Substituting (1.6) in (1.4) and using (1.1) , we obtain two sets of values for N_1 and N_2 as follows:

Set1: $N_1 = 2(k^2+1)^2, N_2 = 2s^2$ (1.7)

Set2: $N_1 = -2s^2, N_2 = -2(k^2+1)^2$ (1.8)

Note that the values of N_1 and N_2 in (1.8) are nothing but the replacement of N_2 by $-N_1$ and N_1 by $-N_2$ in (1.7) respectively.

In addition to (1.7) and (1.8) , we have two other choices for N_1 and N_2 & they are illustrated below:

Choice I : (1.5) is equivalent to the system of equations

$$\left.\begin{aligned} Y + p &= (k^2+1)q \\ Y - p &= q \end{aligned}\right\} \qquad (1.9)$$

Solving the above system of equations , we have

$$Y = k^2 q/2 + q,\ p = k^2 q/2 \qquad (1.10)$$

As our interest is in finding integer solutions, the values of Y, p in (1.10) are integers provided

(i) k is even or (ii) q is even or (iii) both k and q are even.

After performing a few calculations, the corresponding values N_1 and N_2 are as follows:

Values of N_1 and N_2

k	q	N_1	N_2
2K	Arbitrary	$(4K^2+1)q$, $-q$	q, $-(4K^2+1)q$
arbitrary	2Q	$2(K^2+1)Q$, $-2Q$	$2Q$, $-2(K^2+1)Q$
2K	2Q	$2(4K^2+1)Q$, $-2Q$	$2Q$, $-2(4K^2+1)Q$

Choice II : (1.5) is equivalent to the system of equations

$$\left.\begin{aligned} Y + p &= k^2 + 1 \\ Y - p &= q^2 \end{aligned}\right\}$$

Following the procedure as presented in choice I, the corresponding sets of solutions are presented in the Table below:

Values of N_1 and N_2

k	q	N_1	N_2
2K	2Q+1	$4K^2+1$, $-(4Q^2+4Q+1)$	$1+4Q^2+4Q$, $-(1+4K^2)$
2K+1	2Q	$4K^2+4K+2$, $-4Q^2$	$4Q^2$, $-(4K^2+4K+2)$

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ON NANO πgp-CLOSED SETS

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Abstaract — In this paper, new classes of sets called πgp-closed sets in nano topological spaces is introduced and its properties and studied of nano πgp-closed sets.

Keywords — *Nano π-closed set, nano πg-closed set, nano πgp-closed sets and nano gpr-closed set.*

1 Introduction

Thivagar et al. [4] introduced a nano topological space with respect to a subset X of an universe which is defined in terms of lower approximation and upper approximation and boundary region. The classical nano topological space is based on an equivalence relation on a set, but in some situation, equivalence relations are nor suitable for coping with granularity, instead the classical nano topology is extend to general binary relation based covering nano topological space

Bhuvaneswari et al. [3] introduced and investigated nano g-closed sets in nano topological spaces. Recently, Parvathy and Bhuvaneswari the notions of nano gpr-closed sets which are implied both that of nano rg-closed sets. In 2017, Rajasekaran et.al [7] introduced the notion of nano πgp-closed sets in nano topological spaces. new classes of sets called πgp-closed sets in nano topological spaces is introduced and its properties and studied of nano πgp-closed sets.

2 Preliminaries

Throughout this paper $(U, \tau_R(X))$ (or X) represent nano topological spaces on which no separation axioms are assumed unless otherwise mentioned. For a subset H of a

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space $(U, \tau_R(X))$, $Ncl(H)$ and $Nint(H)$ denote the nano closure of H and the nano interior of H respectively. We recall the following definitions which are useful in the sequel.

Definition 2.1. *[6] Let U be a non-empty finite set of objects called the universe and R be an equivalence relation on U named as the indiscernibility relation. Elements belonging to the same equivalence class are said to be indiscernible with one another. The pair (U, R) is said to be the approximation space. Let* $X \subseteq U$.

1. *The lower approximation of X with respect to R is the set of all objects, which can be for certain classified as X with respect to R and it is denoted by* $L_R(X)$. *That is,* $L_R(X) = \bigcup_{x \in U}\{R(x) : R(x) \subseteq X\}$, *where R(x) denotes the equivalence class determined by x.*

2. *The upper approximation of X with respect to R is the set of all objects, which can be possibly classified as X with respect to R and it is denoted by* $U_R(X)$. *That is,* $U_R(X) = \bigcup_{x \in U}\{R(x) : R(x) \cap X \neq \phi\}$.

3. *The boundary region of X with respect to R is the set of all objects, which can be classified neither as X nor as not - X with respect to R and it is denoted by* $B_R(X)$. *That is,* $B_R(X) = U_R(X) - L_R(X)$.

Property 2.2. *[4] If* (U, R) *is an approximation space and* $X, Y \subseteq U$; *then*

1. $L_R(X) \subseteq X \subseteq U_R(X)$;
2. $L_R(\phi) = U_R(\phi) = \phi$ *and* $L_R(U) = U_R(U) = U$;
3. $U_R(X \cup Y) = U_R(X) \cup U_R(Y)$;
4. $U_R(X \cap Y) \subseteq U_R(X) \cap U_R(Y)$;
5. $L_R(X \cup Y) \supseteq L_R(X) \cup L_R(Y)$;
6. $L_R(X \cap Y) \subseteq L_R(X) \cap L_R(Y)$;
7. $L_R(X) \subseteq L_R(Y)$ *and* $U_R(X) \subseteq U_R(Y)$ *whenever* $X \subseteq Y$;
8. $U_R(X^c) = [L_R(X)]^c$ *and* $L_R(X^c) = [U_R(X)]^c$;
9. $U_R U_R(X) = L_R U_R(X) = U_R(X)$;
10. $L_R L_R(X) = U_R L_R(X) = L_R(X)$.

Definition 2.3. *[4] Let U be the universe, R be an equivalence relation on U and* $\tau_R(X) = \{U, \phi, L_R(X), U_R(X), B_R(X)\}$ *where* $X \subseteq U$. *Then by the Property 2.2, R(X) satisfies the following axioms:*

1. U *and* $\phi \in \tau_R(X)$,
2. *The union of the elements of any sub collection of* $\tau_R(X)$ *is in* $\tau_R(X)$,
3. *The intersection of the elements of any finite subcollection of* $\tau_R(X)$ *is in* $\tau_R(X)$.

That is, $\tau_R(X)$ is a topology on U called the nano topology on U with respect to X. We call $(U, \tau_R(X))$ as the nano topological space. The elements of $\tau_R(X)$ are called as nano open sets and $[\tau_R(X)]^c$ is called as the dual nano topology of $[\tau_R(X)]$.

Remark 2.4. *[4] If $[\tau_R(X)]$ is the nano topology on U with respect to X, then the set $B = \{U, \phi, L_R(X), B_R(X)\}$ is the basis for $\tau_R(X)$.*

Definition 2.5. *[4] If $(U, \tau_R(X))$ is a nano topological space with respect to X and if $H \subseteq U$, then the nano interior of H is defined as the union of all nano open subsets of H and it is denoted by $Nint(H)$.*

That is, $Nint(H)$ is the largest nano open subset of H. The nano closure of H is defined as the intersection of all nano closed sets containing H and it is denoted by $Ncl(H)$.

That is, $Ncl(H)$ is the smallest nano closed set containing H.

Definition 2.6. *A subset H of a nano topological space $(U, \tau_R(X))$ is called*

1. *nano semi open [4] if $H \subseteq Ncl(Nint(H))$.*
2. *nano regular-open [4] if $H = Nint(Ncl(H))$.*
3. *nano π-open [1] if the finite union of nano regular-open sets.*
4. *nano pre-open [4] if $H \subseteq Nint(Ncl(H))$.*

The complements of the above mentioned sets is called their respective closed sets.

Definition 2.7. *A subset H of a nano topological space $(U, \tau_R(X))$ is called;*

1. *nano g-closed [2] if $Ncl(H) \subseteq G$, whenever $H \subseteq G$ and G is nano open.*
2. *nano rg-closed set [8] if $Ncl(H) \subseteq G$ whenever $H \subseteq G$ and G is nano regular-open.*
3. *nano πg-closed [7] if $Ncl(H) \subseteq G$, whenever $H \subseteq G$ and G is nano π-open.*
4. *nano gp-closed set [3] if $Npcl(H) \subseteq G$, whenever $H \subseteq G$ and G is nano open.*
5. *nano gpr-closed set [5] if $Npcl(H) \subseteq G$, whenever $H \subseteq G$ and G is nano regular open.*

3 On Nano πgp-closed Sets

Definition 3.1. *A subset H of a space $(U, \tau_R(X))$ is nano πgp-closed if $Npcl(H) \subseteq G$ whenever $H \subseteq G$ and G is nano π-open.*

The complement of nano πgp-open if $H^c = U - H$ is nano πgp-closed.

Example 3.2. *Let $U = \{a, b, c, d\}$ with $U/R = \{\{a, b\}, \{c\}, \{d\}\}$ and $X = \{a, d\}$. Then the nano topology $\tau_R(X) = \{\phi, \{d\}, \{a, b\}, \{a, b, d\}, U\}$.*

1. *then $\{a\}$ is nano πgp-closed set.*

2. *then* $\{b\}$ *is not nano* πgp*-closed set.*

Theorem 3.3. *In a space* $(U, \tau_R(X))$*,*

1. *If* H *is nano* π*-open and nano* πgp*-closed, then* H *is nano pre-closed and hence nano clopen.*

2. *If* H *is nano semi-open and nano* πgp*-closed, then* H *is nano* πg*-closed.*

Proof. 1. If H is nano π-open and nano πgp-closed, then $Npcl(H) \subseteq H$ and so H is nano pre-closed. Hence H is nano clopen, since nano π-open set is nano open and nano pre-closed open set is nano closed.

2. Let $H \subseteq G$ and G be nano π-open. Since H is nano πgp-closed, $Npcl(H) \subseteq G$. Since H is nano semi-open, $Npcl(H) = Ncl(H) \subseteq G$ and hence H is nano πg-closed.

Remark 3.4. *For a subset of a space* $(U, \tau_R(X))$*, we have the following implications:*

$$\begin{array}{ccccc} \textbf{\textit{nano closed}} & & & & \\ \Downarrow & & & & \\ \textbf{\textit{nano }}g\textbf{\textit{-closed}} & \Rightarrow & \textbf{\textit{nano }}\pi g\textbf{\textit{-closed}} & \Rightarrow & \textbf{\textit{nano }}rg\textbf{\textit{-closed}} \\ \Downarrow & & \Downarrow & & \Downarrow \\ \textbf{\textit{nano }}gp\textbf{\textit{-closed}} & \Rightarrow & \textbf{\textit{nano }}\pi gp\textbf{\textit{-closed}} & \Rightarrow & \textbf{\textit{nano }}gpr\textbf{\textit{-closed}} \end{array}$$

None of the above implications are reversible as shown by the following Examples.

Example 3.5. *Let* $U = \{a, b, c\}$ *with* $U/R = \{\{a, c\}, \{b\}\}$ *and* $X = \{c\}$*. Then the nano topology* $\tau_R(X) = \{\phi, \{a, c\}, U\}$*. Then* $\{a, c\}$ *is nano* πgp*-closed set but not nano gp-closed.*

Example 3.6. *In Example 3.2,*

1. *then* $\{a\}$ *is nano* πgp*-closed set but not nano* πg*-closed.*

2. *then* $\{a, d\}$ *is nano gpr-closed set but not nano* πgp*-closed.*

Lemma 3.7. *In a space* $(U, \tau_R(X))$*,*

1. *every nano open set is nano* πgp*-closed.*

2. *every nano closed set is nano* πgp*-closed.*

Remark 3.8. *The converses of statements in Lemma 3.7 are not necessarily true as seen from the following Examples.*

Example 3.9. *In Example 3.2,*

1. *then* $\{a, c, d\}$ *is nano* πgp*-closed set but not nano open.*

2. *then* $\{b, c, d\}$ *is nano* πgp*-closed set but not nano closed.*

Theorem 3.10. *Let* H *be nano* πgp*-closed. Then* $Npcl(H) - H$ *does not contain any non-empty nano* π*-closed set.*

Proof. Let K be a nano π-closed set such that $K \subseteq Npcl(H) - H$. Then $H \subseteq U - K$. Since H is nano πgp-closed and $U - K$ is nano π-open, $Npcl(H) \subseteq U - K$, i.e. $K \subseteq U - Npcl(H)$. Hence $K \subseteq Npcl(H) \cap (U - Npcl(H)) = \phi$. This shows that $K = \phi$.

Corollary 3.11. *Let H be nano πgp-closed. Then H is nano pre-closed $\iff$ $Npcl(H) - H$ is nano π-closed $\iff$ $H = Npcl(Nint(H))$.*

Theorem 3.12. *In a space $(U, \tau_R(X))$, the union of two nano πgp-closed sets is nano πgp-closed.*

Proof. Let $H \cup Q \subseteq G$, then $H \subseteq G$ and $Q \subseteq G$ where G is nano π-open. As H and Q are πgp-closed, $Ncl(H) \subseteq G$ and $Ncl(Q) \subseteq G$. Hence $Ncl(H \cup Q) = Ncl(H) \cup Ncl(Q) \subseteq G$.

Example 3.13. *In Example 3.2, then $H = \{a\}$ and $Q = \{c\}$ is nano πgp-closed. Clearly $H \cup Q = \{a, c\}$ is nano πgp-closed.*

Theorem 3.14. *In a space $(U, \tau_R(X))$, the intersection of two nano πgp-open sets are nano πgp-open.*

Proof. Obvious by Theorem 3.12.

Example 3.15. *In Example 3.2, then $H = \{a, d\}$ and $Q = \{b, d\}$ is nano πgp-open. Clearly $H \cap Q = \{d\}$ is nano πgp-open.*

Remark 3.16. *In a space $(U, \tau_R(X))$, the union of two nano πgp-closed sets but not nano πgp-closed.*

Example 3.17. *In Example 3.2, then $H = \{a\}$ and $Q = \{b\}$ is nano πgp-closed. Clearly $H \cup Q = \{a, b\}$ is but not nano πgp-closed.*

Remark 3.18. *In a space $(U, \tau_R(X))$, the intersection of two nano πgp-open sets but not nano πgp-open.*

Example 3.19. *In Example 3.2, then $H = \{a, c, d\}$ and $Q = \{b, c, d\}$ is nano πgp-open sets. Clearly $H \cup Q = \{c, d\}$ is but not nano πgp-open.*

Corollary 3.20. *If H ia nano πgp-closed and nano regular open and P is nano pre-closed in U, then $H \cap P$ is nano πgp-closed.*

Proof. Let $H \cap P \subseteq G$ and G is nano π-open in H. Since P is nano pre-closed in U, $H \cap P$ is nano pre-closed in H and so $Npcl_H(H \cap P) = H \cap P$. That is $Npcl_H(H \cap P) \subseteq G$. Then $H \cap P$ is nano πgp-closed in the nano πgp-closed and nano regular open set H and hence $H \cap P$ is nano πgp-closed in U.

Theorem 3.21. *If H is nano πgp-closed in U and $H \subseteq P \subseteq Npcl(H)$, then P is nano πgp-closed.*

Proof. Let $P \subseteq G$ and G be nano π-open in U. Since $H \subseteq G$ and H is nano πgp-closed, $Npcl(H) \subseteq G$ and then $Npcl(P) = Npcl(H) \subseteq G$. hence P is nano πgp-closed.

Theorem 3.22. *A set H of a space $(U, \tau_R(X))$ is called nano πgp-open $\iff$ if $K \subseteq Npint(H)$ whenever K is nano π-closed and $K \subseteq H$.*

Proof. Obvious.

Theorem 3.23. *A subset H of U is nano πgp-open $\iff$ $G = U$ whenever G is nano π-open and $Npint(H) \cup (U - H) \subseteq G$.*

Proof. Let G ba a nano π-open set and $Npint(H) \cup (U - H) \subseteq G$. Then $U - G \subseteq (U - Npint(H)) \cap H$, i.e., $(U - G) \subseteq Npcl(U - H) - (U - H)$. Since $U - H$ is nano πgp-closed, by Theorem 3.10, $U - G = \phi$ and hence $G = U$.

Conversely, let K be a nano π-open set of U and $K \subseteq H$. Since $Npint(H) \cup (U - H) = Nint(Ncl(H)) \cup (U - K)$ is nano π-open and $Npint(H) \cup (U - H) \subseteq Npint(H) \cup (U - K)$, by hypothesis, $Npint(H) \cup (U - K) = U$ and hence $K \subseteq Npint(H)$.

Theorem 3.24. *Let $H \subseteq V \subseteq U$ and V nano π-open and nano closed in U. If H is nano πgp-open in V, then H is nano πgp-open in U.*

Proof. Let K be any nano π-closed set and $K \subseteq H$. Since K is nano π-closed in V and H is nano πgp-open in V, $K \subseteq Npint_V(H)$ and then $K \subseteq Npint_U(H) \cap V$. Hence $K \subseteq Npint_U(H)$ and so H is nano πgp-open in U.

Theorem 3.25. *If H is nano πgp-open in U and $Npint(H) \subseteq P \subseteq H$, then P is nano πgp-open.*

Proof. Let $K \subseteq P$ and K be nano π-closed in U. Since H is nano πgp-open and $K \subseteq H$. $K \subseteq Npint(H)$ and then $K \subseteq Npint(P)$. Hence P is nano πgp-open.

Theorem 3.26. *A subset H of U is nano πgp-closed $\iff$ $Npcl(H) - H$ is nano πgp-open.*

Proof. Let $K \subseteq Npcl(H) - H$ and K be nano π-closed in U. Then by Theorem 3.10, $K = \phi$ and so $K \subseteq Npint(Npcl(H) - H)$. This shows that $Npcl(H) - H$ is nano πgp-open.

Conversely, let G be a nano π-open set of U and $H \subseteq G$. Then $Npcl(H) \cap (U - G) = Ncl(Nint(H)) \cap (U - G)$ is nano π-closed set contained in $Npcl(H) - H$. Since $Npcl(H) - H$ is nano πgp-open, by Theorem 3.22, $Npcl(H) \cap (U - G) \subseteq Npint(Npcl(H) - H = \phi)$ and hence $Npcl(H) \subseteq G$.

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New nano generalized classes of $\tau_R(X)$

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Abstract

In this paper, another generalized class of $\tau_R(X)$ called mildly nano g-closed sets is introduced and the notion of mildly nano g-open sets in nano topological spaces is introduced and studied. The relationships of mildly nano g-closed sets with various other sets are investigated.

AMS subject classification: 54A05, 54C10, 54B05.
Keywords: mildly nano g-closed set, nano g-closed set, nano pre-closed set, nano pre-open set.

1. Introduction

Lellis Thivagar et al [3] introduced a nano topological space with respect to a subset X of an universe which is defined in terms of lower approximation and upper approximation and boundary region. The classical nano topological space is based on an equivalence relation on a set, but in some situation, equivalence relations are nor suitable for coping with granularity, instead the classical nano topology is extend to general binary relation based covering nano topological space

The main aim of this paper is to introduce another nano generalized class called mildly nano g-open sets in nano topological spaces. Moreover, this nano generalized class of $\tau_R(X)$, generalize nano g-open sets and mildly nano g-open sets. The relationships of mildly nano g-closed sets with various other sets are discussed.

2. Preliminaries

Throughout this paper $(U, \tau_R(X))$ (or X) represent nano topological spaces on which no separation axioms are assumed unless otherwise mentioned. For a subset H of a space $(U, \tau_R(X))$, $Ncl(H)$ and $Nint(H)$ denote the nano closure of H and the nano interior of H respectively. We recall the following definitions which are useful in the sequel.

Definition 2.1. [5] Let U be a non-empty finite set of objects called the universe and R be an equivalence relation on U named as the indiscernibility relation. Elements belonging to the same equivalence class are said to be indiscernible with one another. The pair (U, R) is said to be the approximation space. Let $X \subseteq U$.

1. The lower approximation of X with respect to R is the set of all objects, which can be for certain classified as X with respect to R and it is denoted by $L_R(X)$. That is, $L_R(X) = \bigcup_{x \in U} \{R(x) : R(x) \subseteq X\}$, where R(x) denotes the equivalence class determined by x.

2. The upper approximation of X with respect to R is the set of all objects, which can be possibly classified as X with respect to R and it is denoted by $U_R(X)$. That is, $U_R(X) = \bigcup_{x \in U} \{R(x) : R(x) \cap X \neq \phi\}$.

3. The boundary region of X with respect to R is the set of all objects, which can be classified neither as X nor as not - X with respect to R and it is denoted by $B_R(X)$. That is, $B_R(X) = U_R(X) - L_R(X)$.

Property 2.2. [3] If (U, R) is an approximation space and $X, Y \subseteq U$; then

1. $L_R(X) \subseteq X \subseteq U_R(X)$;

2. $L_R(\phi) = U_R(\phi) = \phi$ and $L_R(U) = U_R(U) = U$;

3. $U_R(X \cup Y) = U_R(X) \cup U_R(Y)$;
4. $U_R(X \cap Y) \subseteq U_R(X) \cap U_R(Y)$;
5. $L_R(X \cup Y) \supseteq L_R(X) \cup L_R(Y)$;
6. $L_R(X \cap Y) \subseteq L_R(X) \cap L_R(Y)$;
7. $L_R(X) \subseteq L_R(Y)$ and $U_R(X) \subseteq U_R(Y)$ whenever $X \subseteq Y$;
8. $U_R(X^c) = [L_R(X)]^c$ and $L_R(X^c) = [U_R(X)]^c$;
9. $U_R U_R(X) = L_R U_R(X) = U_R(X)$;
10. $L_R L_R(X) = U_R L_R(X) = L_R(X)$.

Definition 2.3. [3] Let U be the universe, R be an equivalence relation on U and $\tau_R(X) = \{U, \phi, L_R(X), U_R(X), B_R(X)\}$ where $X \subseteq U$. Then by the Property 2.2, R(X) satisfies the following axioms:

1. U and $\phi \in \tau_R(X)$,
2. The union of the elements of any sub collection of $\tau_R(X)$ is in $\tau_R(X)$,
3. The intersection of the elements of any finite subcollection of $\tau_R(X)$ is in $\tau_R(X)$.

That is, $\tau_R(X)$ is a topology on U called the nano topology on U with respect to X. We call $(U, \tau_R(X))$ as the nano topological space. The elements of $\tau_R(X)$ are called as nano open sets and $[\tau_R(X)]^c$ is called as the dual nano topology of $[\tau_R(X)]$.

Remark 2.4. [3] If $[\tau_R(X)]$ is the nano topology on U with respect to X, then the set $B = \{U, \phi, L_R(X), B_R(X)\}$ is the basis for $\tau_R(X)$.

Definition 2.5. [3] If $(U, \tau_R(X))$ is a nano topological space with respect to U and if $H \subseteq U$, then the nano interior of H is defined as the union of all nano open subsets of A and it is denoted by $Nint(H)$.

That is, $Nint(H)$ is the largest nano open subset of H. The nano closure of H is defined as the intersection of all nano closed sets containing H and it is denoted by $Ncl(H)$.

That is, $Ncl(H)$ is the smallest nano closed set containing H.

Definition 2.6. [3] A subset H of a nano topological space $(U, \tau_R(X))$ is called;

1. nano pre-open set if $H \subseteq Nint(Ncl(H))$.

   The complement of nano pre-open set is called nano pre-closed.

2. nano regular open set if $H = Nint(Ncl(H))$.

   The complement of nano regular-open set is called nano regular-closed.

Definition 2.7. [4] Let $(U, \tau_R(X))$ be a nano topological space and let $H \subseteq U$, then H is called nano nowhere dense if $Nint(Ncl(H)) = \phi$.

Definition 2.8. [1] A subset H of a nano topological space $(U, \tau_R(X))$ is called nano g-closed if $Ncl(H) \subseteq G$, whenever $H \subseteq G$ and G is nano open.

Theorem 2.9. [2] In any nano topological space, every nano regular-closed set is nano closed but not conversely.

3. New nano generalized classes of $\tau_R(X)$

Definition 3.1. In a nano topological space $(U, \tau_R(X))$, a subset H of U is said to be

1. weakly nano g-closed if $Ncl(Nint(H)) \subseteq G$ whenever $H \subseteq G$ and G is nano open in U;
2. mildly nano g-closed if $Ncl(Nint(H)) \subseteq G$ whenever $H \subseteq G$ and G is nano g-open in U;
3. strongly nano g-closed if $Ncl(H) \subseteq G$ whenever $H \subseteq G$ and G is nano g-open in U.

The complements of the above mentioned sets are called their respective nano open sets.

Example 3.2. Let $U = \{a, b, c, d\}$ with $U/R = \{\{a\}, \{c\}, \{b, d\}\}$ and $X = \{a, b\}$. Then the nano topology $\tau_R(X) = \{\phi, \{a\}, \{b, d\}, \{a, b, d\}, U\}$. Then $\{c\}$ is weakly nano g-closed, mildly nano g-closed and strongly nano g-closed.

Theorem 3.3. In a nano topological space $(U, \tau_R(X))$, a subset H of U is mildly nano g-closed $\Leftrightarrow Ncl(Nint(H)) \subseteq H$.

Proof. $\Rightarrow$ If $Ncl(Nint(H)) \nsubseteq H$, there exists $x \in U$ such that $x \in Ncl(Nint(H)) - H$. Then $x \in Ncl(Nint(H)) - H \subseteq U - H$ and so $H \subseteq U - \{x\}$ where $U - \{x\}$ is nano g-open being nano open. Thus $H \subseteq U - \{x\}$ where $U - \{x\}$ is nano g-open. But $Ncl(Nint(H)) \nsubseteq U - \{x\}$ since $x \in Ncl(Nint(H))$. This implies that H is not mildly nano g-closed which proves the necessary part.

$\Leftarrow$ Let $Ncl(Nint(H)) \subseteq H$ and G be any nano g-open subset such that $H \subseteq G$. Then $Ncl(Nint(H)) \subseteq H \subseteq G$. This implies that H is mildly nano g-closed which proves the sufficiency part. ■

Theorem 3.4. In a nano topological space $(U, \tau_R(X))$, a subset H of U is weakly nano g-closed $\Leftrightarrow Ncl(Nint(H)) \subseteq H$.

Proof. $\Rightarrow$ If $Ncl(Nint(H)) \nsubseteq H$, there exists $x \in U$ such that $x \in Ncl(Nint(H)) - H$. Then $x \in Ncl(Nint(H)) - H \subseteq U - H$ and so $H \subseteq U - \{x\}$ where $U - \{x\}$ is nano open. Thus $H \subseteq U - \{x\}$ where $U - \{x\}$ is nano open. But $Ncl(Nint(H)) \nsubseteq U - \{x\}$

since $x \in Ncl(Nint(H))$. This implies that H is not weakly nano g-closed which proves the necessary part.

$\Leftarrow$ Let $Ncl(Nint(H)) \subseteq H$ and G be any nano open set such that $H \subseteq G$. Then $Ncl(Nint(H)) \subseteq H \subseteq G$. This implies that H is weakly nano g-closed which proves the sufficiency part. ■

Theorem 3.5. In a nano topological space $(U, \tau_R(X))$, a subset H of U is mildly nano g-closed $\Leftrightarrow$ H is weakly nano g-closed.

Proof. Proof follows by Theorem 3.3 and Theorem 3.4. ■

Theorem 3.6. In a nano topological space $(U, \tau_R(X))$, a subset H of U is strongly nano g-closed $\Leftrightarrow$ $Ncl(H) \subseteq H$.

Proof. $\Rightarrow$ If $Ncl(H) \nsubseteq H$, there exists $x \in U$ such that $x \in Ncl(H) - H$. Then $x \in Ncl(H) - H \subseteq U - H$ and so $H \subseteq U - \{x\}$ where $U - \{x\}$ is nano g-open being nano open. Thus $H \subseteq U - \{x\}$ where $U - \{x\}$ is nano g-open. But $Ncl(H) \nsubseteq U - \{x\}$ since $x \in Ncl(H)$. This implies that H is not strongly nano g-closed which proves the necessary part.

$\Leftarrow$ Let $Ncl(H) \subseteq H$ and G be any nano g-open set such that $H \subseteq G$. Then $Ncl(H) \subseteq H \subseteq G$. This implies that H is strongly nano g-closed which proves the sufficient part. ■

Theorem 3.7. In a nano topological space $(U, \tau_R(X))$, a subset H of U is nano g-closed $\Leftrightarrow$ $Ncl(H) \subseteq H$.

Proof. $\Rightarrow$ If $Ncl(H) \nsubseteq H$, there exists $x \in U$ such that $x \in Ncl(H) - H$. Then $x \in Ncl(H) - H \subseteq U - H$ and so $H \subseteq U - \{x\}$ where $U - \{x\}$ is nano open. Thus $H \subseteq U - \{x\}$ where $U - \{x\}$ is nano open. But $Ncl(H) \nsubseteq U - \{x\}$ since $x \in Ncl(H)$. This implies that H is not nano g-closed which proves the necessary part.

$\Leftarrow$ Let $Ncl(H) \subseteq H$ and G be any nano open set such that $H \subseteq G$. Then $Ncl(H) \subseteq H \subseteq G$. This implies that H is nano g-closed which proves the sufficient part. ■

Theorem 3.8. In a nano topological space $(U, \tau_R(X))$, a subset H of U is strongly nano g-closed $\Leftrightarrow$ H is nano g-closed.

Proof. Proof follows from Theorem 3.6 and Theorem 3.7. ■

Proposition 3.9. In a nano topological space $(U, \tau_R(X))$,

1. Every nano g-closed set is weakly nano g-closed.

2. Every strongly nano g-closed set is mildly nano g-closed.

Proof. Obvious. ■

Remark 3.10. The converses of Proposition 3.9 are not true in general as shown in the following Example.

Example 3.11. In Example 3.2,

1. then $\{b\}$ is weakly nano g-closed set but not nano g-closed.
2. then $\{d\}$ is mildly nano g-closed set but not strongly nano g-closed.

Remark 3.12. In a nano topological space $(U, \tau_R(X))$, the following relations hold for a subset H of U.

$$\begin{array}{ccc} \text{strongly nano } g\text{-closed} & \longleftrightarrow & \text{nano } g\text{-closed} \\ \downarrow & & \downarrow \\ \text{mildly nano } g\text{-closed} & \longleftrightarrow & \text{weakly nano } g\text{-closed} \end{array}$$

Where $A \longleftrightarrow B$ means A implies and is implied by B and $A \rightarrow B$ means A implies B but not conversely.

Theorem 3.13. In a nano topological space $(U, \tau_R(X))$, for a subset H of U, the following properties are equivalent.

1. H is mildly nano g-closed;
2. $Ncl(Nint(H))\backslash H = \phi$;
3. $Ncl(Nint(H)) \subseteq H$;
4. H is nano pre-closed.

Proof. (1) $\Leftrightarrow$ (2) H is mildly nano g-closed $\Leftrightarrow$ $Ncl(Nint(H)) \subseteq H$ by Theorem 3.3 $\Leftrightarrow$ $Ncl(Nint(H))\backslash H = \phi$.

(2) $\Leftrightarrow$ (3) $Ncl(Nint(H))\backslash H = \phi \Leftrightarrow Ncl(Nint(H)) \subseteq H$.

(3) $\Leftrightarrow$ (4) $Ncl(Nint(H)) \subseteq H \Leftrightarrow H$ is nano pre-closed by (1) of Definition 3.1. ■

Theorem 3.14. In a nano topological space $(U, \tau_R(X))$, if H is mildly nano g-closed, then $H \cup (U - Ncl(Nint(H)))$ is mildly nano g-closed.

Proof. Since H is mildly nano g-closed, $Ncl(Nint(H)) \subseteq H$ by Theorem 3.3. Then $U - H \subseteq U - Ncl(Nint(H))$ and $H \cup (U - H) \subseteq H \cup (U - Ncl(Nint(H)))$. Thus $U \subseteq H \cup (U - Ncl(Nint(H)))$ and so $H \cup (U - Ncl(Nint(H))) = U$. Hence $H \cup (U - Ncl(Nint(H)))$ is mildly nano g-closed. ■

Theorem 3.15. In a nano topological space $(U, \tau_R(X))$, the following properties are equivalent:

1. H is a nano closed set and an nano open set,

2. H is a nano regular-closed set and an nano open set,

3. H is a mildly nano g-closed set and an nano open set.

Proof. (1) $\Rightarrow$ (2): Since H is nano closed and nano open, $H = Ncl(H)$ and $H = Nint(H)$ implies $H = Ncl(Nint(H))$ and $H = Nint(H)$. Hence H is nano regular-closed and nano open.

(2) $\Rightarrow$ (3): Since H is nano regular-closed and nano open, $H = Ncl(Nint(H))$ and $H = Nint(H)$. Since $H = Ncl(Nint(H))$, $Ncl(Nint(H)) \subseteq H$. By Theorem 3.3, H is mildly nano g-closed and nano open.

(3) $\Rightarrow$ (1): Since H is mildly nano g-closed, $Ncl(Nint(H)) \subseteq H$ by Theorem 3.3. Again H is nano open implies $Ncl(H) \subseteq H$. Thus H is nano closed and nano open. ■

Proposition 3.16. In a nano topological space $(U, \tau_R(X))$, every nano closed set is mildly nano g-closed.

Proof. Let G be any nano g-open subset of U such that $H \subseteq G$. Then $cl(int(H)) \subseteq cl(H) = H \subseteq G$ and hence H is mildly nano g-closed. This shows that H is nano closed $\Rightarrow$ mildly nano g-closed. ■

Remark 3.17. The converse of Proposition 3.16 is not true in general as shown in the following example.

Example 3.18. In Example 3.2, then $\{b\}$ is mildly nano g-closed set but not nano closed.

Theorem 3.19. In a nano topological space $(U, \tau_R(X))$, if H is mildly nano g-closed and G is a subset such that $H \subseteq G \subseteq Ncl(Nint(H))$, then G is mildly nano g-closed.

Proof. Since H is mildly nano g-closed, $Ncl(Nint(H)) \subseteq H$ by (3) of Theorem 3.13. Thus by assumption, $H \subseteq G \subseteq Ncl(Nint(H)) \subseteq H$. Then $H = G$ and so G is mildly nano g-closed. ■

Corollary 3.20. In a nano topological space $(U, \tau_R(X))$, if H is a mildly nano g-closed set and an nano open set, then $Ncl(H)$ is mildly nano g-closed.

Proof. Since H is nano open in U, $H \subseteq Ncl(H) = Ncl(Nint(H))$. H is mildly nano g-closed implies $Ncl(H)$ is mildly nano g-closed by Theorem 3.19. ■

Theorem 3.21. In a nano topological space $(U, \tau_R(X))$, a nano nowhere dense subset is mildly nano g-closed.

Proof. If H is a nano nowhere dense subset in U then $Nint(Ncl(H)) = \phi$. Since $Nint(H) \subseteq Nint(Ncl(H))$, $Nint(H) = \phi$. Hence $Ncl(Nint(H)) = Ncl(\phi) = \phi \subseteq H$. Thus, H is mildly nano g-closed in $(U, \tau_R(X))$ by Theorem 3.3. ■

Remark 3.22. The converse of Theorem 3.21 is not true in general as shown in the following Example.

Example 3.23. In Example 3.2, then $\{b\}$ is mildly nano g-closed set but not nano nowhere dense.

Remark 3.24. In a nano topological space $(U, \tau_R(X))$, the intersection of two mildly nano g-closed subsets is mildly nano g-closed.

Proof. Let P and Q be mildly nano g-closed subsets in $(U, \tau_R(X))$. Then $Ncl(Nint(P)) \subseteq P$ and $Ncl(Nint(Q)) \subseteq Q$ by Theorem 3.3. Also $Ncl[Nint(P \cap Q)] = Ncl[Nint(P) \cap Nint(Q)] \subseteq Ncl(Nint(P)) \cap Ncl(Nint(Q)) \subseteq P \cap Q$. This implies that $P \cap Q$ is mildly nano g-closed by Theorem 3.3. ■

Remark 3.25. In a nano topological space $(U, \tau_R(X))$, the union of two mildly nano g-closed subsets need not be mildly nano g-closed.

Example 3.26. Let $U = \{a, b, c\}$ with $U/R = \{\{a\}, \{b, c\}\}$ and $X = \{b, c\}$. Then the nano topology $\tau_R(X) = \{\phi, \{b, c\}, U\}$. Then $\{\phi, \{a\}, \{b\}, \{c\}, \{a, b\}, \{a, c\}, U\}$ is mildly nano g-closed set. Then $P = \{b\}$ and $Q = \{c\}$ is mildly nano g-closed sets. Hence $P \cup Q = \{b, c\}$ is not mildly nano g-closed.

Theorem 3.27. In a nano topological space $(U, \tau_R(X))$, a subset H is mildly nano g-open if and only if $H \subseteq Nint(Ncl(H))$.

Proof. H is mildly nano g-open $\Leftrightarrow$ $U \backslash H$ is mildly nano g-closed $\Leftrightarrow$ $U \backslash H$ is nano pre-closed by (4) of Theorem 3.13 $\Leftrightarrow$ H is nano pre-open $\Leftrightarrow$ $G \subseteq Nint(Ncl(H))$. ■

Theorem 3.28. In a nano topological space $(U, \tau_R(X))$, if the subset H is mildly nano g-closed, then $Ncl(Nint(H)) \backslash H$ is mildly nano g-open in $(U, \tau_R(X))$.

Proof. Since H is mildly nano g-closed, $Ncl(Nint(H)) \backslash H = \phi$ by (2) of Theorem 3.13. Thus $Ncl(Nint(H)) \backslash H$ is mildly nano g-open in $(U, \tau_R(X))$. ■

Theorem 3.29. In a nano topological space $(U, \tau_R(X))$, if H is mildly nano g-open, then $Nint(Ncl(H)) \cup (U - H) = U$.

Proof. Since H is mildly nano g-open, $H \subseteq Nint(Ncl(H))$ by Theorem 3.27. So $(U-H) \cup H \subseteq (U-H) \cup Nint(Ncl(H))$ which implies $U = (U-H) \cup Nint(Ncl(H))$. ■

Theorem 3.30. In a nano topological space $(U, \tau_R(X))$, if H is mildly nano g-open and $Nint(Ncl(H)) \subseteq G \subseteq H$, then G is mildly nano g-open.

Proof. Since H is mildly nano g-open, $H \subseteq Nint(Ncl(H))$ by Theorem 3.27. By assumption $Nint(Ncl(H)) \subseteq G \subseteq H$. This implies $H \subseteq Nint(Ncl(H)) \subseteq G \subseteq H$. Thus $H = G$ and so G is mildly nano g-open. ■

Corollary 3.31. In a nano topological space $(U, \tau_R(X))$, if H is a mildly nano g-open set and a nano closed set, then $Nint(H)$ is mildly nano g-open.

Proof. If H is a mildly nano g-open set and a nano closed set in $(U, \tau_R(X))$, then $Nint(Ncl(H)) = Nint(H) \subseteq Nint(H) \subseteq H$. Thus, by Theorem 3.30, $Nint(H)$ is mildly nano g-open in $(U, \tau_R(X))$. ■

4. Nano $\mathcal{O}$-set

Definition 4.1. A subset H of a nano topological space $(U, \tau_R(X))$ is called a nano $\mathcal{O}$-set if $H = P \cup Q$ where P is nano g-closed and Q is nano pre-open.

Example 4.2. In Example 3.2, then $\{\phi, \{a, c\}, \{b, c\}, \{c, d\}, \{a, b, c\}, \{a, c, d\}, \{b, c, d\}, U\}$ is nano $\mathcal{O}$-set.

Proposition 4.3. Every nano pre-open (resp. nano g-closed) set is a nano $\mathcal{O}$-set.

Remark 4.4. The separate converses of Proposition 4.3 are not true in general as shown in the following Example.

Example 4.5. In Example 3.2, then $\{a, c\}$ is nano $\mathcal{O}$-set but not nano pre-open.

Remark 4.6. The following example shows that the concepts of nano pre-open and nano g-closed are independent of each other.

Example 4.7. In Example 3.2,

1. then $\{c\}$ is nano g-closed set but not nano pre-open.
2. then $\{b\}$ is nano pre-open set but not nano g-closed.

Theorem 4.8. Let $(U, \tau_R(X))$ be a nano topological space and $H \subseteq U$. Then H is mildly nano g-open if and only if $F \subseteq Nint(Ncl(H))$ whenever F is nano g-closed and $F \subseteq H$.

Proof. Suppose H is mildly nano g-open. If F is nano g-closed and $F \subseteq H$, then $U - H \subseteq U - F$ and so $Ncl(Nint(U - H)) \subseteq U - F$. Therefore $F \subseteq U - Ncl(Nint(U - H)) = Nint(Ncl(H))$.

Conversely, the condition holds. Let G be an nano g-open set such that $U - H \subseteq G$. Then $U - G \subseteq H$ and so $U - G \subseteq Nint(Ncl(H))$. Therefore $Ncl(Nint(U - H)) \subseteq G$. Thus $U - H$ is mildly nano g-closed and so H is mildly nano g-open. ■

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EFFECT OF B.K.S. IYENGAR YOGA ON SELECTED PHYSIOLOGICAL AND PSYCHOLOGICAL VARIABLES AMONG COLLEGE GIRLS

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Abstract:

The purpose of the study was to find out the effect of B.K.S. Iyengar yoga on selected physiological and psychological variables among college girls. The investigator randomly selected 60 girls from National College, Tiruchirapalli, Tamilnadu. The age groups of subjects were between 18 and 23 years. They were divided into two equal groups as experimental group (B.K.S. Lyengar yoga) and control group based on their initial score in physiological and psychological variables and each groups consisting 30 subjects. Experimental group are underwent the training for12 weeks, 5 days a week for maximum of one hour in morning. The control group was kept in active rest. The pre test and post test were conducted before and after the training for all three groups. The selected physiological variables, pulse rate and blood pressure were measured by Radial Pulse and Sphygmomanometer respectively and in psychological variables, stress was measured by standardized stress questionnaire constructed by Dr. Latha Satish (1997)consisting of 52 questions and self- confidence was measured by self- confidence questionnaire developed by Rekha Agnihotri (1987) consisting of 52 questions. The collected data were statistically analyzed by using Analysis of covariance (ANCOVA) to determine the significant difference and tested at 0.05 level of significance. The result of the study shows that the experimental group had significant improvement in all the selected physiological and psychological variables than the control group among college girls.

Keywords: Physical Activity Program, B.K.S. Lyengar Yoga, Physiological & Psychological Variables.

Introduction:

Lyengar Yoga is a form of Hatha Yoga in which there is a focus on the structural alignment of the physical body through the development of asanas. Through the practice of a system of asanas, it aims to unite the body, mind and spirit for health and well-being. The discipline is considered by its practitioners to be a powerful tool to relieve the stresses of modern-day life, in turn helping to promote total physical and spiritual well-being.

B.K.S. Lyengar was the founder of Lyengar Yoga and is considered one of the foremost yoga teachers in the world. In his book, *Light on Life*, he explains how physical weaknesses led him to take up the ancient practice of yoga. He used props such as ropes, belts and bricks to help even the elderly, weak, and inflexible experience yoga's therapeutic effects, often allowing yoga student to hold positions for longer periods than might be possible without them.

Lyengar yoga appeals to a huge range of people, of all fitness levels, and is particularly well-suited to yoga students who have a meticulous approach to yoga and an interest in the body's anatomy. It is excellent for people with back problems and for people who suffer from stress, two conditions that often go together, but in reality anyone can benefit from it.

Furthermore, the poses in Lyengar yoga are done with great attention to detail. As a result, the increased body awareness developed allows one to become more aware of posture and its direct effects on psychological states, and to carry this awareness off the yoga mat into everyday life. Practiced regularly, Lyengar yoga is a wonderful, natural way to cope with physical, mental, and emotional stress.

In recent years, researchers have started measuring some of yoga's effects on health, and -not surprisingly- the results are fascinating.

Objectives of Study:

- To determine the physical, physiological and psychological effects of practicing Lyengar Yoga.
- To determine the reason and motivation for practitioners to continue Lyengar Yoga practice.
- To evaluate the perception of all sorts of 'stress'.
- To compare the personality characteristics of Lyengar Yoga practitioners with the no practitioners.

Methodology:

To achieve the purposed of the study, the investigator randomly selected 60 girls from National College, Tiruchirapalli, Tamilnadu. The age groups of subjects were between 18 and 23 years. They were divided into two equal groups as experimental group and control group based on their initial score in physiological and psychological variables and each groups consisting 30 subjects. Experimental group was underwent the training programmed for 12 weeks, 5 days a week for maximum of one hour in morning. The control group was kept in active rest. The pre test and post test were conducted before and after the training for all two groups.

Physiological Variables:

SL.NO	VARIABLE	EQUIPMENT/TEST
1	Systolic Blood Pressure	Sphygmomanometer
2	Diastolic Blood Pressure	Sphygmomanometer
3	Resting Pulse Rate	Radial Pulse

Psychological Variables

SL.NO.	VARIABLES	TEST & MEASUREMENT
1	**Stress**	questionnaire constructed by Dr. Latha Satish (1997)
2	**Self- confidence**	questionnaire developed by Rekha Agnihotri (1987)

The collected data were statistically analyzed by using Analysis of covariance (ANCOVA) to determine the significant difference and tested at 0.05 level of significance.

Results and Discussion:

The analysis of covariance on the data obtained on physiological and psychological variables of experimental and control groups have been analyzed and tabulated in Table I to V

TABLE NO-I

ANALYSIS OF COVARIANCE ON SYSTOLIC BLOOD PRESSURE BETWEEN CONTROL AND EXPERIMENTAL GROUPS

TEST	YOGA GROUP	CONTROL GROUP	SV	SS	DF	MS	F	TV 0.05
Pre test	146.53	142.47	**Between**	124.03	1	124.033	0.35	4.01
			Within	9917.47	58	354.20		
Post test	126.80	147.00	**Between**	3060.30	1	3060.30	11.12*	4.01
			Within	7704.40	58	275.16		
Adjusted	125.52	148.28	**Between**	3835.41	1	3835.41	27.32*	4.01
			within	3790.06	57	140.37		

*Significant at 0.05 level of confidence.

Table I shows that the analysis of covariance on systolic blood pressure and pre test means of experimental group and control group are 146.53 and 142.47 respectively. The obtained 'F' ratio is 0.35. Since the obtained 'F' ratio is lower than the Table value of 4.01, it is indicated that there was no significant at 0.05 level of confidence with the df 1 and 58 is 4.01. The post – test means of Experimental group and Control group are 126.80 and 147.00 respectively. The obtained 'F' value is 11.12. Since this is higher than the Table value 4.01 and indicated that the difference among the groups on post test means was significant at 0.05 level of confidence with the df 1 and 58 is 4.01.

The adjusted post – test means of Experimental group and Control group, are 125.52 and 148.28 respectively. The obtained 'F' ratio is 27.32. Since this is higher than the Table value of 4.01, and indicated that the difference among the groups on adjusted post means is significant at 0.05 level of confidence with the df 1 and 58 is 4.01.

TABLE- II
ANALYSIS OF COVARIANCE ON DIASTOLIC BLOOD PRESSURE BETWEEN CONTROL AND EXPERIMENTAL GROUPS

TEST	YOGA GROUP	CONTROL GROUP	SV	SS	DF	MS	F	TV 0.05
Pre test	84.27	83.60	Between	3.33	1	3.333	0.06	4.01
			Within	1688.53	58	60.30		
Post test	74.93	84.27	Between	653.33	1	653.33	11.11*	4.01
			Within	1645.87	58	58.78		
Adjusted	74.74	84.46	Between	706.19	1	706.19	17.37*	4.01
			within	1097.94	57	40.66		

*Significant at 0.05 level of confidence.

Table II shows that the analysis of covariance on diastolic blood pressure and pre test means of experimental group and control group are 84.27 and 83.60 respectively. The obtained 'F' ratio is 0.06. Since the obtained 'F' ratio is lower than the Table value of 4.01, it is indicated that there was no significant at 0.05 level of confidence with the df 1 and 58 is 4.01. The post – test means of Experimental group and Control group are 74.93 and 84.27 respectively. The obtained 'F' value is 11.11. Since this is higher than the Table value 4.01 and indicated that the difference among the groups on post test means was significant at 0.05 level of confidence with the df 1 and 58 is 4.01. The adjusted post – test means of Experimental group and Control group, are 74.74 and 84.46 respectively. The obtained 'F' ratio is 17.37.

TABLE- III
ANALYSIS OF COVARIANCE ON RESTING PULSE RATE BETWEEN CONTROL AND EXPERIMENTAL GROUPS

TEST	YOGA GROUP	CONTROL GROUP	SV	SS	DF	MS	F	TV 0.05
Pre test	83.60	82.00	Between	19.20	1	19.200	0.29	4.01
			Within	1835.60	58	65.56		
Post test	74.27	83.60	Between	653.33	1	65.33	13.04*	4.01
			Within	1402.53	58	50.09		
Adjusted	73.65	84.22	Between	828.69	1	828.69	71.63*	4.01
			within	312.38	57	11.57		

*Significant at 0.05 level of confidence.

Table III shows that the analysis of covariance on resting pulse rate and pre test means of experimental group and control group are 83.60 and 82.00 respectively. The obtained 'F' ratio is 0.29. Since the obtained 'F' ratio is lower than the Table value of 4.01, it is indicated that there was no significant at 0.05 level of confidence with the df 1 and 58 is 4.01. The post – test means of Experimental group and Control group are 74.27 and 83.60 respectively. The obtained 'F' value is 13.04. Since this is higher than the Table value 4.01 and indicated that the difference among the groups on post test means was significant at 0.05 level of confidence with the df 1 and 58 is 4.01. The adjusted post – test means of Experimental group and Control group, are 73.65 and 84.22 respectively. The obtained 'F' ratio is 71.63. Since this is higher than the Table value of 4.01, and indicated that the difference among the groups on adjusted post means is significant at 0.05 level of confidence with the df 1 and 58 is 4.01.

TABLE- IV
ANALYSIS OF COVARIANCE ON STRESS BETWEEN CONTROL AND EXPERIMENTAL GROUPS

TEST	YOGA GROUP	CONTROL GROUP	SV	SS	DF	MS	F	TV 0.05
Pre test	82.83	79.267	Between	190.82	1	190.817	0.26	4.01
			Within	42740.03	58	736.90		
Post test	67.13	83.17	Between	3856.02	1	3856.02	6.05*	4.01
			Within	36965.63	58	637.34		
Adjusted	65.52	84.78	Between	5533.75	1	5533.75	143.28*	4.01
			within	2201.509	57	38.62		

*Significant at 0.05 level of confidence.

Table IV shows that the analysis of covariance on stress between and pre test means of experimental group and control group are 82.83 and 79.26 respectively. The obtained 'F' ratio is 0.26. Since the obtained 'F' ratio is lower than the Table value of 4.01, it is indicated that there was no significant at 0.05 level of confidence with the df 1 and 58 is 4.01.

The post – test means of Experimental group and Control group are 67.13 and 83.17 respectively. The obtained 'F' value is 6.05. Since this is higher than the Table value 4.01 and indicated that the difference among the groups on post test means was significant at 0.05 level of confidence with the df 1 and 58 is 4.01. The adjusted post – test means of Experimental group and Control group, are 65.52 and 84.78 respectively. The obtained 'F' ratio is 143.28. Since this is higher than the Table value of 4.01, and indicated that the difference among the groups on adjusted post means is significant at 0.05 level of confidence with the df 1 and 58 is 4.01.

TABLE- V

ANALYSIS OF COVARIANCE ON SELF CONFIDENCE BETWEEN CONTROL AND EXPERIMENTAL GROUPS

TEST	YOGA GROUP	CONTROL GROUP	SV	SS	DF	MS	F	TV 0.05
Pre test	29.53	28.5	**Between**	16.02	1	16.017	0.12	4.01
			Within	7864.97	58	135.60		
Post test	21.93	29.07	**Between**	763.27	1	763.27	7.27*	4.01
			Within	6091.73	58	105.03		
Adjusted	21.52	29.48	**Between**	950.16	1	950.16	55.67*	4.01
			within	972.847	57	17.07		

Significant at 0.05 level (the table value required for significance at 0.05 level with df 1 and 58 is 4.01)

Table V shows that the analysis of covariance on self confidence and pre test means of experimental group and control group are 29.53 and 28.5 respectively. The obtained 'F' ratio is 0.12. Since the obtained 'F' ratio is lower than the Table value of 4.01, it is indicated that there was no significant at 0.05 level of confidence with the df 1 and 58 is 4.01.

The post – test means of Experimental group and Control group are 21.93 and 29.07 respectively. The obtained 'F' value is 7.27. Since this is higher than the Table value 4.01 and indicated that the difference among the groups on post test means was significant at 0.05 level of confidence with the df 1 and 58 is 4.01.

The adjusted post – test means of Experimental group and Control group, are 21.52 and 29.48 respectively. The obtained 'F' ratio is 143.28. Since this is higher than the Table value of 4.01, and indicated that the difference among the groups on adjusted post means is significant at 0.05 level of confidence with the df 1 and 58 is 4.01.

All the above tables shows the systolic blood pressure, diastolic blood pressure, resting pulse rate, stress and self confidence among the experimental and control groups before and after scores of B.K.S. Lyengar yoga practices. There was a significance changes in all the variables. The pre test means of all the variables does not show any significance difference. After the B.K.S. Lyengar yoga practices the experimental group shows significant changed in all physiological and psychological variables. Whereas the control group shows no significant difference in all the above mentioned variables.

Conclusions:

- It was conclude that due to 12 weeks yogic practices improved the physiological and psychological variables among college girls.
- The physiological variable of systolic blood pressure was significantly reduced due to influence of 12 weeks training of yogic practices group compared to control group.
- The physiological variable of diastolic blood pressure was significantly reduced due to influence of 12 weeks training of yogic practices group compared to control group.
- The physiological variable of resting heart rate was significantly reduced due to influence of 12 weeks training of yogic practices group compared to control group.
- The psychological variable of stress was significantly reduced due to influence of 12 weeks training of yogic practices group compared to control group.
- The physiological variable of self confidence was significantly reduced due to influence of 12 weeks training of yogic practices group compared to control group.

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Synthesis, growth and characterization of L-Phenylalaninium methanesulfonate nonlinear optical single crystal

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ABSTRACT

The titled compound, L-Phenylalaninium methanesulfonate (LPA-MS) was synthesized and grown into single crystals by slow solvent evaporation solution growth technique in aqueous solution containing equimolar concentrations of L-phenylalanine and methanesulfonic acid at room temperature. The grown crystals were subjected to single crystal X-ray diffraction studies. It crystallizes in the monoclinic crystal structure with P_{21} space group and the unit cell parameters are a = 5.312 (10) Å, b = 8.883 (2) Å and c = 25.830 (7) Å. The functional groups of the LPA-MS crystal were confirmed with FT-IR and FT-Raman analysis. The carbon-hydrogen skeleton was confirmed with ^{1}H NMR and ^{13}C NMR analysis. TG–DTG and DSC studies were carried out to determine the thermal stability of the crystals. The optical transparency ranges were studied through UV–vis–spectroscopy and the crystal was found to be transparent in the visible region. The second Harmonic generation (SHG) efficiency of the grown LPA-MS crystal was measured by the Kurtz–Perry powder technique. The dipolar nature of the L-phenylalaninium methanesulfonate and the presence of the intermolecular hydrogen bonding between the molecules are the vital factors responsible for the existence of SHG activity in the crystal.

1. Introduction

The crystal growth and analysis of novel non linear optical (NLO) materials have been strongly encouraged due to their extensive use in the field of optical communication, laser technology, optical computing, data storage, dynamic holography, harmonic generators, frequency mixing, and electro-optic switching [1,2]. Researcher has put great effort to develop high performance optoelectronic devices than the existing ones with higher efficiency with low costs. Varieties of materials including inorganic, organometallic, organic and polymeric materials have been studied for their NLO activity [3]. However, organic NLO materials are receiving major attention in nonlinear optics because, they have fast response, high NLO efficiency and high laser damage threshold compared to inorganic NLO materials [2]. The limitless architectural flexibility of the organic molecules gives tailor-made molecular engineering to find novel nonlinear optical materials with customized NLO properties [2]. Among the organic molecules, amino acids are playing vital role because of their specific features of interest such as molecular chirality, wide optical transparency window in the entire UV, Visible and NIR regions [4,5]. Many amino acids, individually and their complexes or salts with various compounds, are showing good second order nonlinearity because of the presence of chiral carbon atom, non-centrosymmetric crystal structure and the dipolar donor and acceptor groups that provide the ground state charge asymmetry of the molecule allows the intermolecular charge transfer possible [6]. In addition, these crystals can be easily grown using conventional slow evaporation technique (SET). By considering these aspects, several novel organic NLO materials with excellent properties have been developed and reported in the literature [7–10].

Among various amino acid investigated, L-phenylalanine is one of the essential amino acids used by the body to build neurotransmitters [11]. The single crystals of L-phenylalanine salts of various acids were investigated for NLO applications [12–14]. The crystal structures of LPA compounds involve alternating polar and non-polar zones that are stabilized by hydrogen bonds and Van der Waals interactions. Hence they are optically more nonlinear than inorganic materials [15]. The present work deals with the growth

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and crystal structure determination of a newly synthesized L-phenylalaninium methanesulfonate single crystal by slow solvent evaporation technique at room temperature. The structure of the grown crystal is analyzed by single crystal XRD, NMR, FT-IR, FT-Raman analysis. Further, systematic studies are carried out through UV–Visible absorption studies, thermal analysis and powder SHG for exploring the NLO applications of the crystal for the first time in literature.

2. Experimental

2.1. Material synthesis

The titled compound, LPA-MS, was synthesized from L-phenylalanine and methanesulfonic acid taken in the equimolar ratio (1:1) from aqueous solution. The precursor chemicals were dissolved in de-ionized water and stirred well using a magnetic stirrer for about 1 h. The reaction was preceded according to Scheme 1 at room temperature. The solvent was evaporated to obtain the LPA-MS as salt from the solution. The purity of the synthesized compound was improved by repeated re-crystallization process with water.

2.2. Solubility study

The solubility of LPA-MS was analyzed at temperature ranging between 30 and 50 °C in water. The solubility was determined by dissolving the LPA-MS salt in water taken in an air-tight container with continuous stirring. After attaining the saturation the concentration of the solute was estimated gravimetrically. This study shows that the solubility of LPA-MS increases with increase in temperature and the material has positive temperature coefficient of solubility.

2.3. Growth of single crystals

Slow evaporation solution growth method was used to grow the single crystals of the newly synthesized compound, LPA-MS. The saturated solution was prepared in accordance with solubility data and it was constantly stirred for about 3 h using a magnetic stirrer. It was then filtered and kept undisturbed for crystal growth. The grown crystal was harvested after a period of 12 days. A small single crystal with characteristic shape and size was used as a seed for bulk growth. Bulk crystal growth was attempted by submerged seed growth method by just immersing the seed inside the prepared supersaturated solution. The photograph of the as grown crystal is presented in Fig. 1a.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The three dimensional X-ray intensity data were collected by employing single crystal X-ray diffraction measurement using ENRAF nonius CAD4 with graphite monochromatic MoKα radiation of wavelength 0.71073 Å at room temperature. A suitable good quality crystal was selected to subject X-ray diffraction and mounted perfectly on goniometer. Precise unit cell parameters were calculated by least square refinement with the setting angle of 25 well centered reflections using auto-indexing procedure [16]. The program SIR92 and SHELXL-97 were used to solve and refine the structure by full matrix least square refinement on F^2 respectively [17]. The h, k and l index ranges are $-6 \le h \le 6$, $-11 \le k \le 11$ and $-33 \le l \le 33$ respectively [18]. The positions of cation and anion were predicted by prominent peaks of calculated E-map. All the non-hydrogen atoms were refined isotropically monitored by anisotropic refinement [19]. The hydrogen atom attached with carboxyl oxygen atom was refined isotropically and all other hydrogen atoms were positioned in geometrically calculated position with riding model approximation [20,21].

Table 1 represents the crystallographic data and refinement parameter. From this table, it is clearly found that the compound was crystallized in orthorhombic spacegroup with Z = 4. The bond length and bond angle for crystal are listed in Table 2. The final atomic coordinates and isotropic displacement parameters of non-hydrogen atoms are listed in Table 3. The anisotropic thermal parameters for non-hydrogen atoms with their s.u,'s parentheses are shown in Table 4. Table 5 gives the isotropic thermal parameters of hydrogen atoms.

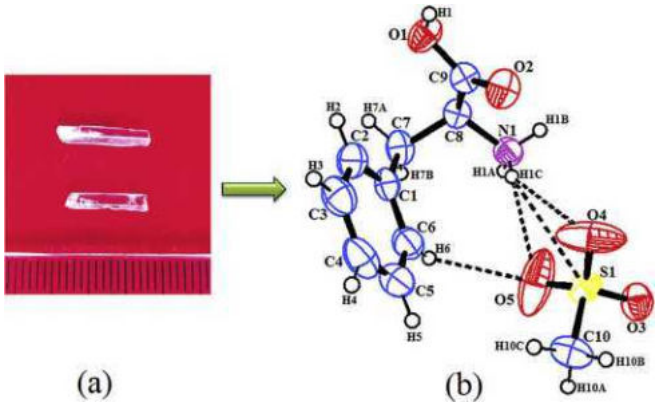
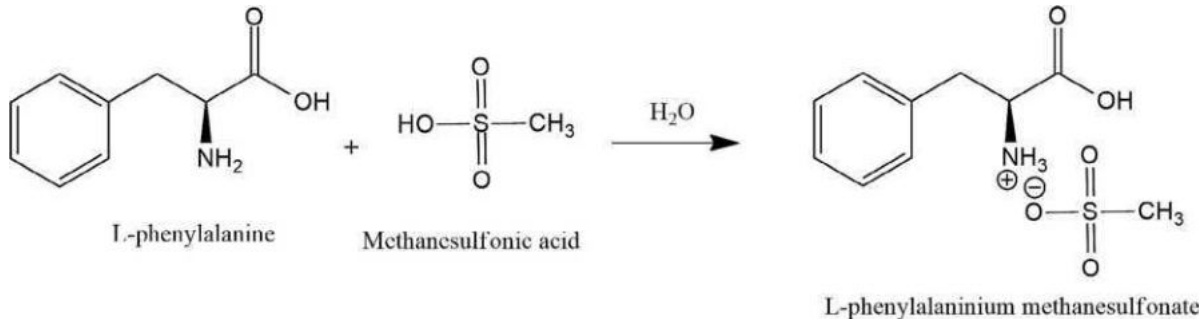


Fig. 1. (a) Photograph of grown LPA-MS single crystal (b) The molecular structure of LPA-MS with atomic numbering scheme.



Scheme 1. Reaction scheme of L-phenylalaninium methanesulfonate.

Table 1
Crystal data and structure refinement for LPA-MS.

Empirical formula	$C_{10}H_{14}NO_5S$
Formula weight	260.28
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 5.312 (10) Å a = 90°
	b = 8.883 (2) Å β = 90°
	c = 25.830 (7) Å γ = 90°
Volume	1219.1 (3) $Å^3$
Z	4
Density (calculated)	1.418 Mg/m^3
Absorption coefficient	0.275 mm^{-1}
F (000)	548
Crystal size	0.3 × 0.2 × 0.2 mm^3
Theta range for data collection	1.577–27.464°
Index ranges	$-6 \le h \le 6$, $-11 \le k \le 11$, $-33 \le l \le 33$
Reflections collected	19540
Independent reflections	2786 [R (int) = 0.0220]
Completeness to theta = 25.242°	100.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2786/0/155
Goodness-of-fit on F^2	1.098
Final R indices [I > 2sigma(I)]	R1 = 0.0457, w*R*2 = 0.1305
R indices (all data)	R1 = 0.0509, w*R*2 = 0.1442
Absolute structure parameter	0.046 (14)
Extinction coefficient	0.063 (9)
CCDC No.	1050462

Fig. 1b gives the molecular structure of titled compound with 50% probability thermal ellipsoids showing atomic numbering scheme. The asymmetric unit of title crystal consists of positively charged cation of carboxy phenylethanaminium and negatively charged anion of methane sulfonate. This obviously explained the proton transfer from the sulfonic derivative leads to the amino group of propaionic derivative which forms ion pair adducts. Moreover, the protonation is confirmed from elongated C–N bond distance of 1.495 (4)º and it was established at N1 atom [22]. From Table 2 it is revealed that the sulfonate anion molecule exhibit tetrahedral geometry with the average S–O bond distances being 1.415(3), 1.428 (4) and 1.442 (3)º. The bond angle between O (4)–S (1)–O (5) and O (4)–S (1)–O (3) are 112° and 115° respectively. Similarly, 109° is for angle between O (5)–S (1)–O (3). In sulfonate anion ring, atom S1 has pyramidal coordination whose bond angle sum is 336° and this indicates sp^3 hybridization. Hence, the atom S1 in sulfonate anion occupies an equatorial position. Gayathri et al. has reported the sum of bond angle as 330° which leads the sp^3 hybridization [23]. The bond distance between C_9 and O_2 is about 1.204 (4) Å, which matches with the standard value of 1.20 Å with the negligible deviation indicating that it is the double bond i.e. [-C=O-].

Intermolecular hydrogen bonding forces play prominent role in forming supramolecular system and determining the physico-chemical properties. In the titled crystal, anions are playing crucial role to form three dimensional hydrogen bonding networks via connecting cations [24]. In hydrogen bonding interactions, except O2, all other oxygens are playing a role as acceptor or donors. In this way, The N–H···O, C–H···O and O–H···O intermolecular hydrogen bonds are formed between the nitrogen, carbon and oxygen atom from cation to oxygen atom of anion which stabilize the crystal structure and are listed in Table 6. There are two three-centered bifurcated and three two-centered hydrogen bonding were observed. In addition, the sulfonate anion is making bifurcated two-centered hydrogen bond in which one of the H bond is observed through self-associated S (4) motif. Therefore, it forms two chain $C_1^2(6)$ and $C_2^1(7)$ motif which is extended along the b axis

Table 2
Bond lengths [Å] and angles [°] for LPA-MS.

Connected Atoms	Bond length [Å]
S (1)–O (4)	1.415 (3)
S (1)–O (5)	1.428 (4)
S (1)–O (3)	1.442 (3)
S (1)–C (10)	1.735 (4)
O (1)–C (9)	1.305 (4)
O (2)–C (9)	1.204 (4)
N (1)–C (8)	1.495 (4)
C (8)–C (9)	1.505 (4)
C (8)–C (7)	1.543 (4)
C (2)–C (1)	1.390 (5)
C (2)–C (3)	1.397 (6)
C (7)–C (1)	1.502 (5)
C (3)–C (4)	1.375 (7)
C (1)–C (6)	1.391 (5)
C (6)–C (5)	1.384 (6)
C (5)–C (4)	1.388 (7)
Connected Atoms	**Bond Angle [°]**
O (4)-S (1)-O (5)	112.1 (4)
O (4)-S (1)-O (3)	115.3 (3)
O (5)-S (1)-O (3)	109.4 (2)
O (4)-S (1)-C (10)	107.5 (2)
O (5)-S (1)-C (10)	106.4 (3)
O (3)-S (1)-C (10)	105.5 (2)
N (1)-C (8)-C (9)	108.4 (3)
N (1)-C (8)-C (7)	112.4 (3)
C (9)-C (8)-C (7)	110.8 (3)
O (2)-C (9)-O (1)	125.2 (3)
O (2)-C (9)-C (8)	123.5 (3)
O (1)-C (9)-C (8)	111.2 (3)
C (1)-C (2)-C (3)	121.0 (4)
C (1)-C (7)-C (8)	115.0 (3)
C (4)-C (3)-C (2)	119.9 (4)
C (2)-C (1)-C (6)	118.1 (3)
C (2)-C (1)-C (7)	120.6 (3)
C (6)-C (1)-C (7)	121.4 (3)
C (5)-C (6)-C (1)	121.2 (4)
C (6)-C (5)-C (4)	120.0 (4)
C (3)-C (4)-C (5)	119.8 (4)

Table 3
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) of non-hydrogen atoms for LPA-MS.

	x	y	z	U (eq)
S (1)	6567 (2)	503 (1)	8396 (1)	44 (1)
O (1)	2429 (5)	7530 (3)	8041 (1)	57 (1)
O (2)	5353 (4)	5758 (3)	7936 (1)	56 (1)
O (3)	6622 (6)	−816 (3)	8071 (1)	61 (1)
N (1)	1979 (6)	3507 (3)	7962 (1)	48 (1)
C (8)	1088 (6)	5049 (4)	8103 (1)	39 (1)
C (9)	3211 (6)	6140 (4)	8013 (1)	40 (1)
O (4)	7645 (10)	1813 (4)	8178 (2)	116 (2)
C (2)	3240 (8)	6422 (4)	9255 (1)	54 (1)
C (7)	145 (6)	5141 (5)	8667 (1)	49 (1)
C (3)	5170 (9)	6391 (5)	9623 (1)	61 (1)
C (1)	2176 (6)	5097 (4)	9071 (1)	43 (1)
C (6)	3056 (9)	3741 (4)	9270 (1)	56 (1)
C (5)	4967 (10)	3704 (6)	9634 (2)	68 (1)
O (5)	4054 (8)	756 (6)	8573 (3)	127 (2)
C (10)	8323 (10)	41 (6)	8940 (2)	68 (1)
C (4)	6012 (8)	5037 (6)	9813 (1)	66 (1)

of the unit cell (Fig. 2a). Further, the secondary $R_4^2(13)$ ring motifs are formed by interconnected with these two primary chain motifs (Fig. 2b). These arrangements are leading to the hydrophilic layers at x = ¼ & ¾ and hydrophobic layers at x = 0, ½ & 1.Here, the hydrophobic layers at x = ½ is sandwiched between the two hydrophilic layers of x = ¼ & ¾ is shown in Fig. 3. In higher order

Table 4
Anisotropic displacement parameters ($Å^2 x\ 10^3$) for the non-hydrogen atoms for LPA-MS.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S (1)	41 (1)	33 (1)	57 (1)	−3 (1)	−10 (1)	−3 (1)
O (1)	47 (1)	39 (1)	84 (2)	−5 (1)	5 (1)	−3 (1)
O (2)	28 (1)	66 (2)	73 (2)	−8 (1)	−1 (1)	−2 (1)
O (3)	65 (2)	55 (2)	62 (2)	−14 (1)	5 (1)	−9 (1)
N (1)	56 (2)	43 (1)	43 (1)	−1 (1)	2 (1)	−7 (1)
C (8)	30 (1)	44 (2)	45 (1)	−3 (1)	−3 (1)	−3 (1)
C (9)	29 (1)	48 (2)	42 (1)	−2 (1)	−4 (1)	−5 (1)
O (4)	152 (4)	74 (2)	120 (3)	52 (2)	−75 (3)	−70 (3)
C (2)	58 (2)	52 (2)	51 (2)	−10 (1)	−2 (2)	−2 (2)
C (7)	32 (1)	61 (2)	52 (2)	−9 (2)	8 (1)	−7 (2)
C (3)	66 (2)	70 (3)	46 (2)	−10 (2)	−3 (2)	−13 (2)
C (1)	38 (2)	52 (2)	40 (1)	−7 (1)	10 (1)	−2 (1)
C (6)	73 (3)	52 (2)	44 (2)	−1 (1)	4 (2)	−6 (2)
C (5)	78 (3)	76 (3)	48 (2)	9 (2)	5 (2)	13 (2)
O (5)	50 (2)	147 (4)	184 (5)	−97 (4)	−12 (2)	20 (2)
C (10)	77 (3)	76 (3)	52 (2)	15 (2)	−13 (2)	−8 (2)
C (4)	58 (2)	103 (3)	39 (2)	−2 (2)	−3 (2)	1 (2)

Table 5
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 x\ 10^3$) of hydrogen atoms for LPA-MS.

	x	y	z	U (eq)
H (1)	3615	8103	7991	85
H (1A)	743	2848	8013	71
H (1B)	2434	3492	7630	71
H (1C)	3292	3262	8159	71
H (2)	2660	7343	9132	64
H (7A)	−803	6066	8708	58
H (7B)	−1001	4310	8728	58
H (3)	5884	7286	9738	73
H (6)	2347	2842	9156	68
H (5)	5550	2786	9759	81
H (10A)	7636	−847	9097	103
H (10B)	10036	−145	8840	103
H (10C)	8270	859	9182	103
H (4)	7279	5015	10062	80

Table 6
Hydrogen bonding geometry of LPA-MS

D-H … A	D-H [Å]	H … A [Å]	D … A [Å]	D … H.A [°]
O1–H1···S1#1	0.820 (1)	2.846 (2)	3.556 (2)	146.09 (1)
O1–H1···O3#1	0.820 (1)	1.876 (2)	2.670 (2)	162.71 (2)
N1–H1A … O4#2	0.890 (2)	1.932 (3)	2.806 (2)	166.99 (2)
N1–H1B···O3#3	0.890 (2)	1.978 (1)	2.834 (1)	161.04 (2)
N1–H1C···O4	0.890 (2)	2.647 (1)	3.411 (1)	144.48 (1)
N1–H1C···O5	0.890 (2)	2.503 (2)	3.111 (2)	125.99 (1)
C10–H10B···O5#4	0.960 (1)	2.382 (2)	3.251 (1)	150.40 (2)

Symmetry transformations used to generate equivalent atoms.
#1 x, y+1, z #2 x-1, y, z #3 −x+1, y+1/2, -z+3/2 #4 x+1, y, z.

packing, the above said intermolecular hydrogen bonds N–H···O and O–H···O are interlinked and thereby supramolecular sheet-like structure are formed [25]. The dihedral angle between the cation and anion plane is 15.56° which indicates these two planes are parallel to each other.

3.2. FT-IR and FT-Raman studies

Fourier transform infra-red (FT-IR) and Raman (FT-Raman) spectral studies have been performed to identify the functional groups of LPA-MS single crystal. The FT-IR spectrum of the grown LPA-MS single crystal was recorded in the frequency region of 4000–400 cm^{-1} using a Thermo Fisher, Nicolet-iS10 spectrometer,

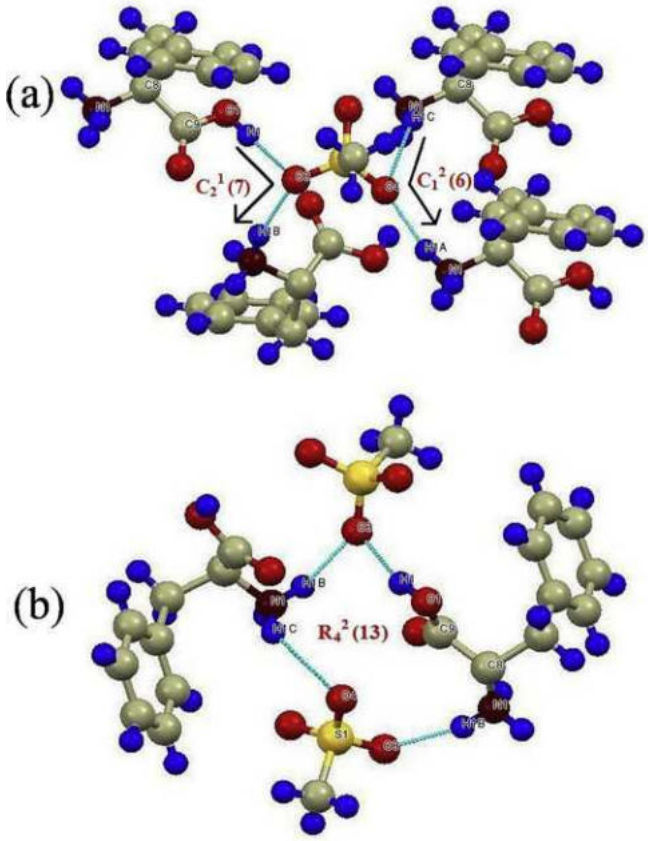


Fig. 2. (a) A molecular aggregations formed in LPA-MS showing chain C_2^1 (7) and C_1^2 (6) motifs. Hydrogen bonds are shown in dashed lines (b) A primary chain motifs are cross linked to form ring R_4^2 (13) motif. Hydrogen bonds are shown in dashed lines.

by KBr pellet technique. The FT-Raman spectrum was recorded in BRUKER RFS27: Stand alone FT-Raman Spectrometer with Nd:YAG 1064 nm laser source. These analyses provide information about the chemical bonding and molecular structure of a material. FT-IR and FT-Raman spectra of the LPA-MS single crystal were recorded and presented in Fig. 4a and b respectively. The characteristic FT-IR peak at 3440 cm^{-1} is assigned to –OH stretching vibration of –COOH group. The peak observed at 3058 cm^{-1} is assigned to NH_3^+ group of LPA-MS crystal. Further, the asymmetric and symmetric vibrations of NH_3^+ are observed at 1624 and 1487 cm^{-1} respectively [26]. In FT-Raman, NH_3^+ asymmetric stretching vibrations are obtained at 3060 cm^{-1} and the peak at 3017 cm^{-1} is attributed to the symmetric stretching vibrations. The strong peak in FT-IR at 2927 cm^{-1} is assigned to –C–H stretching vibrations. The Raman peaks for –C–H asymmetric and symmetric stretching vibrations are obtained at 2937 cm^{-1} and 2872 cm^{-1} [26]. The FT-IR band at 1199 cm^{-1} can be assigned to the –C–C– stretching and the –C–S stretching vibrations is observed at 786 cm^{-1}. The FT-Raman peak for C–S stretching is obtained at 772 cm^{-1}. FT-IR peak observed at 703 cm^{-1} is due to the presence of benzene ring. The ring deformation is also noted in FT-Raman at 616 cm^{-1}. In FT-IR, the C–C deformation and COO rocking is observed at 559 cm^{-1} and 455 cm^{-1} but in Raman the ring deformation is observed at 616 cm^{-1} and COO rocking is observed at 479 cm^{-1} [26]. Further, the C–N deformation is observed at 819 cm^{-1}. In FT-Raman, peak at 1463 cm^{-1} is assigned to $-CH_3$ stretching and peak at 1324 cm^{-1} is assigned to $-CH_2$ stretching vibrations. The characteristic –C=O stretching vibrations of LPA-MS is observed in FT-IR at 1773 cm^{-1} and the same in FT-Raman is observed at 1731 cm^{-1}. The presence

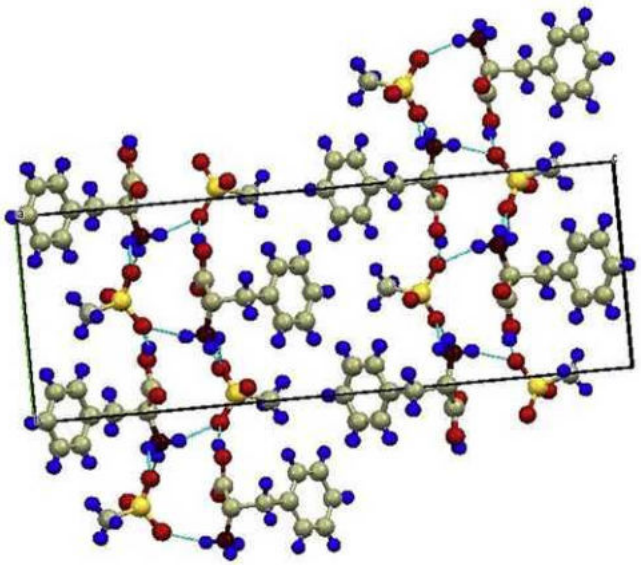


Fig. 3. Packing diagram of LPA-MS viewed along b-axis.

of methanesulfonate anion is confirmed from the sharp peak from FT-IR at 1041 cm^{-1} which is assigned to the stretching vibrations of $-SO_3$. Further it is confirmed from Raman peaks for SO_3 asymmetric and symmetric stretching vibrations which are observed at 1208 cm^{-1} and 1012 cm^{-1} respectively [27]. Also an additional weak peak from FT-Raman at 559 cm^{-1} is attributed to SO_3 symmetric stretching vibrations [27].

3.3. FT-NMR studies

The ^1H NMR and ^{13}C NMR spectral techniques are used to study the carbon and hydrogen skeleton of the LPA-MS single crystal. NMR spectra were recorded in D_2O solvent using BRUKER Avance 400 MHz FT-NMR spectrometer. ^1H NMR spectrum of the LPA-MS crystal is shown in Fig. 5. The insets show the expanded view of the spectrum. It could be observed from the spectrum that there are six set of signals. The peaks with chemical shift values around the δ 3.106 to δ 3.301 ppm are assigned to the two methylene protons of L-phenylalaninium moiety. Due to the influence of −CH protons on methylene protons, the $-CH_2$ signals split as doublet of doublet. The chemical shift of −CH proton is observed at δ 4.215 ppm. Further this signal is split as triplet because of the influence of methylene proton on −CH proton. The phenyl ring protons of the L-phenylalaninium moiety are observed as multiplet between δ 7.242 and δ 7.372 ppm due the spin-spin splitting of adjacent C−H protons. The singlet observed at δ2.721 ppm is due to the methyl group protons of methane sulfonate moiety. The protons of NH_3^+ and COOH groups are not observed due to the fast proton exchange reactions [28]. Further water peak of D_2O is observed as singlet at δ4.70 ppm. The ^{13}C NMR spectrum of LPA-MS is presented in Fig. 6. The signals at the chemical shift values δ35.90 ppm and δ54.46 ppm are attributed to the $-CH_2$ and −CH groups of the L-phenylalaninium moiety. The presence of the signal at δ128.35–δ134.28 ppm is attributed to the carbons of the phenyl ring. The signal observed at δ171.81 ppm is attributed to the carbonyl carbon of the acid group of L-phenylalanine. The signal at chemical shift value δ 38.75 ppm is due the methyl carbon of methane sulfonate group. The NMR spectra analysis confirms the LPA-MS carbon hydrogen framework.

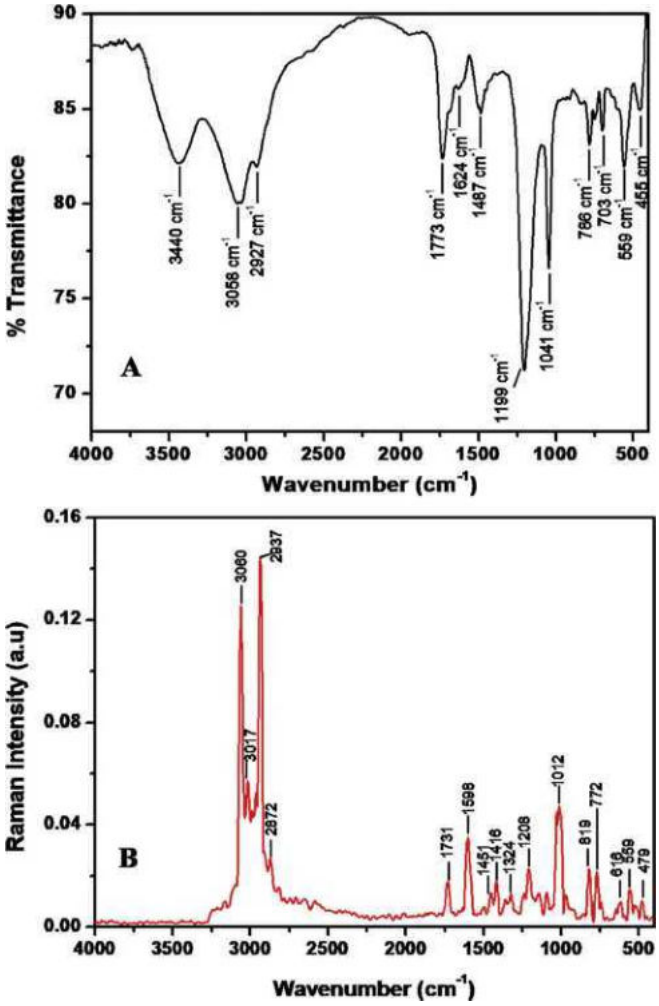


Fig. 4. (a) FT-IR and (b) FT-Raman spectra of LPA-MS crystal.

3.4. Thermal analyses

Thermogravimetry (TG) and differential thermal (DTA) analyses were performed to study the thermal stability and melting point of the grown crystals by using TA Instruments SDT Q600 (V20.9 Build 20) thermal analyzer. The sample was heated in nitrogen (100 mL min^{-1}) atmosphere in alumina crucible at the rate of 10 °C min^{-1}.The TGA and DTA thermograms of the grown crystal is presented in Fig. 7a.

The TGA curve shows no major weight loss upto 260 °C, indicates the suitability of the crystal for high temperature usage like laser applications where crystals should withstand high temperature. There is no evidence for entrapped water in the crystal lattice or physically adsorbed water on the surface of the crystal. Further heating shows, steady weight loss about 80% in between 260 and 360 °C and decomposition up to 450 °C. This is attributed to the decomposition of the compound through bond breaking with the loss of volatile decomposition products like ammonia, carbon dioxide and sulphur trioxide.

In DTA curve, the sharp endothermic peak at 188.9 °C was attributed to the melting point of the crystal which was also confirmed by the melting point apparatus using capillary tube method. The sharpness of endothermic peaks indicates good degree of crystallinity of the LPA-MS. Another sharp peak around 280 °C is due to the decomposition and volatilization of the material

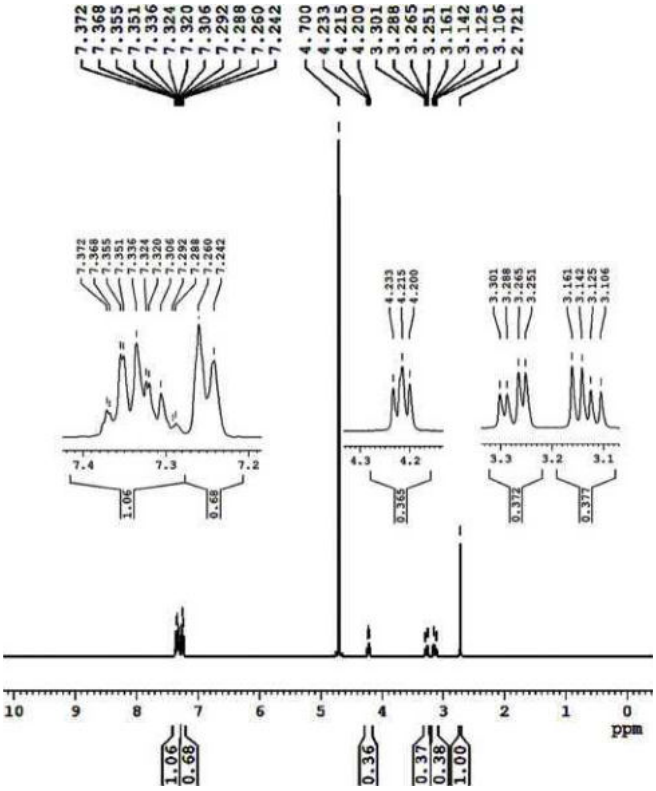


Fig. 5. ^{1}H NMR spectrum of LPA-MS single crystal recorded in D_2O.

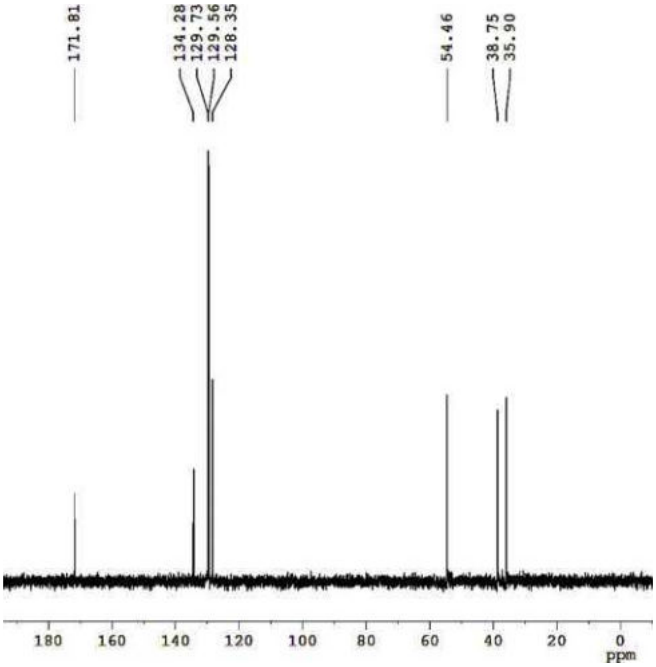


Fig. 6. ^{13}C NMR spectrum of LPA-MS recorded in D_2O.

that matches with the decomposition observed in TGA curve.

The differential scanning calorimeter (DSC) measurements were made using a NETZSCH-DSC 204 PC differential scanning calorimetry (DSC) in the temperature range of 30–350 °C at a heating rate of 10 Kmin^{-1} (Fig. 7b). According to DSC, the sharp endothermic peak observed at 189 °C give the melting point of the crystal which

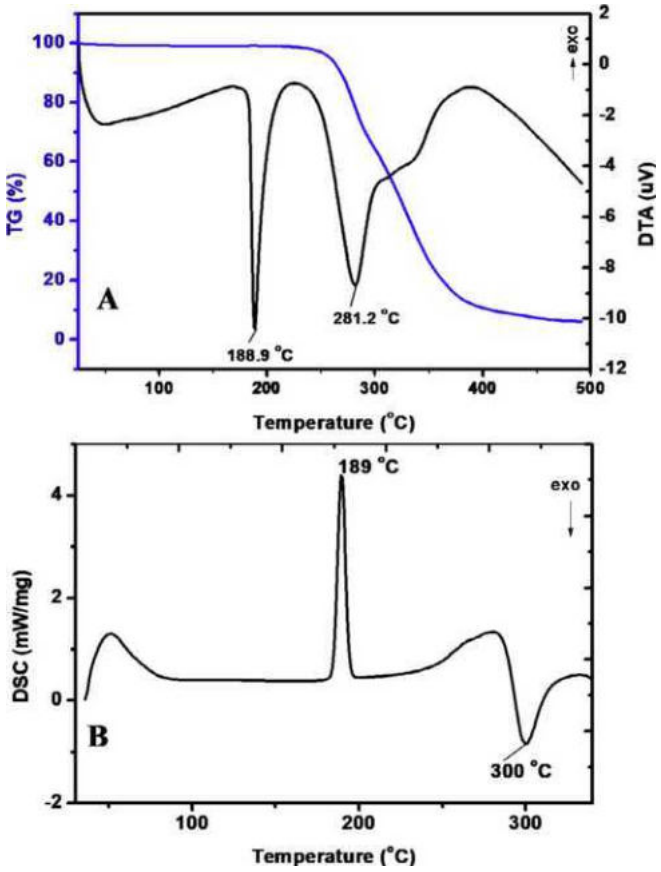


Fig. 7. (a) TG/DTA curve and (b) DSC curve of LPA-MS single crystal.

is exactly matches with the TGA/DTA results. The decomposition was further confirmed by the exothermic peak around 300 °C. Thus from thermal analyses, it is seen that the crystal can be utilized for device applications in the field of optoelectronics and photonics up to 188 °C.

3.5. UV–vis absorption studies

Optical transparency is very important characteristics for any NLO material. Optical properties of crystalline materials give information regarding the compositional nature and quality of the crystal. UV–vis transmission spectrum has been recorded using JASCO V-760 (Tokyo, Japan) spectrophotometer in the spectral region between 190 and 850 nm to measure the optical transparency of the grown crystal. Fig. 8 shows the plot of absorbance against the wavelength. It is observed from Fig. 8 that the grown single crystal has good transparency in the entire visible region. The lower edge cut-off wavelength of LPA-MS single crystal is obtained around 282 nm. The optical absorption coefficient (α) was calculated from the transmittance using the relation.

$$\alpha = \left(\frac{2.303}{d}\right)\log\left(\frac{100}{T}\right)$$

where d is the thickness and T is the transmittance. The optical band gap E_g is calculated from the following Tauc's relationship,

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where, α is the absorption coefficient, Eg is the optical band gap and

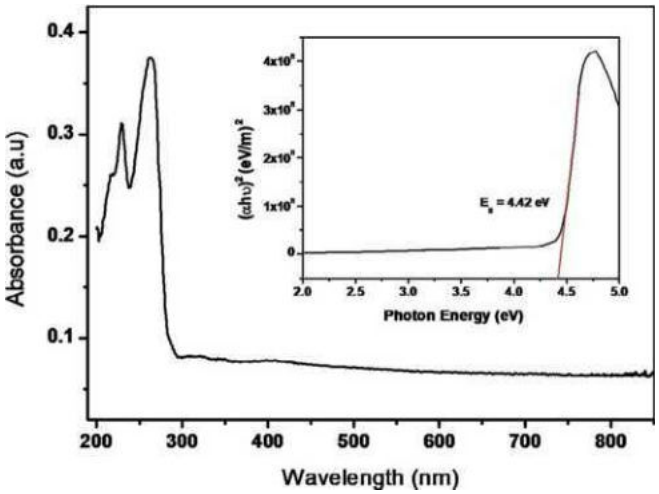


Fig. 8. UV–Vis spectrum of LPA-MS single crystal. Inset shows the Tauc's plot of $(\alpha h\upsilon)^2$ vs photon energy for band gap calculation.

A is a constant.

Optical band gap was determined by extrapolating the linear portion of the plot, $(\alpha h\nu)^2$ vs photon energy (inset of Fig. 8). Optical band gap of the title crystal is found to be 4.42 eV. The high value of band gap energy and the very good transmittance in the entire visible region shows the suitability of the crystal for optoelectronic applications.

3.6. Powder SHG measurement

The band gap of the material plays an important in SHG activity. It must be greater than 2.33eV (cut off >532 nm). Also, the SHG efficiency of the organic materials very much depend on the molecular structure [29]. SHG conversion efficiency of the LPA-MS crystal was measured using Kurtz and Perry powder SHG technique [30]. The crystal was grounded into a homogenous powder of particles and densely packed glass capillary tube. A Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064 nm with an input power of 1.9 mJ and pulse width of 8 ns with a repetition rate of 10 Hz was used. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532 nm collected a monochromator after separating the 1064 nm pump beam with an IR-blocking filter. A photomultiplier tube is used as detector. It is observed that the measured SHG efficiency of LPA-MS crystal was 1.2 times that of potassium dihydrogen phosphate (KDP).

4. Conclusion

A single crystal of L-phenylalaninium methanesulfonate was grown by slow evaporation solution technique. The lattice parameter and space group of LPA-MS were identified by Single-crystal X-ray diffraction studies. The studies showed that LPA-MS belongs to ~~monoclinic~~ system with space group P21. FT-IR and FT-Raman analyses gave the evidences for the functional groups of the LPA-MS single crystal. Further, ^{1}H NMR and ^{13}C NMR analysis confirmed the carbon-hydrogen framework. The linear optical property studies by UV–Vis absorption studies revealed that the crystal has 80% of transparency in the entire visible region, with the UV cut-off around 290 nm. The thermal behavior of the grown crystal was studied by the TG/DTA and DSC curves and results show that the LPA-MS crystal is extremely stable up to 280 °C with sharp melting point at 189 °C. Moreover, it is observed that no structural transformation was observed before melting. Hence, LPA-MS crystal can be exploited for any suitable application up to its melting point (189 °C). The Kurtz test reveals that the SHG efficiency of LPA-MS is about 1.2 times that of KDP. The result obtained in the present study indicates that LPA-MS is a potential material for frequency conversion applications.

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Hydrogen-bonding patterns in bis(cytosinium) tartarate monohydrate

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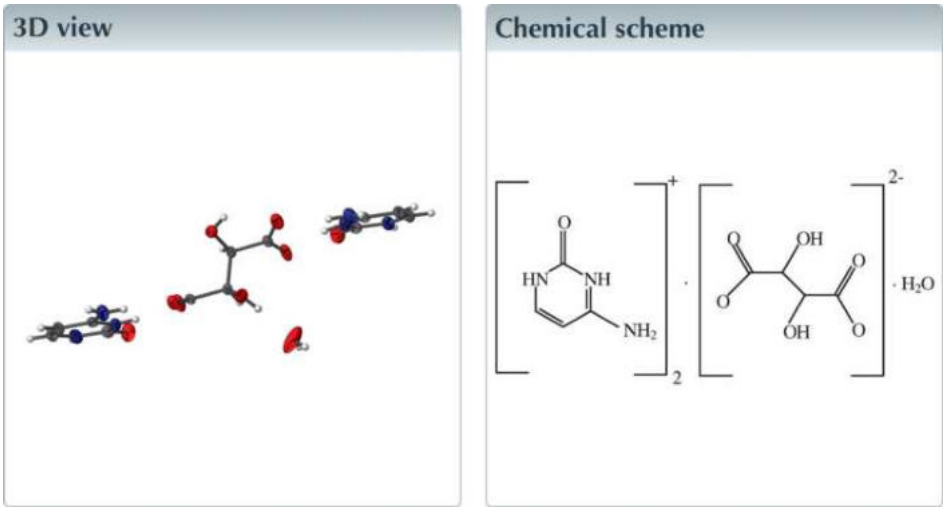
The asymmetric unit of the title cytosinium salt derivative, $2C_4H_6N_3O^+\cdot C_4H_4O_6^{2-}\cdot H_2O$, contains two cytosinium cations, one tartaric acid anion and a water molecule. The two cytosinium cations are almost planar (r.m.s. deviations of the fitted atoms are 0.0151 and 0.0213 Å). The crystal structure features C—H···O, N—H···O and O—H···O interactions. Further C—O···π and π–π interactions are observed along the *ab* plane, contributing to the crystal stability.



Structure description

Pyrimidine-based derivatives have attracted a great deal of attention in terms of their hydrogen-bonding patterns. Cytosinium is one of the naturally occurring base molecules found in DNA and RNA (Portalone *et al.*, 2009). Many cytosinium salts of organic acids have been reported previously, *viz*. cytosinium hydrogen sulfate, cytosinium perchlorate (Bensegueni *et al.*, 2009), cytosinium dihydrogen phosphite (Messai *et al.*, 2009), cytosinium hydrogen chloranilate monohydrate (Gotoh *et al.*, 2006) and cytosinium zoledronate trihydrate (Sridhar & Ravikumar, 2011). As part of our investigations on the growth and characterization of semi-organic crystals containing the nucleic acid component cytosine, we report herein the crystal structure determination and the geometry optimization of the title compound.

A perspective view of the title compound with the atomic numbering scheme is illustrated in Fig. 1. It crystallizes in the orthorhombic space group $P2_12_12_1$ with two cytosinium cations, a tartarate anion and one water molecule. The two cytosinium

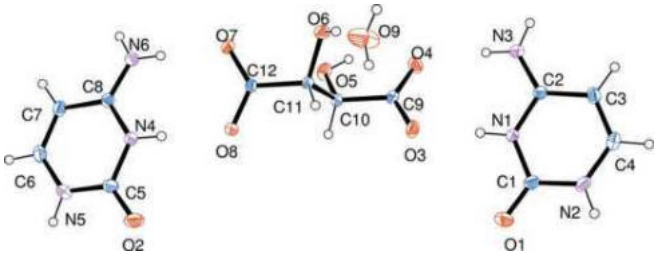


Figure 1
The molecular structure with displacement ellipsoids for the non-H atoms drawn at the 30% probability level.

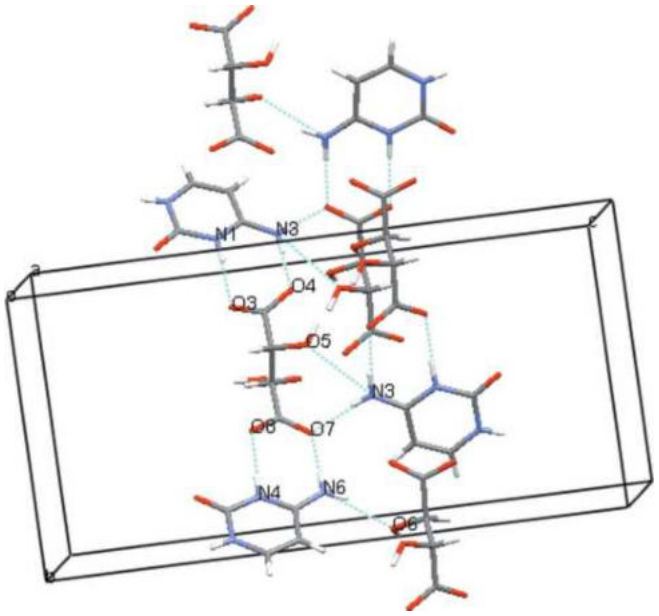


Figure 2
Crystal packing of the title compound, showing the N—H···O interactions in the $R_2^2(12)$ motif along the *c* axis and in parallel chains along the *a* and *c* axes as dashed lines. Other H atoms have been omitted for clarity.

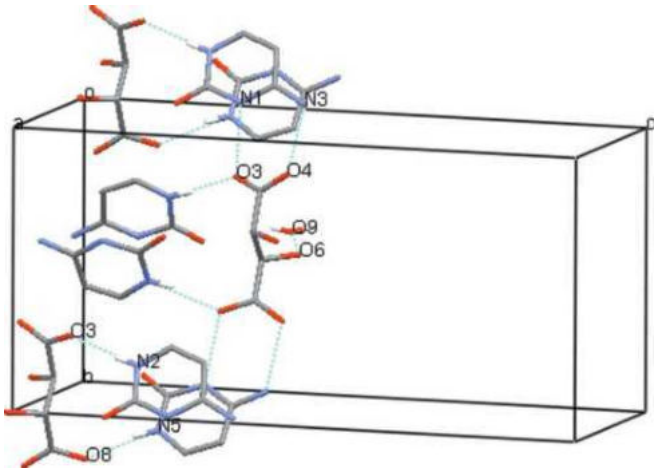


Figure 3
Crystal packing of the title compound, showing the N—H···O interactions enclosing parallel chains along the *c* and *a* axes and O—H···O interactions enclosing parallel chains along the *ab* plane, as dashed lines. Other H atoms have been omitted for clarity.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.93	2.53	3.098 (2)	120
C10—H10···O2^{ii}	0.98	2.33	3.312 (2)	175
C11—H11···O1^{iii}	0.98	2.38	3.361 (2)	179
O5—H5···O4	0.82	2.12	2.6140 (19)	118
O6—H6*A*···O9	0.82	1.87	2.688 (2)	172
N1—H1*A*···O3	0.86 (2)	1.80 (2)	2.656 (2)	171 (3)
N2—H2*A*···O3^{i}	0.86 (2)	1.91 (2)	2.768 (2)	175 (3)
N3—H3*A*···O4	0.84 (2)	2.04 (2)	2.873 (2)	171 (2)
N3—H3*B*···O7^{iv}	0.83 (2)	2.04 (2)	2.865 (2)	172 (2)
N4—H4*A*···O8	0.85 (2)	1.90 (2)	2.748 (2)	173 (3)
N5—H5*A*···O8^{v}	0.86 (2)	1.93 (2)	2.766 (2)	166 (3)
N6—H6*B*···O7	0.85 (2)	1.96 (2)	2.808 (2)	179 (3)
N6—H6*C*···O6^{vi}	0.83 (2)	2.01 (2)	2.812 (2)	163 (2)
O9—H9*A*···O2^{i}	0.83 (2)	2.24 (3)	3.040 (3)	162 (4)
O9—H9*B*···O5^{vii}	0.84 (2)	2.00 (3)	2.812 (2)	161 (3)

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (v) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vii) $x-1, y, z$.

cations are almost planar, the r.m.s deviations of the fitted atoms C1–C4/N1–N3/O1 and C5–C8/N4–N6/O2 being 0.0151 and 0.0213 Å, respectively. An overlay analysis of the two cations gives an r.m.s. deviation of 1.128 Å. Bond distances and angles in the cations are comparable to those in the cation of cytosinium zoledronate trihydrate (Sridhar & Ravikumar, 2011).

The crystal structure features C—H···O, N—H···O and O—H···O interactions. The interaction between N4 and O8 through H4*A*, N6 and O7 through H6*B* and N1 and O3 through H1*A*, N3 and O4 through H3*A* occur alternately as chain links and form a three-dimensional network enclosing $R_2^2(8)$ ring motifs. The interaction between N3 and O7 through H3*B* and N6 and O6 through H6*C* form parallel chains along the *a*- and *c*-axis directions, respectively (Fig. 2). Similarly the interactions between N2 and O3 through H2*A* and N5 and O8 through H5*A* form infinite parallel chains along the *c*- and *a*-axis directions, respectively. The O6—H6*A*···O9 interaction encloses parallel chains along the *ab* plane (Fig. 3). Also the interactions of C4, C11 with O1 through H4, H11 form infinite parallel chains along the *b*- and *c*-axis directions, respectively (Fig. 4). The O9 interactions with O2, O5 through H9*A*, H9*B*

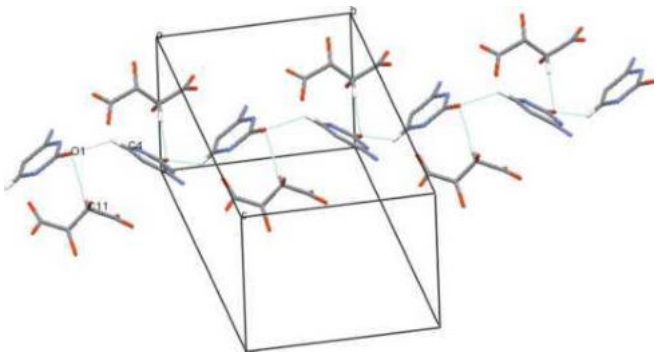


Figure 4
Crystal packing of the title compound, showing the C—H···O interactions enclosing parallel chains along the *b* and *c* axes as dashed lines. Other H atoms have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$2C_4H_6N_3O^+\cdot C_4H_4O_6^{2-}\cdot H_2O$
M_r	390.32
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, b, c (Å)	7.6932 (8), 10.1152 (8), 20.9336 (17)
V (Å^3)	1629.0 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.14
Crystal size (mm)	0.25 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.705, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22011, 4920, 4299
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.713
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.087, 1.11
No. of reflections	4920
No. of parameters	284
No. of restraints	13
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.22
Absolute structure	Flack x determined using 1669 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.1 (3)

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *XPREP* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Qmol* (Gans & Shalloway, 2001), *Mercury* (Macrae *et al.*, 2008), *ORTEPIII* (Burnett & Johnson, 1996), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

and the interaction between C10 and O2 through H10 forms an $R_3^3(7)$ ring motif along the *ab* plane (Fig. 5). A short contact is observed in the tartarate anion between atoms O4 and O5. Details are given in Table 1.

C—O$\cdots\pi$ interactions are observed along the *ab* plane [C9$\cdots$*Cg*2(x, $-1+y$, z) = 3.876 (2) Å, C9—O3$\cdots$*Cg*2(x, $-1+y$, z) = 15°; C12$\cdots$*Cg*1(x, $1+y$, z) = 3.497 (2) Å, C12—O8$\cdots$*Cg*1 = 2°; *Cg*1 and *Cg*2 are the centroids of the N1/C1/N2/C4/C3/C2 and N4/C5/N5/C6/C7/C8 rings, respectively]. In addition, weak π–π interactions are observed between the two symmetry-related cytosinium rings, with *Cg*1$\cdots$*Cg*2($-1+x$, $-1+y$, z) = 3.401 (2) Å.

Synthesis and crystallization

A hot supersaturated water solution of cytosine (0.111 g, from Spectrochem) and tartaric acid (0.150 g, from Loba Chemie, India) were mixed in a 1:1 molar ratio and the solution was allowed to evaporate slowly, resulting in the formation of transparent plate-like crystals of cytosinium tartrate monohydrate in 15 days (m.p. 491–493 K).

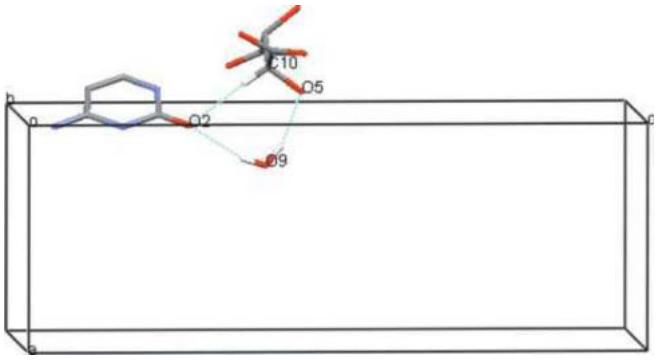


Figure 5
Crystal packing of the title compound, showing the C—H$\cdots$O and O—H$\cdots$O interactions enclosing an $R_3^3(7)$ ring motif and parallel chains along the *ab* plane as dashed lines. Other H atoms have been omitted for clarity.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2017). **2**, x170448 [https://doi.org/10.1107/S2414314617004485]

Hydrogen-bonding patterns in bis(cytosinium) tartarate monohydrate

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Bis(cystosinium) tartarate monohydrate

Crystal data

$2C_4H_6N_3O^+·C_4H_4O_6^{2-}·H_2O$
M_r = 390.32
Orthorhombic, $P2_12_12_1$
a = 7.6932 (8) Å
b = 10.1152 (8) Å
c = 20.9336 (17) Å
V = 1629.0 (3) Å^3
Z = 4
$F(000)$ = 816
D_x = 1.592 Mg m^{-3}
Melting point: 493 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7834 reflections
θ = 2.8–28.9°
μ = 0.14 mm^{-1}
T = 296 K
Plate, colourless
0.25 × 0.25 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan SADABS
T_{min} = 0.705, T_{max} = 0.746
22011 measured reflections
4920 independent reflections
4299 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 30.5°, θ_{min} = 2.2°
h = −10→10
k = −14→14
l = −29→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.087
S = 1.11
4920 reflections
284 parameters
13 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.2224P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack x determined using 1669 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.1 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5157 (3)	−0.12312 (19)	0.28216 (8)	0.0271 (4)
C2	0.4512 (2)	−0.13171 (17)	0.39524 (8)	0.0227 (3)
C3	0.3533 (3)	−0.24948 (18)	0.38552 (9)	0.0280 (4)
H3	0.3003	−0.2928	0.4195	0.034*
C4	0.3402 (3)	−0.29593 (18)	0.32550 (10)	0.0302 (4)
H4	0.2755	−0.3721	0.3182	0.036*
C5	1.0040 (3)	0.91530 (19)	0.27540 (9)	0.0282 (4)
C6	1.1517 (3)	1.09471 (19)	0.32643 (10)	0.0311 (4)
H6	1.2200	1.1700	0.3220	0.037*
C7	1.1029 (3)	1.05652 (18)	0.38512 (9)	0.0279 (4)
H7	1.1340	1.1050	0.4211	0.033*
C8	1.0018 (2)	0.93903 (17)	0.39043 (8)	0.0228 (3)
C9	0.6955 (2)	0.21335 (16)	0.40007 (8)	0.0223 (3)
C10	0.7829 (2)	0.34860 (16)	0.39920 (8)	0.0205 (3)
H10	0.8548	0.3549	0.3607	0.025*
C11	0.6476 (2)	0.45940 (16)	0.39747 (8)	0.0191 (3)
H11	0.5796	0.4511	0.3581	0.023*
C12	0.7400 (2)	0.59383 (15)	0.39722 (8)	0.0203 (3)
N1	0.5288 (2)	−0.07644 (15)	0.34392 (7)	0.0244 (3)
N2	0.4183 (3)	−0.23531 (17)	0.27525 (8)	0.0313 (4)
N3	0.4693 (3)	−0.07353 (16)	0.45057 (8)	0.0303 (4)
N4	0.9555 (2)	0.87599 (16)	0.33577 (7)	0.0245 (3)
N5	1.1043 (3)	1.02646 (17)	0.27297 (8)	0.0327 (4)
N6	0.9557 (3)	0.88801 (16)	0.44485 (8)	0.0303 (4)
O1	0.5847 (2)	−0.06662 (17)	0.23794 (7)	0.0443 (4)
O2	0.9624 (2)	0.85238 (17)	0.22833 (7)	0.0438 (4)
O3	0.6214 (2)	0.17628 (13)	0.34904 (7)	0.0366 (4)
O4	0.7027 (2)	0.14814 (14)	0.44995 (7)	0.0347 (3)
O5	0.89220 (18)	0.36252 (13)	0.45351 (7)	0.0308 (3)
H5	0.8871	0.2952	0.4752	0.046*
O6	0.53350 (18)	0.44816 (13)	0.45043 (6)	0.0276 (3)
H6A	0.4348	0.4328	0.4376	0.041*
O7	0.74807 (19)	0.65974 (12)	0.44753 (6)	0.0273 (3)
O8	0.8050 (2)	0.63023 (14)	0.34462 (6)	0.0348 (3)
O9	0.2191 (3)	0.4089 (3)	0.39776 (10)	0.0725 (8)
H1A	0.569 (4)	0.003 (2)	0.3477 (12)	0.051 (8)*
H2A	0.403 (3)	−0.258 (3)	0.2363 (9)	0.038 (7)*
H3A	0.529 (3)	−0.004 (2)	0.4530 (11)	0.037 (7)*
H3B	0.411 (3)	−0.094 (2)	0.4827 (9)	0.026 (6)*
H4A	0.902 (3)	0.802 (2)	0.3369 (11)	0.041 (7)*
H5A	1.138 (4)	1.046 (3)	0.2351 (10)	0.044 (7)*
H6B	0.895 (3)	0.8185 (19)	0.4459 (11)	0.036 (7)*
H6C	0.986 (3)	0.921 (2)	0.4795 (9)	0.037 (6)*
H9A	0.190 (5)	0.401 (4)	0.3598 (11)	0.096 (14)*
H9B	0.134 (4)	0.397 (4)	0.4223 (14)	0.088 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0325 (9)	0.0277 (8)	0.0211 (8)	0.0014 (8)	−0.0023 (7)	−0.0016 (7)
C2	0.0259 (8)	0.0190 (7)	0.0232 (7)	0.0033 (7)	0.0007 (7)	0.0005 (6)
C3	0.0308 (10)	0.0211 (8)	0.0323 (10)	−0.0018 (7)	0.0024 (8)	0.0032 (7)
C4	0.0320 (10)	0.0210 (8)	0.0377 (10)	−0.0018 (8)	−0.0044 (8)	−0.0034 (8)
C5	0.0304 (10)	0.0314 (9)	0.0227 (8)	0.0018 (8)	0.0024 (7)	0.0013 (7)
C6	0.0324 (10)	0.0222 (8)	0.0387 (10)	−0.0020 (8)	0.0023 (8)	0.0040 (8)
C7	0.0318 (10)	0.0217 (8)	0.0302 (9)	−0.0028 (8)	−0.0024 (8)	−0.0028 (7)
C8	0.0237 (8)	0.0209 (7)	0.0237 (8)	0.0025 (6)	−0.0011 (6)	0.0002 (7)
C9	0.0280 (9)	0.0174 (7)	0.0217 (8)	−0.0007 (7)	0.0011 (7)	−0.0019 (6)
C10	0.0232 (8)	0.0177 (7)	0.0205 (7)	−0.0020 (6)	0.0006 (6)	−0.0020 (6)
C11	0.0228 (8)	0.0187 (7)	0.0158 (7)	−0.0018 (6)	−0.0009 (6)	−0.0026 (6)
C12	0.0235 (8)	0.0166 (7)	0.0209 (7)	0.0004 (6)	−0.0016 (6)	0.0001 (6)
N1	0.0330 (8)	0.0200 (7)	0.0202 (7)	−0.0036 (6)	0.0005 (6)	−0.0011 (6)
N2	0.0410 (10)	0.0278 (8)	0.0250 (8)	−0.0017 (7)	−0.0048 (7)	−0.0077 (6)
N3	0.0435 (10)	0.0264 (8)	0.0210 (7)	−0.0037 (7)	0.0051 (7)	−0.0014 (6)
N4	0.0287 (8)	0.0225 (7)	0.0223 (7)	−0.0036 (6)	0.0004 (6)	−0.0009 (6)
N5	0.0414 (10)	0.0311 (8)	0.0256 (8)	−0.0027 (7)	0.0056 (7)	0.0065 (7)
N6	0.0422 (10)	0.0278 (8)	0.0210 (7)	−0.0083 (7)	−0.0002 (7)	−0.0018 (6)
O1	0.0591 (11)	0.0519 (10)	0.0219 (6)	−0.0129 (9)	0.0033 (7)	0.0021 (6)
O2	0.0543 (10)	0.0535 (10)	0.0235 (6)	−0.0138 (9)	0.0041 (7)	−0.0069 (7)
O3	0.0632 (11)	0.0226 (6)	0.0241 (6)	−0.0123 (7)	−0.0124 (7)	0.0010 (5)
O4	0.0496 (9)	0.0285 (7)	0.0261 (6)	−0.0091 (7)	−0.0056 (6)	0.0074 (6)
O5	0.0306 (7)	0.0262 (6)	0.0355 (7)	−0.0010 (6)	−0.0120 (6)	−0.0019 (6)
O6	0.0240 (6)	0.0311 (6)	0.0277 (6)	−0.0020 (6)	0.0056 (5)	−0.0044 (5)
O7	0.0398 (8)	0.0208 (6)	0.0212 (6)	−0.0040 (5)	−0.0013 (5)	−0.0042 (5)
O8	0.0563 (10)	0.0249 (6)	0.0233 (6)	−0.0100 (7)	0.0110 (6)	−0.0027 (5)
O9	0.0402 (10)	0.137 (2)	0.0409 (10)	−0.0349 (13)	0.0010 (9)	−0.0080 (13)

Geometric parameters (Å, º)

C1—O1	1.211 (2)	C9—C10	1.524 (2)
C1—N2	1.367 (3)	C10—O5	1.421 (2)
C1—N1	1.380 (2)	C10—C11	1.530 (2)
C2—N3	1.307 (2)	C10—H10	0.9800
C2—N1	1.350 (2)	C11—O6	1.419 (2)
C2—C3	1.424 (3)	C11—C12	1.534 (2)
C3—C4	1.345 (3)	C11—H11	0.9800
C3—H3	0.9300	C12—O7	1.248 (2)
C4—N2	1.358 (3)	C12—O8	1.264 (2)
C4—H4	0.9300	N1—H1A	0.86 (2)
C5—O2	1.216 (2)	N2—H2A	0.857 (18)
C5—N5	1.364 (3)	N3—H3A	0.842 (18)
C5—N4	1.377 (2)	N3—H3B	0.834 (17)
C6—C7	1.341 (3)	N4—H4A	0.854 (19)
C6—N5	1.365 (3)	N5—H5A	0.857 (19)

C6—H6	0.9300	N6—H6B	0.846 (18)
C7—C8	1.425 (3)	N6—H6C	0.833 (17)
C7—H7	0.9300	O5—H5	0.8200
C8—N6	1.300 (2)	O6—H6A	0.8200
C8—N4	1.358 (2)	O9—H9A	0.83 (2)
C9—O4	1.236 (2)	O9—H9B	0.84 (2)
C9—O3	1.267 (2)		

O1—C1—N2	123.44 (18)	C11—C10—H10	108.5
O1—C1—N1	121.52 (18)	O6—C11—C10	110.11 (14)
N2—C1—N1	115.04 (17)	O6—C11—C12	111.12 (13)
N3—C2—N1	118.14 (17)	C10—C11—C12	109.52 (14)
N3—C2—C3	124.05 (17)	O6—C11—H11	108.7
N1—C2—C3	117.81 (16)	C10—C11—H11	108.7
C4—C3—C2	117.74 (18)	C12—C11—H11	108.7
C4—C3—H3	121.1	O7—C12—O8	124.04 (15)
C2—C3—H3	121.1	O7—C12—C11	119.58 (15)
C3—C4—N2	122.18 (18)	O8—C12—C11	116.38 (15)
C3—C4—H4	118.9	C2—N1—C1	124.84 (16)
N2—C4—H4	118.9	C2—N1—H1A	118.0 (18)
O2—C5—N5	123.37 (18)	C1—N1—H1A	115.5 (18)
O2—C5—N4	121.41 (18)	C4—N2—C1	122.35 (16)
N5—C5—N4	115.20 (17)	C4—N2—H2A	123.5 (17)
C7—C6—N5	122.05 (18)	C1—N2—H2A	113.8 (17)
C7—C6—H6	119.0	C2—N3—H3A	119.2 (16)
N5—C6—H6	119.0	C2—N3—H3B	123.3 (15)
C6—C7—C8	117.66 (18)	H3A—N3—H3B	117 (2)
C6—C7—H7	121.2	C8—N4—C5	124.52 (16)
C8—C7—H7	121.2	C8—N4—H4A	121.0 (16)
N6—C8—N4	118.70 (16)	C5—N4—H4A	114.1 (16)
N6—C8—C7	123.27 (17)	C5—N5—C6	122.51 (17)
N4—C8—C7	118.01 (16)	C5—N5—H5A	113.3 (18)
O4—C9—O3	125.05 (17)	C6—N5—H5A	124.2 (18)
O4—C9—C10	117.97 (16)	C8—N6—H6B	120.2 (16)
O3—C9—C10	116.98 (15)	C8—N6—H6C	121.8 (16)
O5—C10—C9	109.89 (14)	H6B—N6—H6C	118 (2)
O5—C10—C11	110.42 (13)	C10—O5—H5	109.5
C9—C10—C11	110.95 (14)	C11—O6—H6A	109.5
O5—C10—H10	108.5	H9A—O9—H9B	111 (3)
C9—C10—H10	108.5		

N3—C2—C3—C4	177.53 (19)	O6—C11—C12—O8	−160.68 (16)
N1—C2—C3—C4	−1.9 (3)	C10—C11—C12—O8	77.45 (19)
C2—C3—C4—N2	0.9 (3)	N3—C2—N1—C1	−177.22 (18)
N5—C6—C7—C8	1.4 (3)	C3—C2—N1—C1	2.3 (3)
C6—C7—C8—N6	175.8 (2)	O1—C1—N1—C2	177.9 (2)
C6—C7—C8—N4	−2.5 (3)	N2—C1—N1—C2	−1.4 (3)
O4—C9—C10—O5	13.0 (2)	C3—C4—N2—C1	0.1 (3)

O3—C9—C10—O5	−166.62 (16)	O1—C1—N2—C4	−179.1 (2)
O4—C9—C10—C11	−109.38 (19)	N1—C1—N2—C4	0.1 (3)
O3—C9—C10—C11	71.0 (2)	N6—C8—N4—C5	−176.22 (18)
O5—C10—C11—O6	−65.06 (17)	C7—C8—N4—C5	2.2 (3)
C9—C10—C11—O6	57.03 (17)	O2—C5—N4—C8	177.85 (19)
O5—C10—C11—C12	57.41 (17)	N5—C5—N4—C8	−0.6 (3)
C9—C10—C11—C12	179.50 (14)	O2—C5—N5—C6	−179.1 (2)
O6—C11—C12—O7	19.7 (2)	N4—C5—N5—C6	−0.6 (3)
C10—C11—C12—O7	−102.17 (18)	C7—C6—N5—C5	0.2 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.93	2.53	3.098 (2)	120
C10—H10···O2^{ii}	0.98	2.33	3.312 (2)	175
C11—H11···O1^{iii}	0.98	2.38	3.361 (2)	179
O5—H5···O4	0.82	2.12	2.6140 (19)	118
O6—H6*A*···O9	0.82	1.87	2.688 (2)	172
N1—H1*A*···O3	0.86 (2)	1.80 (2)	2.656 (2)	171 (3)
N2—H2*A*···O3^{i}	0.86 (2)	1.91 (2)	2.768 (2)	175 (3)
N3—H3*A*···O4	0.84 (2)	2.04 (2)	2.873 (2)	171 (2)
N3—H3*B*···O7^{iv}	0.83 (2)	2.04 (2)	2.865 (2)	172 (2)
N4—H4*A*···O8	0.85 (2)	1.90 (2)	2.748 (2)	173 (3)
N5—H5*A*···O8^{v}	0.86 (2)	1.93 (2)	2.766 (2)	166 (3)
N6—H6*B*···O7	0.85 (2)	1.96 (2)	2.808 (2)	179 (3)
N6—H6*C*···O6^{vi}	0.83 (2)	2.01 (2)	2.812 (2)	163 (2)
O9—H9*A*···O2^{i}	0.83 (2)	2.24 (3)	3.040 (3)	162 (4)
O9—H9*B*···O5^{vii}	0.84 (2)	2.00 (3)	2.812 (2)	161 (3)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) −*x*+2, *y*−1/2, −*z*+1/2; (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) *x*−1/2, −*y*+1/2, −*z*+1; (v) −*x*+2, *y*+1/2, −*z*+1/2; (vi) *x*+1/2, −*y*+3/2, −*z*+1; (vii) *x*−1, *y*, *z*.

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Influence of Sm doped ZnO nanoparticles with enhanced photoluminescence and antibacterial efficiency

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Abstract Samarium doped Zinc Oxide nanoparticles are prepared by using soft chemical route with different doping concentrations. The structural studies indicated that doping does not affect the structure of ZnO lattice. The shape and size of the nanoparticles are analyzed using the FESEM and TEM images. The photoluminescence spectrum shows the increases in the intensity of violet and blue emission peaks as the concentration of dopant increases. Antibacterial activities against Staphylococcus aureus (*S. Aureus*) and Escherichia coli (*E. coli*) bacterial strains using the agar well diffusion method were studied. The increased diameter of the zone of inhibition at the higher concentration of samarium shows the enhanced efficiency of antibacterial activity.

1 Introduction

A new perspective has acquired over the past years in the field of science and technology of nanomaterials. Applications such as optical coatings, solid state window layer, electro-optical modulators and other light emitting materials are extensively being studied by II–VI compound semiconductors. In the recent decade, one of the most significant challenges is due to infectious diseases and bacterial or fungal contamination in all kinds of materials. In order to prevent them several antibacterial and antifungal agents are widely used for the public health issues [1]. The new materials with antibacterial or antifungal properties are much needed as they have their ability which depends on the size, structure and surface properties of the nanomaterials [2].

Several metal oxides such as TiO_2, ZnO, and CuO have gained much attention of the researchers in the fields. Among them, ZnO is a promising II–VI group semiconductor material, which has direct band gap of about 3.37 eV. Also, it absorbs UV radiation due to band to band transition and it is a good transparent conductive oxide (TCO) material which are mainly for solar cells, LED and heat mirror applications [3, 4]. Above all oxide materials, ZnO is one of the most promising material due to its optical, electrical, chemical and mechanical property. Unlike the materials IFO & SnO2, the semiconductor materials ZnO is abundant in nature, inexpensive, chemically stable, non-toxic and biocompatible [5].

Several synthesis routes have been employed to improve the performance of ZnO. Synthesis routes such as sol–gel technique [6], combustion method [7], polyol method [8], sonochemical method [9], hydrothermal method [10] and simple soft chemical route [11, 12] have been employed to improve the performance of ZnO nanoparticles.

Among all the methods, simple soft chemical route offers good tailoring of the size, and morphology of the nanoparticles. It is also very fascinating, facile and inexpensive method which is suitable for the nano structured materials in large scale [13]. Recent research has been on doping of rare-earth metal with the metal oxide semiconductors due to their unique applications in visible light emitting phosphorous in displays, high power lasers, and other opto-electronic applications. It is because, Nair.et.al reported that they have partially filled 4 f shells, and if incorporated into suitable materials, their infra-4 f optical

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transitions become possible because of splitting induced by the crystal field in the matrix [14]. Liu.et.al reported Nd^{3+} into ZnO and studied its luminescence properties [15] and Karthikeyan.et.al reported linear and nonlinear optical properties of Dy^{3+} doped ZnO nanoparticles [16]. In order to increase the carrier concentration samarium is added as the dopant. Also, Sm^{3+} has a standard has an ionic radius of 1.04 Å which is appreciably higher than that of Zn which is 0.74 Å [17]. In this paper, we have extensively reviewed the effects of antibacterial efficiency and photoluminescence property of rare-earth (Sm) doped ZnO nanoparticles. To the best our knowledge, this is the first report on the work of Sm doped ZnO nanoparticles synthesized by simple soft chemical route for biomedical applications.

2 Experimental details

2.1 Synthesis process

ZnO:Sm nanoparticles were synthesized using a simple soft chemical route. Zinc Acetate dihydrate (0.2 M) was dissolved in de-ionized water. Samarium nitrate was used as a dopant precursor with various concentrations as 2, 4, 6 at.% respectively. A suitable amount of sodium hydroxide (NaOH) solution was added to keep the pH of the starting solution at 7. The obtained mixture solution is stirred for 2h under the temperature of 85 °C. The precipitate formed is separated out carefully by filtration and washed several times thoroughly with a mixture of ethanol and water in the ratio 1:3. The product is then dried in an oven at a temperature of 100 °C for 2 h and the powder finally calcined at 550 °C for 3 h to get the ZnO nanoparticles in its final form.

2.2 Characterization of Bi doped ZnO nanoparticles

The structural properties of synthesized nanoparticles were obtained using X-ray diffractometer (PANalytical-PW 340/60 X'pert PRO) with Cu-Kα radiation (1.5406 Å). Photoluminescence (PL) spectra were studied using Spectroflurometer (JobinYvon_FLUROLOG-FL3-11). Morphology of the sample was observed using Field Emission Scanning Electron Microscope (FESEM) (Hitachi SU8000), Transition Electron Microscopy (TEM, Hitachi H-7100) and the elemental composition analyses were made using Energy Dispersive X-ray analysis (EDX) (Model: JEOL-JSM 6390 with attachment INCA-Penta FETX3 OXFORD).

2.3 Antibacterial activity

The antibacterial activity of the synthesized ZnO nanoparticles was tested against Staphylococcus aureus (*S. Aureus*) (Gram-positive) and Escherichia coli (*E. coli*) (Gram-negative) bacteria using the well diffusion method. The both microorganisms were inoculated on Luria broth (LB) agar plate, and then the concentration of Sm:ZnO nanoparticles (200 µL/mL) were added to the well present in the LB agar plate. A reaction mixture containing no ZnO nanoparticles was put in the well in the LB plate and cultured under the same condition as the control test. All the LB plates were incubated at 37 °C overnight. After incubation, the plates were observed in the presence of a zone of inhibition.

3 Results and discussions

3.1 X-ray diffraction (XRD) analysis

Figure 1 shows the X-ray diffraction pattern of the undoped and Sm doped ZnO nanoparticles. All the diffraction peaks are well matched with JCPDS card (34-1451) which confirms the hexagonal wurtzite structure of ZnO nanoparticles. No other peaks such as metallic zinc and ZnO_2 phase were observed. The intensity of the peaks is found to be decreased as the concentration of Sm is increased. Furthermore, the diffraction peaks of Sm doped ZnO nanoparticles, indicating the substitution of Sm^{3+} ions into the Zn^{2+} sites in the lattice of ZnO because, the ionic radius of Sm is little larger than that of Zn.

The particle size was calculated using Scherr's formula [18],

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where λ is wavelength of X-ray used (1.5406 Å), β is the (101) Full-width Half maximum (FWHM) intensity and θ is the angle of the diffraction.

The lattice constant 'a', and 'c' are calculated using the relation [19],

$$1/d^2 = (4/3(h^2 + hk + k^2)/a^2) + (l^2/c^2) \quad (2)$$

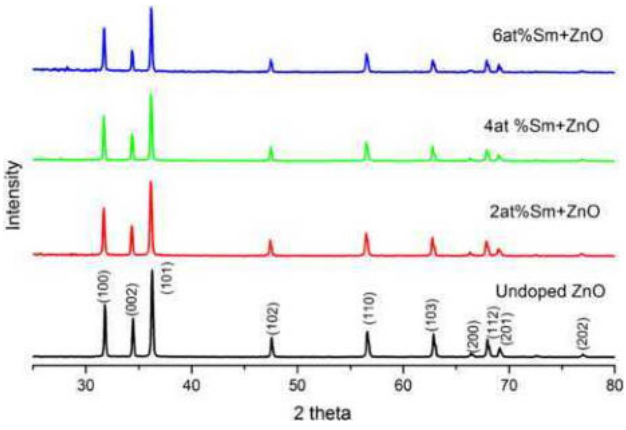

Fig. 1 XRD patterns of undoped and Sm doped ZnO nanoparticles

The volume of the unit cell (v) is calculated using the Equation [20],

$$V = \sqrt{3}/2\ (a^2c) \quad (3)$$

Micro strain of the nanoparticles were calculated using the formula [21],

$$\varepsilon = (C - C_0/C_0) \quad (4)$$

The calculated lattice parameters and particle size of the nanoparticles are listed in Table 1. The average particle size decreases as Sm concentration increases, which is possibly due to the interference of the Sm cation to the ZnO lattice. The calculated lattice parameters 'a' and 'c' values show small variations as the doping level increases, which is due to the substitutional incorporation of Sm^{3+} ions into the ZnO lattice. The undoped ZnO clearly shows the compressive strain, whereas the doped ZnO samples exhibit tensile strain. The compressive strain created in the former may be due to the oxygen vacancies in the lattice. The transition from the compressive strain to the tensile strain may be due to the incorporation of the Sm ions into the ZnO lattice either by substitution, interstitial and/or anti-site incorporation.

3.2 Morphology and EDX

The FESEM images of undoped and Sm doped ZnO nanoparticles were shown in Fig. 2. These images clearly show that the average particle size is of the order of nano region. The average particle size decreases with the increase of the Sm concentration in ZnO lattice. This smaller particle more readily allows them to interact and penetrate to the interior of the bacteria by destroying it. The particle size is also evidenced from the TEM image Fig. 3b. From the TEM image, no aggregate is observed, in addition, no impurities have been found in ZnO material. The EDX spectra of the undoped and Sm doped ZnO nanoparticles are shown in Fig. 3a. The components present in the synthesized nanoparticles were confirmed by the presence of Zn, O, and Sm atoms.

3.3 Photoluminescence

Figure 4 shows the photoluminescence spectra of undoped and Sm doped ZnO nanoparticles. A strong emission peak at 397 and 420 nm is absorbed. There is a gradual increase of intensity as the dopant level increases. The blue emission band at centered at 420 nm may be originated from the reconstruction of the photogenerated hole with an electron occupying the oxygen vacancy. The strong peak at around 420 nm is assigned to the zinc interstitials (Zn_i) [22]. It is observed that the broad emission peak in the visible region, centered at 397 nm is associated with the near band-edge emission (NBE) of ZnO results due to the band to band electronic transition [23–26].

The variation of the emission intensity in Sm content could be ascribed to the variation of the average particle size with Sm content. The peak at 466 nm is associated with the blue emission that originates from the transition of electrons from the donor level of singly ionized oxygen vacancies to the valence band [27]. The presence of excess surface defects leads to the stronger blue emission corresponding to the formation of hydroxyl radicals [28]. These hydroxyl radicals are responsible for the inhibition of bacterial growth.

3.4 Antibacterial efficiency

The antibacterial activity of ZnO and Sm doped ZnO nanopowders were investigated against gram negative (*E. Coli*) and Gram positive (*S. Aureus*) bacteria respectively. From the Fig. 5 it is observed that there is no zone of inhibition over the control. The variation in the diameter of the zone of inhibition is plotted as a bar diagram (Fig. 6). It is observed that Sm influences the higher antibacterial activity than that of the undoped ZnO nanoparticle. This increase in the efficiency of the antibacterial activity may be due to the following reasons (i) the generation of reactive oxygen species (ROS) (ii) size of the particle (iii) release of Zn^{2+} ions. Release of more number of Zinc ions is induced in the system as the substitution of Sm ions into the Zn sites results in a larger number of Zn interstitials. It is well known that interstitial Zn ions have more probability to become free

Table 1 Structural parameters of undoped and Sm doped ZnO nanoparticles

Sm doping level (at.%)	2θ	D (nm)	*Lattice constants (Å)		v $(Å)^3$	Strain $\varepsilon \times 10^{-4}$
			a	c		
0	36.284	56.04	3.270	5.211	47.606	9.604
2	36.204	56.79	3.256	5.218	49.032	0.235
4	36.188	42.59	3.258	5.220	47.990	0.026
6	36.178	42.60	3.260	5.223	48.079	0.331

*Standard values: a = 3.2498 Å, c = 5.2066 Å (JCPDSCardNo. 36-1451)

2θ bragg's angle, *D* crystallite size, *v* volume of the unit cell and *ε* micro strain

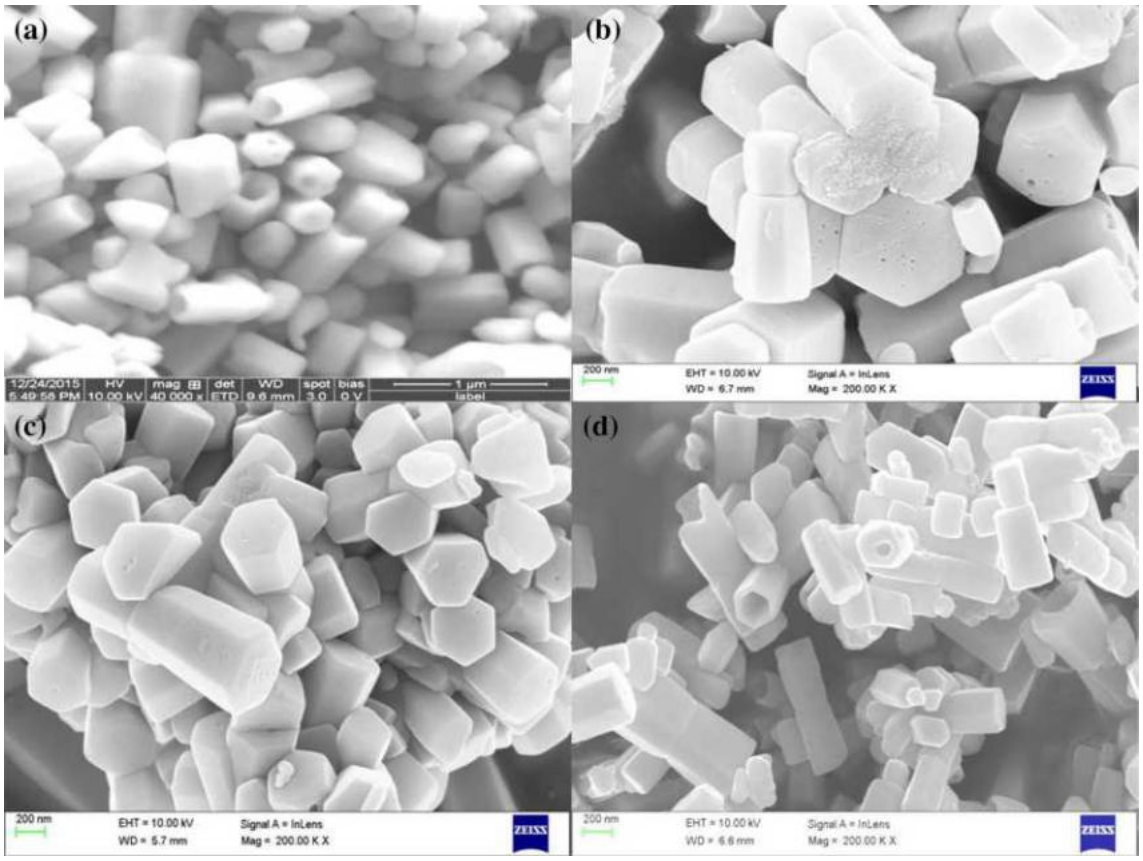

Fig. 2 FESEM images of undoped and Sm doped ZnO nanoparticles **a** undoped, **b** 2 at.%, **c** 4 at.% and **d** 6 at.%

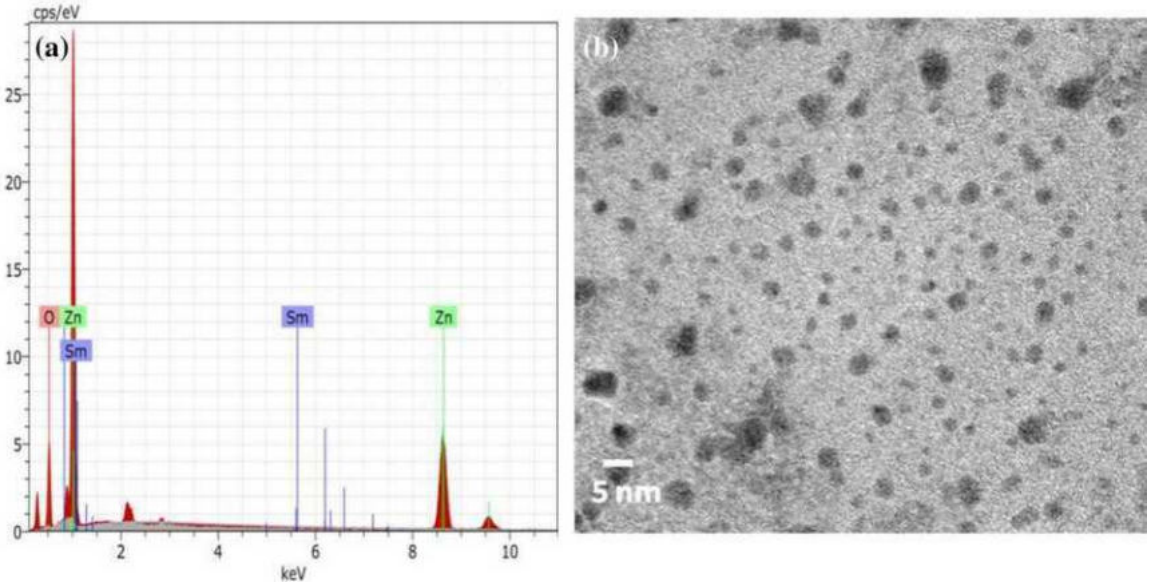

Fig. 3 **a** EDAX profile of 6 at.% Sm :ZnO, **b** TEM image of undoped ZnO nanoparticles

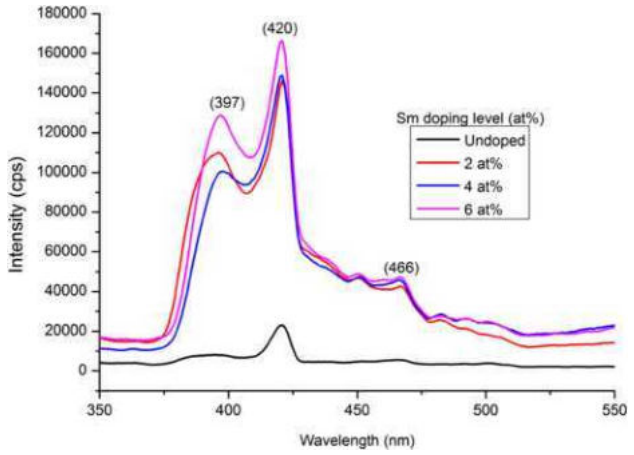

Fig. 4 Photoluminescence spectra of undoped and Sm doped ZnO nanoparticles

from the lattice. This released Zn^{2+} ions have strong electrostatic interaction with the membranes of bacteria cells, leading to a considerable damage to the bacterial cell. This generation of ROS can be written as follows [29–32]:

$$ZnO + h\nu \rightarrow h^+ + e^- \quad (5)$$

$$h^+ + H_2O \rightarrow OH^* + H^+ \quad (6)$$

$$O_2 + e^- \rightarrow O_2^{*-} \quad (7)$$

$$O_2^{*-} + H^+ \rightarrow HO_2^* \quad (8)$$

$$H^+ + HO_2^* + e^- \rightarrow H_2O_2 \quad (9)$$

$$H_2O_2 + O_2^{*-} \rightarrow OH^* + O_2^{*-} + OH^- \quad (10)$$

When compared with the hydroxyl radicals and superoxide anions, hydrogen peroxide is more toxic so that it can easily damage the cell wall of the bacteria. The peak observed at 466 nm at the PL spectra is the evidence for the presence of singlet oxygen. This singlet oxygen is produced in the presence of superoxide anion by hydrogen peroxide which is more toxic than it. The presence of ionized vacancy is evidenced from the observed peak centered at 466 nm in the PL spectra. The release of Zn^{2+} ions is also one of the reasons for the efficiency of antibacterial activity. It is noteworthy to mention here that the antibacterial efficiency is found to be higher than that of the undoped when the Sm doping level was at 6 at%.

4 Conclusion

Undoped and Sm doped ZnO nanoparticles have been successfully prepared by simple soft chemical route. These ZnO nanoparticles were demonstrating antibacterial

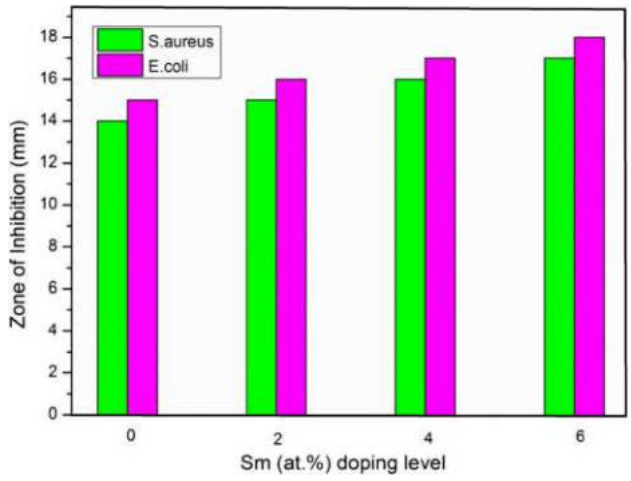

Fig. 6 Variation in the zone of Inhibition caused by ZnO+Sm nanoparticles

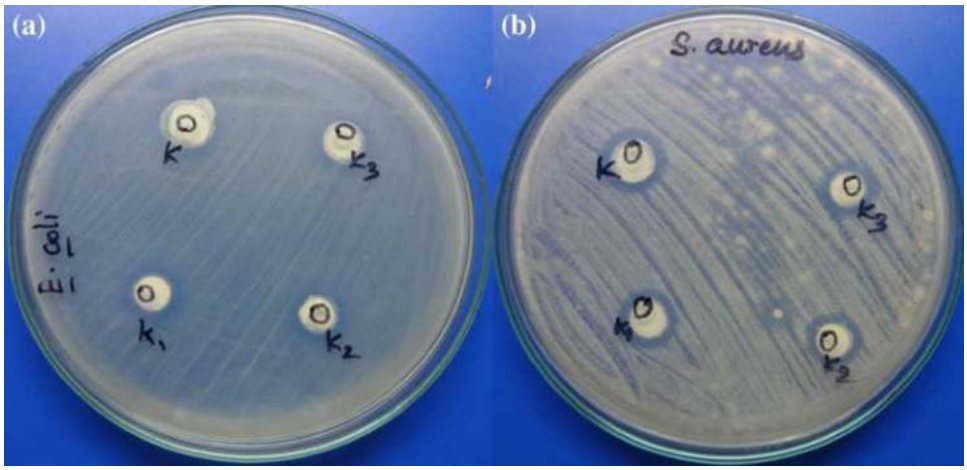

Fig. 5 Antibacterial activity of ZnO:Sm nanoparticles against **a** *E. coli* and **b** *S. aureus* bacteria

activity with the model bacterial the *E. coli* and *S. aureus*. The zone of inhibition increases as the dopant concentration is increased. The antibacterial activity of ZnO nanoparticles was apparent from the zone of inhibition so these nanoparticles are bellowed to act as preventive for bacterial contamination. An effect and effectiveness in changing bacterial growth, a finding which may be lead to valuable invention in the future in various fields like in antimicrobial systems as well as medical devices.

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Investigations on the growth, Structural, Optical, Mechanical and Cytotoxicity Properties of a Semiorganic Single Crystal: Cytosinium Nitrate

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ABSTRACT

Aim: To synthesize and grow pyrimidine based cytosinium nitrate single crystals and characterize the grown crystals for structural, optical, mechanical, dielectric and proliferation assay. Methodology

Cytosinium nitrate, a semi organic material was synthesized and single crystals were grown from aqueous solution employing the technique of controlled slow evaporation.

Results and Discussion: The lattice parameter of the grown crystal was determined using single crystal X – ray diffractometer. Fourier transform infrared spectral analysis is carried out to identify the functional group of the grown crystal. The grown crystals were characterized using UV – Vis – NIR and dielectric analysis. Mechanical strength was estimated using Vickers microhardness test. The crystal exhibits reverse indentation size effect and belongs to soft material category. A sharp emission peak was observed in photoluminescence spectrum at 378 nm. The anti – proliferative property of grown crystal was tested on human lung cancer cell line A549.

Conclusion: All these investigations were used to reveal the properties like structural, dielectric parameters, optical, mechanical, surface morphology and biological activity.

Key Words: Crystal growth, Optical materials, Mechanical properties, Dielectric measurements, Photoluminescence

INTRODUCTION

In the past few decades, there has been extensive investigation made in the design and characterization study of inorganic, organic and semiorganic nonlinear optical(NLO) materials [1]. Nonlinear optical materials are very significant because of its wide applications in the field of laser technology, laser communication, optoelectronic and photonic applications [2]. In particular organic materials possessing a large third – order non linearity have attracted many researchers owing to their potential application in optical switching and sensor protection [3]. Synthesis and characterization of novel materials for third order nonlinear optical application has gained much attention by the researchers [4]. Cytosine is one of the five main nucleic acids used in storing and transporting genetic information within a cell [5]. The single crystal structure of anhydrous cytosine [6] and cytosine monohydrate [7] was reported. Several researchers reported the single crystal structure of cytosine derivatives [8-11]. Most of these complexes are dealt with application of crystal engineering to active pharmaceutical and biological applications. The epigenetic mechanism such as methylation of cytosine in DNA was discussed by Plitta et al [12]. The molecular recognition of cytosine based on proton–transfer reaction elucidated by Portalone et al [13]. Kistenmacher et al [14] made systematic study on enzyme – metal – nucleic

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acid ternary complexes with cytosine. It is identified that cytosine may be an interesting material to optimize them for nonlinear optical limiting applications. Because the protonation of cytosine base pair carries important structural implications in crystal engineering. In particular the base pair ability known to self – assemble in acidic media. Though, the structure of cytosinium nitrate has been reported earlier [15], there are no earlier reports on the bulk crystal growth of cytosimium nitrate. In our present investigation we report the single crystal XRD, powder XRD, FTIR, UV – Vis - NIR optical analysis, photoluminescence, dielectric, Vickers microhardness, etching studies and proliferation Assay on cytosinium nitrate single crystal.

MATERIALS AND METHODS

Crystal Growth

Cytosine ($C_4H_5N_3O$) and nitric acid (HNO_3) was dissolved in deionised Millipore water at room temperature. The resultant solution was stirred well to obtain clear homogeneous solution. The prepared solution was filtered using Whatman filter paper and taken in a beaker. Beaker containing the solution was closed with perforated polythene paper and kept in an undisturbed dust free condition. Slow evaporation at room temperature yielded transparent single crystals of cytosinium nitrate (CN) of 7 mm × 2 mm × 1 mm size were harvested in a growth period of 15 days. The as grown single crystals of CN are shown in Fig. 1.

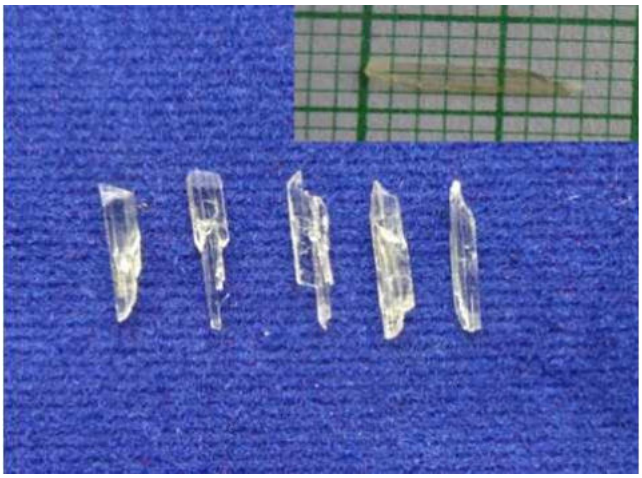

Figure 1: As grown single crystals of cytosinium nitrate.

RESULTS AND DISCUSSION

X – ray Diffraction Analysis

Single crystal X – ray diffraction data of the grown CN crystal were collected on a BRUKER NONIUS X – ray diffractometer using monochromated Cu Kα radiation (λ = 1.5408Å) at 293K. From the single crystal X – ray diffraction analysis it is confirmed that grown CN belongs to triclinic system. The obtained cell parameters are in good agreement with the corresponding reported values of Cherouana et al. [15] as is evident from Table. 1

Table 1: Crystallographic data of CN

S. No	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β*(°)	γ (°)	Volume (Å³)
1. Present work	6.509	6.726	9.222	72.02	72.85	73.75	358.9
2.Reported [15]	6.530	6.724	9.211	71.96	72.84	73.75	359.4

Powder X – ray diffraction

The powder X – ray diffraction pattern of the grown single crystal of CN was recorded on a REICH SIEFERT X – ray diffractometer instrument using Cu Kα (1.540 Å) radiation employing the reflection mode for scanning. The finely crushed sample was scanned in the 2θ values ranging from 10 – 80° at a rate of 1°/min. All the observed reflection lines were indexed with the help of computer program AUTOX 93 (Fig. 2).

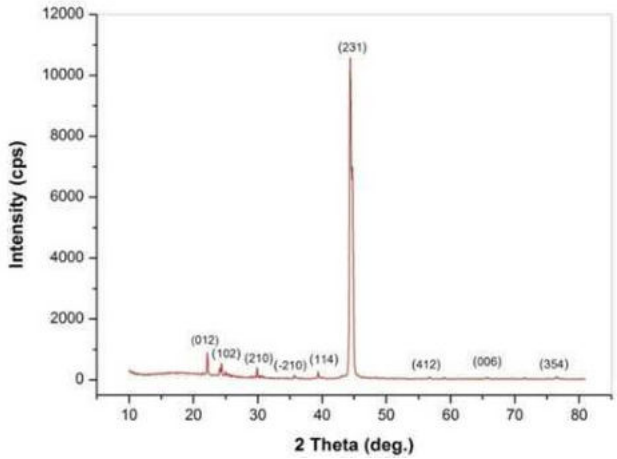

Figure 2: Powder X-ray diffraction pattern of CN.

Fourier Transform Infrared (FTIR) spectrum

In order to identify the functional groups, the FTIR spectral analysis of CN was carried out in the middle infrared region extending from 400 – 4000 cm^{-1} using a Perkin Elmer FTIR spectrometer by KBr pellet technique. The recorded FTIR spectrum is shown in Fig. 3. In the higher energy region, the NH_2 asymmetric and symmetric stretching vibrational frequencies are observed at 3342 and 3214 cm^{-1} respectively. The peak at 2932 cm^{-1} is attributed to the symmetric stretching vibration of NH. The strong band at 1728 cm^{-1} is due to the C=O stretching vibration. The NH_2 deformation and

wagging vibrations are observed at 1665 cm^{-1}. The intense peak at 1546 cm^{-1} arises due to C – NH stretching vibration. The strong band appears at 1381 cm^{-1} in the spectrum is assigned to C=C stretching vibration C–N stretching vibration observed at 1201 cm^{-1}. The peak at 792 cm^{-1} is due to the C = O bending vibration. The peaks due to NO_2 deformation are observed at 632 and 576 cm^{-1}. The prominent vibrational frequencies of FT-IR spectra with tentative assignments of CN crystal are listed in Table.2.

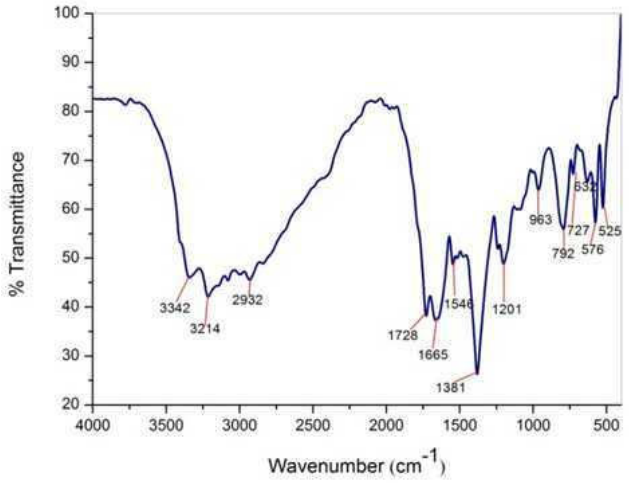

Figure 3: FT – IR spectrum of CN crystal.

Table 2: FT-IR band assignments of CN single crystal

Wave number (cm^{-1})	Assignments
3342	NH_2 asymmetric stretching vibration
3214	NH_2 symmetric stretching vibration
2932	NH symmetric stretching vibration
1728	C = O stretching vibration
1665	NH_2 deformation
1546	C – N – H stretching vibration
1381	C = C stretching vibration
1201	C – N stretching vibration
963	C – C – H deformation
792	C = O bending vibration
727	NO_2 deformation
632	–O – N = O deformation
576	–O – N = O deformation

Linear optical analysis

The UV – Vis – NIR spectrum gives more information about the band structure and optical quality of material. The absorption or emission of radiation and cut – off wavelength of grown crystals are prime factor for optical applications [16]. The UV – visible optical transmission spectrum of CN crystal was recorded between 190 – 1100 nm using Perkin – Elmer Lambda 35 spectrophotometer. The recorded transmittance spectrum of CN single crystal is shown in Fig.4. The crystal has wide transparency in the entire UV and visible region. The CN crystal is optically transparent in the entire visible region with 97% transmittance with lower cut-off wavelength of 291 nm. The optical absorption coefficient (α) was calculated using the following relation.

$$\alpha = \frac{1}{t}\log\left(\frac{1}{T}\right)$$

Where, T is the transmittance and t is the thickness of the crystal. The dependence of the optical absorption coefficient on the photon energy helps us to study the band structure and the types of transition of electrons [17]. The band gap energy of the material is calculated using the following relation

$$\alpha = \frac{A(h\upsilon - Eg)^{1/2}}{h\upsilon}$$

Where, A is a constant, E_g is optical band gap of the crystal, h is Planck's constant and υ is the frequency of the incident photon. The E_g could be estimated from the Tauc's plot of variation of $(\alpha h\upsilon)^2$ versus $h\upsilon$ and shown in Fig. 5. E_g is obtained from the extrapolation and interception of the linear part of the graph with X – axis [18]. The band gap energy was found to be 4.1eV. The extinction coefficient is an essential parameter to examine amount of absorption when electromagnetic waves propagates through a medium. The absorption coefficient (α) is related to the extinction coefficient K by

$$K = \lambda\alpha / 4\pi$$

Where, K is the extinction coefficient, λ is the wavelength and α is the absorption coefficient. Fig. 6 shows that variation of extinction coefficient (K) as a function of wavelength.

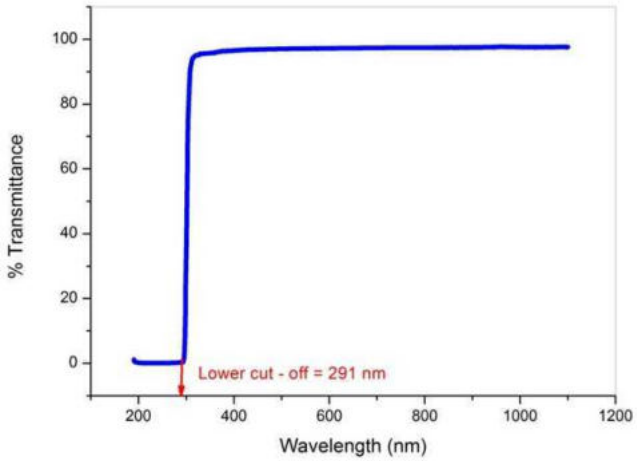

Figure 4: UV – Vis – NIR transmittance spectrum of CN crystal.

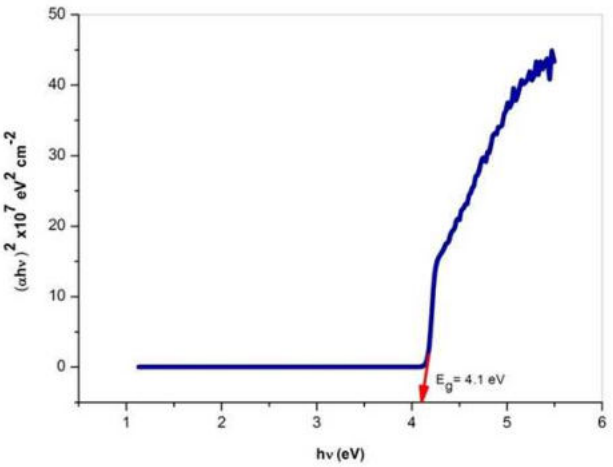

Figure 5: Plot of $(\alpha h\gamma)^2$ versus hγ of CN crystal.

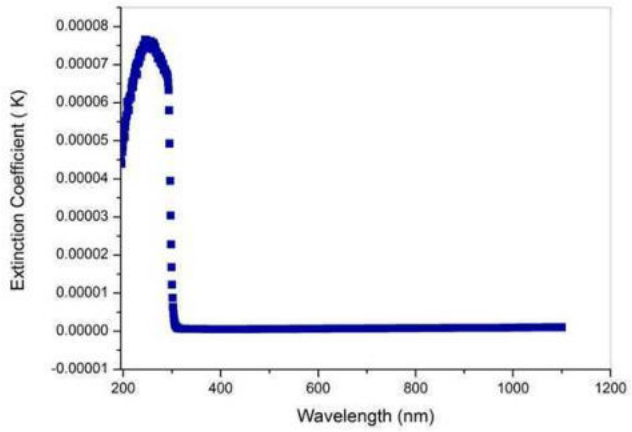

Figure 6: Dependence of extinction coefficient with wavelength of CN crystal.

Dielectric studies

The different polarization effects, relaxation phenomena and optical properties of solids can be explained by analyzing dielectric behaviour [19]. By employing the HIOKI 3536 LCR instrument the dielectric measurement were carried out on CN single crystal in the frequency region from 1 KHz to 5 MHz. Silver coated CN sample of 2mm thickness was used as the parallel plate capacitor to form dielectric medium. The capacitance of the sample was recorded by varying the frequency at different temperatures (Room temp, 50 °C, 70 °C and 90 °C). The dielectric constant of the material was calculated using equation $\varepsilon' = Cd / (A\varepsilon_0)$. Where C is the capacitance of the sample, d is the thickness of the crystal, ε_0 is the permittivity of free space ($\varepsilon_0 \approx 8.854 \times 10^{-12}$ F / m) and A is the area of the sample. The variation of dielectric constant with frequency of CN crystal is shown in Fig. 7. From Fig. 7 it is observed that, the dielectric constant decreases with increasing frequency and reaches a constant value. The high value of dielectric constant at lower frequencies may be due to the contribution of all the four polarizations namely space charge, orientation, electronic and ionic polarizations and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually [20]. The dielectric loss was calculated using the equation $\varepsilon'' = \varepsilon' \tan \delta$ and the variation of dielectric loss with varying frequency is depicted in Fig. 8. From the plot one can understand that the dielectric loss decreases with increase of frequency at different temperatures. The low dielectric loss value in high frequency for the sample suggests that the crystal has good optical quality and lesser defects.

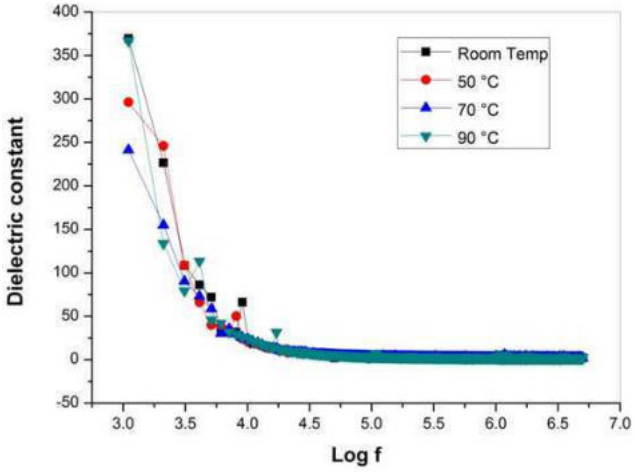

Figure 7: Frequency dependent dielectric constant of CN at various temperatures.

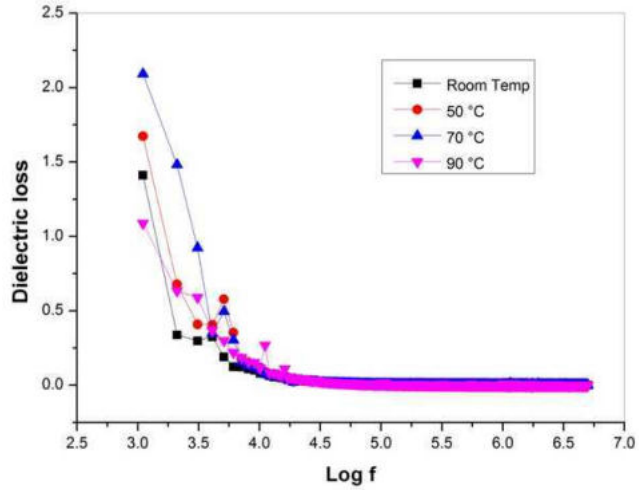

Figure 8: Frequency dependent dielectric loss of CN at various temperatures.

Photoluminescence study

Optical properties of the as grown CN single crystal were analyzed by photoluminescence spectroscopy. The near – band – edge photoluminescence of solids gives important information about the quality and composition of materials by probing the electron [21]. Photoluminescence is the ab-

sorption of photon energy promotes a valence electron from its ground state to an excited state. The excited energy is released as short wavelength light [22]. Photoluminescence of CN crystal is recorded with a Cary Eclipse fluorescence spectrometer (Type – Savitzky Golay) with auto excitation filter mode in the range 340 – 600 nm. The sample was excited at 320 nm. Photoluminescence spectrum of CN crystal is shown in Fig. 9. Spectrum shows a broad emission peaked at 378 nm which may be due to the vibrations in crystal lattice by changing incident power and sample temperature[23]. Intensity is slowly decreases in higher wavelength region. The result indicates that the emission of crystal is in violet region. The energy band gap of CN crystal has been calculated to be 3.2 eV using the formula Eg = 1240/ λ (eV)

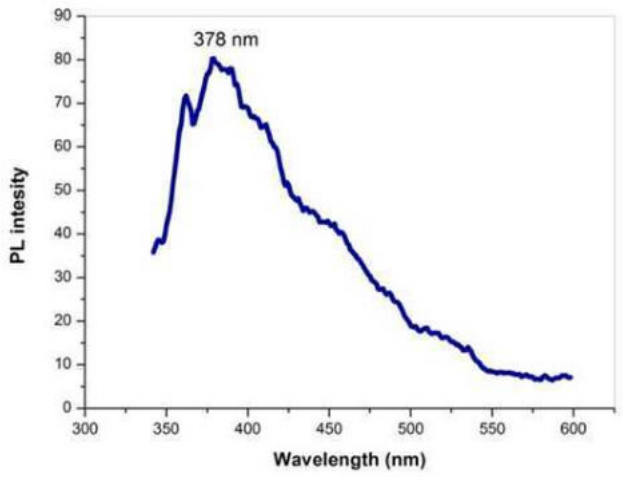

Figure 9: Photoluminescence spectrum of CN crystal.

Vickers microhardness analysis

For the commercial usage and device fabrication microhardness indentation analysis play a major role for conforming the mechanical stability. Microhardness studies were carried out on flat surface of the grown crystal of CN by using Shimadzu HMV-2000 hardness tester. Several trials of indentation were carried out for different loads (5g, 10g, 25g, 50g and 100g) at room temperature. Vickers hardness number (H_v) was calculated using the relation $H_v = 1.8544\ P/d^2$ (kg/mm^2), where P is the applied load in kg and d is the average diagonal length of indentation in mm. For loads above 100 g cracks started developing around the indentation impression. The variation of Vickers hardness values (H_v) with applied is shown in Fig. 10. Hardness (Hv) value increases with the increasing load. This type of variation of hardness is termed as reverse indentation size effect (RISE). In order to analyse the reverse indentation size effect (ISE), Meyers law was used by fitting the experimental data from the relation $P = Ad^n$, where P is the applied load, A is a constant, d is the average diagonal length of the indenter and n is the work hardening coefficient. By plotting log P versus log d (Fig.11), the value of work hardening coefficient (n) is calculated as 2.3. According to Onitsch [24], n lies between 1 and 1.6 for hard materials and for soft materials it is above 1.6. This implies that cytosinium nitrate belongs to soft material category.

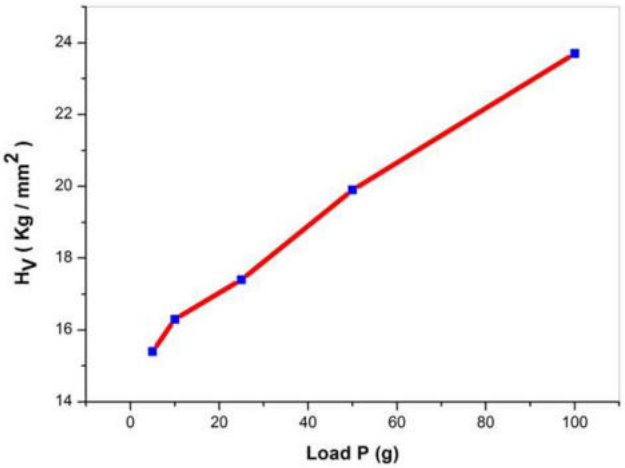

Figure 10: Variation of hardness number (H_v) Vs load (P) for CN crystal.

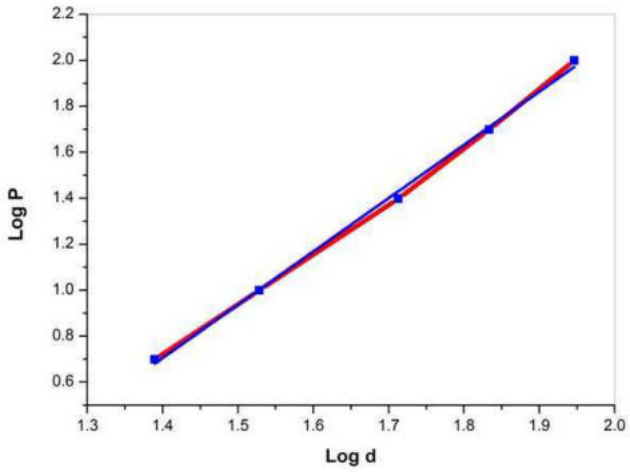

Figure 11: Variation of Log d Vs Log P for CN crystal.

Chemical etching analysis.

The microstructural analysis of the grown crystal by etching the surface gives more information about dislocations, imperfections and surface morphology. Optical behaviour of the NLO material in particular nonlinear efficiency mainly depends on the quality of the crystal. So it is very essential to study the surface morphology by etching of the as-grown crystal [25]. The etching of CN crystal was carried out by using double distilled water as an etchant. The cytosinium nitrate single crystal was immersed in water for few seconds and dried with tissue paper to remove the water molecules. The etch patterns in the crystal was examined using normal incident light type microscope. The photographs of etch

patterns were captured by Motic camera fitted with optical microscope. The microphotograph of CN crystal for etching time 5 s is shown in Fig. 12 (a). The figure shows predominant parallel ridges on crystal. Some of them extended over the surface while others are partly extended. Further the etching period was increased to 10 s and the etch pattern is shown in Fig. 12 (b). After etching for 10 s, the ridges were elongated in large number and forms different etch pattern. From the etching study there is such a periodicity seen in distribution of etch pattern.

Figure 12 (a): Etch pattern of CN single crystal (etching time 5 s).

Figure 12 (b): Etch pattern of CN single crystal (etching time 10 s).

Proliferation Assay

The synthesized cytosinium nitrate was evaluated for its anti-proliferative activity. For this, the cytosinium nitrate was tested for its anti-cancer properties on human lung cancer cell line A549. This assay was performed for determining the IC50. The cells were maintained in Dulbecco's modified Eagle's medium (DMEM) (Sigma-Aldrich Chemie Gmbh), supplemented with 10% fetal bovine serum (HyClone), 100IU/ml penicillin, 100mg/mL Streptomycin, and 2mmol/L L-glutamine (Sigma). Cells were seeded into 96-well plates at 5000 cells per well and incubated overnight. The medium was replaced with a fresh one containing the desired concentrations of CN dissolved in DMEM, ranging from 25µM, 50µM, 75µM, 100µM, 250µM and 500µM. Cells with cytosinium nitrate were incubated further for 24h and 48h. After treatment period, medium with cytosinium nitrate was removed and washed with 1XPBS (Phosphate buffered saline). Thereafter 100µl of MTT (3, 4, 5-dimethylthiazol-2yl)-2, 5-diphenyltetrazolium bromide)dye dissolved in serum free medium at the concentration of 5mg/mL, was added to the cells and incubated for 3h in CO_2 incubator. After 3h, the medium was removed and the formazan crystals were dissolved in 100µl of acidified isopropanol. The purple color of the formazan product was read in Robonik ELISA plate reader at 570nm. The percentage of cell viability was calculated with respect to control cells cultured at conditions similar to treated cells. Triplicate was maintained for all concentrations, including control cells.

Results indicate that cytosinium nitrate in the concentrations from 25µM to 250µM did not show any anti-cancer activity. Both control and treated cells have similar optical density upto 250µM. At 500µM concentration, a drastic decrease was observed in cell viability. At 24h, the viability was about 28%, which further decreased to 23% at 48h (Fig.13). This significant decrease may be due to the change in pH of the medium. At high concentrations such as above 250 µM, the nitric acid, component of cytosine nitric acid, induce change in pH towards acidicity. Change in color of the medium from pink to colorless even before the addition of MTT reagent for the MTT assay was probably the reason of cell death and cannot be considered due to toxicity of the compound *per se*. Study on the pharmacological effects of bioactive compounds on cancer treatments and prevention has increased dramatically over the past few decades. Many novel compounds, complexes of metals and heterocyclic combinations have been demonstrated to be cytotoxic and to possess anticancer activities in various cancer cells without exhibiting significant damage to normal cells [26 – 27]. In the present investigation, there was no significant toxicity demonstrated by the cytosine derivative at lower concentrations upto 250 µM, however, toxicity at 500 µM either did not seem to be evident due to its toxic nature, but due to high acidic nature of the compound itself. Cytosine being a significant bioactive molecule in its physiological perspective, it is believed by the authors that its modification further to make it toxic may provide a potential anti-cancer related bioactive molecule.

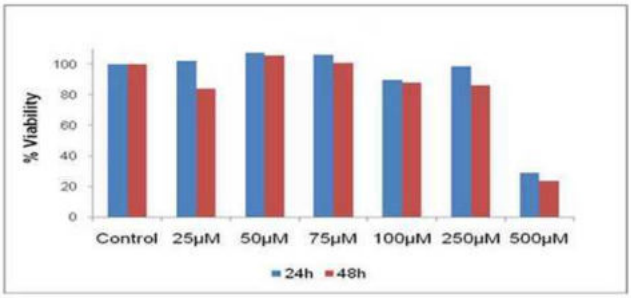

Figure 13: MTT assay for cytosinium nitrate against A549 cell line.

CONCLUSION

Cytosinium nitrate single crystals of size 7 mm × 2 mm × 1 mm were grown from aqueous solution by slow evaporation technique at room temperature. The grown crystal belongs to the triclinic system with centrosymmetric space group P_1. Various functional groups were present in the grown crystal was confirmed by FT IR analysis. It is evident from UV – Vis – NIR optical transmittance, the CN crystal has a wide transparency range in the entire UV visible and near infra red region. The low value of dielectric constant and dielectric loss of CN at higher frequencies revealed from dielectric measurements. The Vickers microhardness value increases with increase of load and shows reverse indentation size effect. The value of Meyer's index n turned out to be higher than 1.6 for CN and the material belongs to soft materials category. The variation of dielectric constant and dielectric loss were studied with varying frequency at different temperatures. Etching analysis shows the presence surface dislocations in the sample. The violet emission was identified by photoluminescence spectrum. Anticancer property was tested on human lung cancer cell line A549. No significant toxicity was demonstrated even by increasing concentrations.

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Conflict of interest: Nil

Ethical approval: Not required

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Revealing the influence of the Bi dopant on the structural, photoluminescence and antibacterial properties of ZnO nanoparticles

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Abstract
Undoped and Bi doped zinc oxide nanoparticles were synthesized by soft chemical method. The effects of doping on structural and optical properties of Bi doped nanoparticles were investigated. The product was subjected to powder X-ray diffraction, field emission scanning electron microscope, transmission electron microscope and photoluminescence techniques. The crystallite sizes of synthesized samples were calculated from the powder XRD patterns, the crystalline size is variable from 42 to 56 nm for undoped and Bi doped ZnO nanoparticles respectively. The photoluminescence intensity of the Bi (7 at.%) doped ZnO was much higher than that of undoped ZnO nanoparticles. The undoped and Bi doped ZnO nanoparticles are subjected to antibacterial bio activity against both *Staphylococcus aureus* and *Escherichia coli* bacteria in order to find the materials efficiency towards the bacterial strains and it is found that there is a good zone of inhibition.

1 Introduction

Nanostructured ZnO particles are very much attractive for several applications in both microelectronic and optoelectronic devices. It has a wideband gap oxide semiconductor with a direct energy gap 3.37 eV, making it attractive nanoelectronic and photonic applications. Therefore, ZnO absorbs UV radiation due to band-to-band transitions. It can be used as transparent conductive oxide (TCO) materials, mainly for applications such as gas sensing, liquid crystal displays and photovoltaics [1, 2]. ZnO is also low-cost, plentiful in the nature and non toxic. Zinc oxide (ZnO) nanoparticles have been demonstrated to have enormous applications like as solar cells, transparent conducting electrode in photovoltaic, gas sensor, acoustic wave devices and laser diodes [3–9]. The semiconductor and optical properties of ZnO are extremely energy harvesting like photo thermal conversion system, gas sensor, and optical position sensors. ZnO is good candidates for solar energy conversion materials [10–13]. A number of investigations on the synthesized a variety of ZnO nanoparticles, including hydrothermal method [14], combustion synthesis technique [15], microwave synthesis [16], wet chemical method [17] and simple soft chemical route [18, 19]. Low temperature solution simple soft chemical route has high potential, simple, cost effective and energy saving route [20–22]. ZnO has been enhancing its properties with suitable doping material for a variety of optoelectronic devices. Doped ZnO nanoparticles have been attracted much attention because their inevitable role in transparent conducting electrodes (III B elements) and ferroelectric (Li, Bi or Mg) in optoelectronic devices. Bismuth has been an important impurity in ZnO is a good candidate as efficient applications due to much bigger radius of Bi^{3+} (0.103 nm) than that of Zn^{2+} (0.072 nm) producing the large mismatch in the lattice [23]. It can be used to favor trapping of photogenerated electrons, reducing the rate of recombination processes between electrons and holes [24, 25].

In this work, undoped and Bi doped ZnO nanoparticles were synthesized by simple soft chemical route. Even though, to our best knowledge, there are few reports of Bi doped ZnO nanoparticles, the study of the combined structural, photoluminescence and antibacterial properties of Bi doped ZnO is not so far. In this present work the structural, optical, morphological and antibacterial activities of Bi

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doped ZnO nanoparticles prepared by soft chemical route were examined.

2 Materials and methods

2.1 Preparation of samples

Undoped and Bi doped ZnO nanoparticles were synthesized by a simple soft chemical method. All starting materials were introduced analytic reagent. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) with 0.2 M concentrations diluted in deionized water. Bismuth nitrate ($Bi(NO_3) \cdot H_2O$) used as a dopant source is added to a small amount in the starting solution. The doping level is varied by changing the atomic percentage of [Bi/Zn], in the solution, from 0, 3, 5 and 7 at.% respectively. Required amount of NaOH (0.5 M) solution is added to maintain the pH value of starting solution at 7. The prepared mixture was stirred magnetically for 2 h at a temperature of 85 °C to get homogeneous solution. After the stirring process it was allowed to cool to room temperature and kept undisturbed for 1 h to get the required precipitate. The precipitate formed is separated out carefully by filtration and washed several times thoroughly with a mixture of ethanol and water in the ratio 1:3. The product is then dried in an oven at a temperature of 100 °C for 2 h and finally the powder was obtained by thermal treatment 550 °C for 3 h.

2.2 Characterization of Bi doped ZnO nanoparticles

Powder X-ray diffraction (XRD) measurements were performed in X-ray diffractometer (PANalytical-PW 340/60 X'pert PRO) with Cu-Kα radiation (1.5406 Å) at scanning rate 1θ/min in the 2θ range from 10° to 80°. FESEM images of the sample were gained using a field emission scanning electron microscope (FESEM) (Hitachi SU8000), Transition Electron Microscopy (TEM, Hitachi H-7100) and the elemental composition analyses were made using energy dispersive X-ray analysis (EDX) (Model: JEOL-JSM 6390 with attachment INCA-Penta FETX3 OXFORD). Photoluminescence (PL) spectra were studied using Spectro-flurometer (JobinYvon_FLUROLOG-FL3-11). All measurements carried out at room temperature.

2.3 Measurement of antibacterial activity

The antibacterial activity of the synthesized ZnO nanoparticles was tested against *Staphylococcus aureus* (*S. aureus*) (Gram-positive) and *Escherichia coli* (*E. coli*) (Gram-negative) bacteria using the well diffusion method. The nutrient agar medium was prepared and sterilized by autoclave at 121 °C for 15 min. The medium was poured into the sterile pertiplates and allowed to solidify. The bacterial broth culture was webbed on the agar plates using sterile buds and five wells were made by well cutter. In each well, discs were loaded and the agar plates were incubated at 37 °C for 24 h. After incubation the plates were observed in the zone of inhibition around the well. The diameter of the inhibition zone is measured in mm using a high accuracy antibiotic zone scale. For comparison the zone of inhibition for a standard antibiotic (Gentamicin) is also measured.

3 Results and discussion

3.1 Powder X-ray diffraction (PXRD) analysis

Figure 1 shows the XRD patterns of undoped and Bi doped ZnO nanoparticles. All the diffraction peaks are a reflection of samples indexed to the hexagonal wurtzite structure of ZnO. It fits well with the standard data of the ZnO hexagonal crystalline system (JCPDS card No. 36-1451). In the case of undoped and Bi doped ZnO, the (101) diffraction peak is predominant to over all other diffraction peaks. Additionally, there were peaks marked '*' at the 2θ of (27.93°, 32.71°, 46.20°, and 55.45°) were ascribed to Bi_2O_3 (JCPDS: 712274 & 501088). It suggested there exhibit a minority phase of Bi_2O_3 apart from the ZnO major phase. From the figure, it is seen that as the Bi doping level increases, the intensity of the peaks decreases gradually. This reduction in the intensity may be due to the immigration of Zn atoms into the interstitial positions of the regular zinc sites caused by the substitution of Bi.

The crystallite size of nanoparticles was estimated using the Scherrer's formula [26],

$$D = 0.9\lambda/\beta \cos\theta \quad (1)$$

where λ is the wavelength, β is the full width half maximum and θ is the Bragg's angle. The strongest peak at (101) at 36.2° was used to determine the average crystallite size of ZnO + Bi nanoparticles.

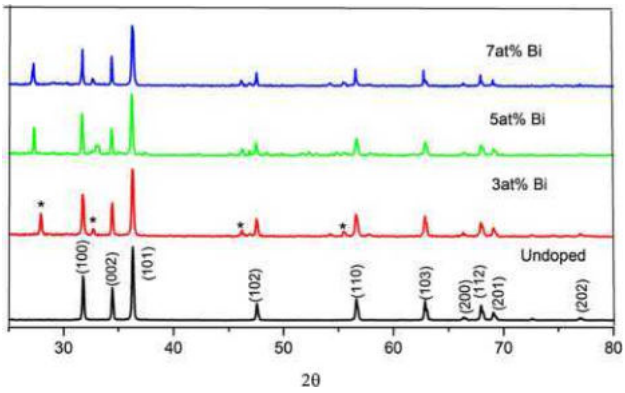

Fig. 1 XRD patterns of undoped and Bi doped ZnO nanoparticles

The lattice constant 'a' and 'c' are calculated using the formula [27],

$$1/d^2 = \left(4/3\left(h^2 + hk + k^2\right)/a^2\right) + \left(l^2/c^2\right) \quad (2)$$

To find out the micro strain for nanoparticles was calculated by the following equation [28],

$$\varepsilon = \left(C - C_0/C_0\right) \times 100 \quad (3)$$

The volume of crystalline (V) is calculated using the relation [28],

$$V = D^3 \quad (4)$$

The calculated structural parameters from XRD studies are given in the Table 1. The average crystallite size of Bi doped ZnO was found, the D value increases up to 7 at.% of Bi doping, which an increase in the particle size ranging from 42 to 56 nm. The obtained result can interpret based on the change depending on the difference in the ionic radii Bi^{3+} (0.103 nm) than that of Zn^{2+} (0.072 nm) of the dopant element. Inclusion of Bi^{3+} in the ZnO nanoparticles structure causes an increase in the stress and increasing crystal imperfection [29–32]. The calculated lattice constants 'a' and 'c' are very close to that of the standard values up to 7 at.% of Bi doping. The above discussion on Bi inclusion up to 7 at.%, due to the incorporation of Bi into the O^- sites. The micro strain of the undoped and Bi doped ZnO nanoparticles, it is found that the undoped ZnO nanoparticle, possesses the micro strain along c-axis changes to a negative sign (compressive). It is also noted that the micro strain along c-axis exhibit a positive sign (tensile) for up to 7 at.% of Bi doping. The minimum micro strain may involve a significant value for the initial Bi_2O_3 phase. The volume of crystallite size indicates that there is proper incorporation of Bi ions into the regular lattice sites of O^-.

3.2 Morphology and compositional analysis

FESEM images of the undoped and Bi doped ZnO nanoparticles are depicted in Fig. 2. It is interesting to see that the morphology is well defined hexagonal wurtzite shape with the doping of Bi. It could be found from the figure that the crystalline quality is increased and the grain size becomes larger because of the Bi doping which is good agreement with the results in XRD. The increase may be due to the impact of ionic radii of Bi with Zn lattice. The crystallite size is also evidence from the TEM image (Fig. 3b). From the TEM image, no aggregate observed, in addition, no impurities have been found in ZnO material. Figure 3a shows the EDAX profile of the chemical compositions of the synthesized nanoparticles. The EDAX spectrum clearly showed the presence of Zn, O and Bi atoms that are very much expected in the system without other impurity peaks.

3.3 Photoluminescence studies

The photoluminescence (PL) spectra are a powerful tool to study the structural defects and crystalline quality of the materials. Figure 4 shows that PL spectra of undoped and Bi doped ZnO nanoparticles. There is no emission peak has been noticed in the UV region. The broad emission peak observed in the visible region, centered at 397 nm is associated with the near band-edge emission (NBE) which is due to the band to band electronic transition. The sharp, intense peak violet emission band at 421 nm may be originated from the intrinsic defects in ZnO, for oxygen vacancy (V_o), interstitial zinc (Zn_i) and antisite oxygen vacancy (O_{zn}) [33–37]. The intensity of violet emission has a structural modification that occurs due to ZnO:Bi^{3+} system. The peak at 468 nm is rising due to blue emission which is originated from the transition of electrons from the donor level of singly ionized oxygen vacancies to the valence band in ZnO [38]. These singly ionized oxygen vacancies to generate the stronger blue emission corresponding to the formation of hydroxyl radicals [39]. This hydroxyl radical plays a crucial role in the inhibition of bacterial growth.

3.4 Antibacterial activity measurement

To determine the variation in the zone of inhibition caused by the synthesized Bi doped ZnO nanoparticles against *E. coli* and *S. aureus* bacteria were estimated by the well diffusion method as shown in Fig. 5. In this work, a complete zone of inhibition of bacterial growth was observed on agar

Table 1 The structural parameters of undoped and Bi doped ZnO nanoparticles

Bi doping level (at.%)	Crystallite size D (nm)	Lattice constant* (Å)		Strain $\varepsilon \times 10^{-4}$	Volume of the unit cell (v) ($Å^3$)
		a	c		
0	42.606	3.2512	5.2062	−0.0078	47.6490
3	42.605	3.2522	5.2112	0.0881	47.7291
5	42.599	3.2633	5.2182	0.2226	48.1237
7	56.797	3.2574	5.2195	0.2475	47.9610

D crystallite size, *v* volume of the unit cell, *ε* micro strain

*Standard value: a = 3.24982, c = 5.20661

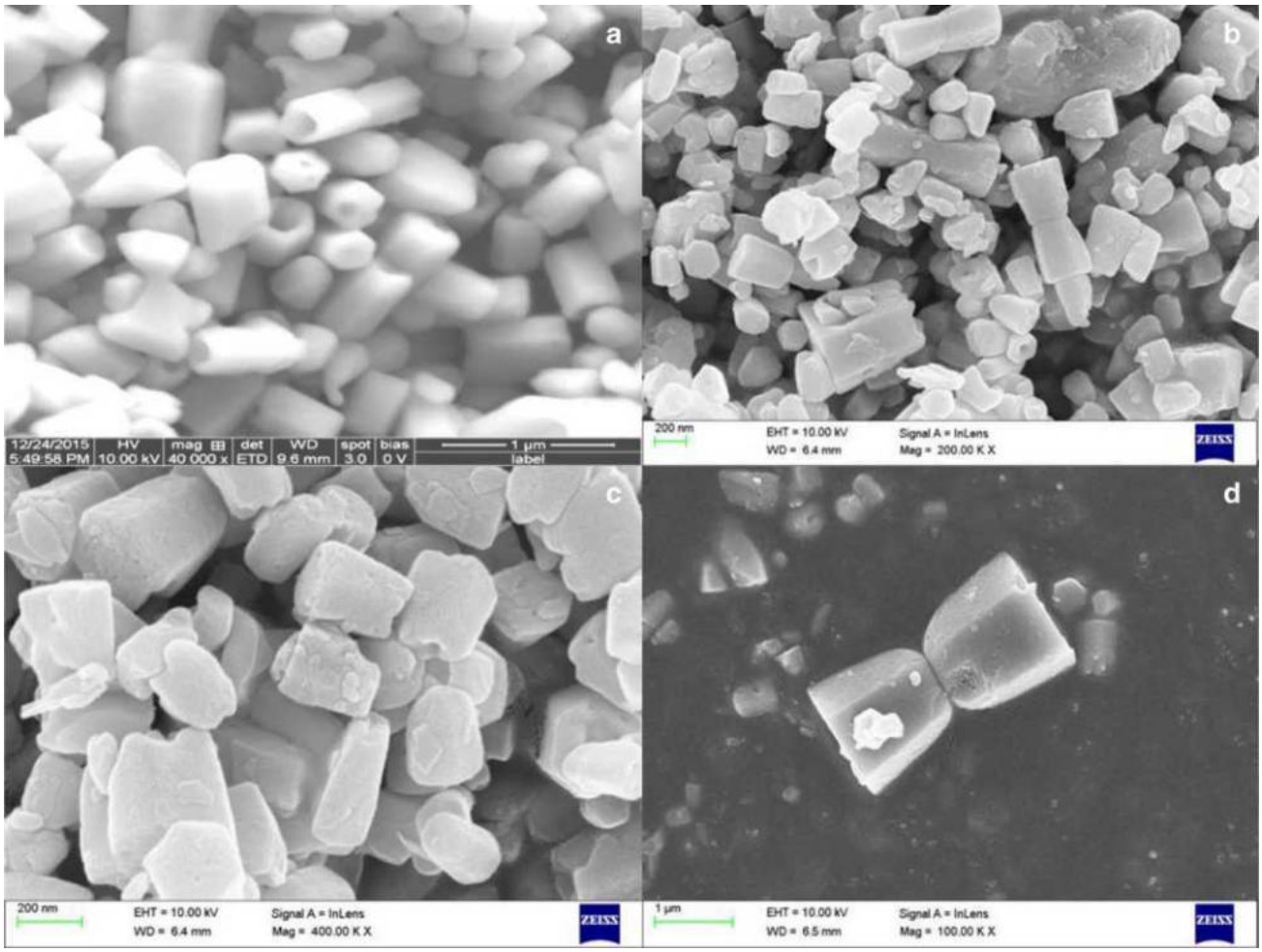

Fig. 2 FESEM images of ZnO: Bi nanoparticles with doping levels **a** undoped, **b** 3 at.%, **c** 5 at.% and **d** 7 at.%

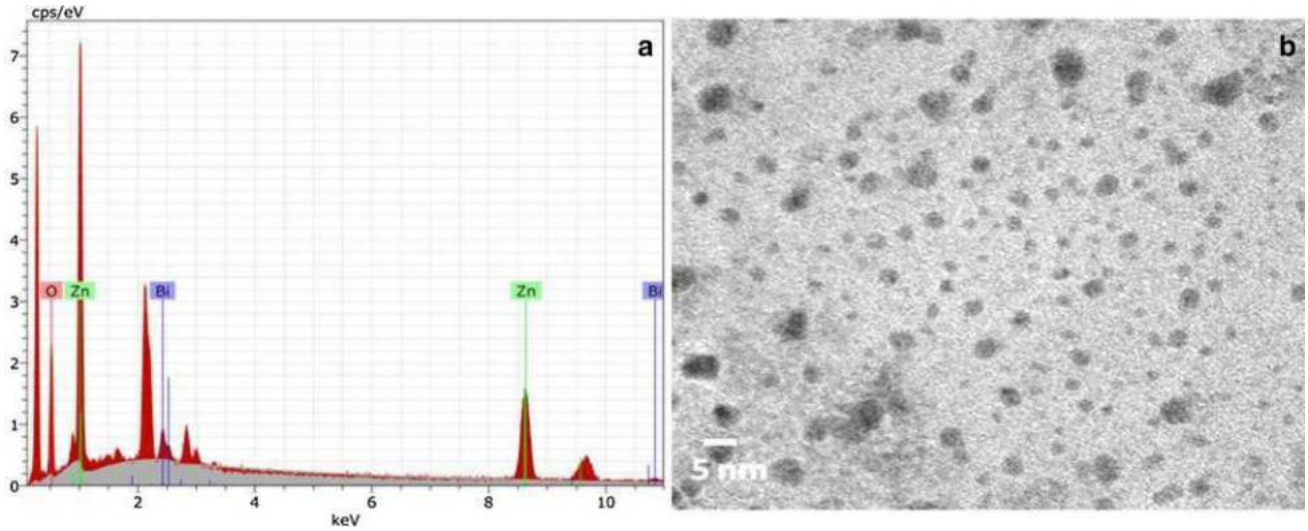

Fig. 3 **a** EDAX profile of Bi (7 at.%) doped ZnO nanoparticle and **b** TEM image of undoped ZnO nanoparticle

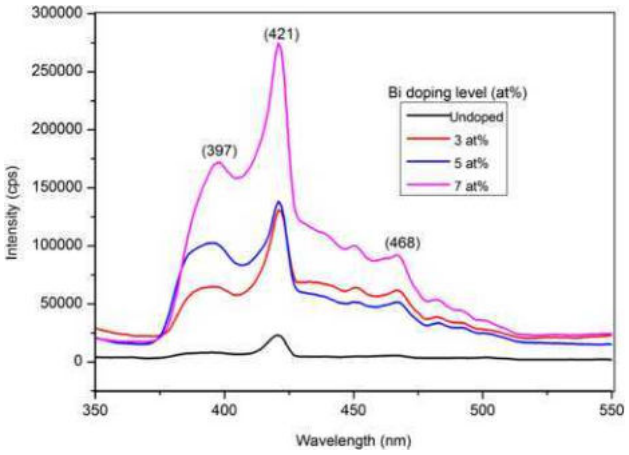

Fig. 4 Photoluminescence spectra of undoped and Bi doped ZnO nanoparticles

plates with undoped and Bi doped ZnO nanoparticles. The Zone of inhibition increased for each of individual microorganisms with increase in the doping ratio of Bi. It is noteworthy that the inhibition depends on the concentration of Bi doped with ZnO nanoparticles as well as on the initial bacteria numbers. It is observed that higher antibacterial activity of synthesized nanoparticles is happened due to three important factors, such as (1) reduced size of the grains, (2) pH (3) highly reactive oxygen spices (ROS) generated including hydroxyl groups (OH), superoxide anions (O^2), and hydrogen peroxide (H_2O_2) [40]. In our work pH of the powder samples dispersed in NaOH in 7, irrespective of the samples. The generation of ROS due to the free electrons caused by incorporation of Bi^{3+} ions into the ZnO lattice plays a crucial role. This could be the reason is ROS has the ability to destroy the bacteria.

The generation of ROS can be represented as follows [41]:

$$ZnO + h\nu \rightarrow h^+ + e^-$$

$$H^+ + H_2O \rightarrow OH^\bullet + H^+$$

$$O_2 + e^- \rightarrow O_2^{\bullet -}$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$$

$$H^+ + HO_2^\bullet + e^- \rightarrow H_2O_2$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^\bullet + O_2 + OH^-$$

From these reactions, it is seen that, the electron hole pairs plays a vital role in the generation of ROS. In this present work, the peak at 468 nm is confirmed as the presence of singly ionized oxygen vacancy observed in the PL spectra. It is clearly found that there is an increase in the efficiency of Zone of Inhibition with an increase in the Bi doping level. Also, it is well noted that Bi doped ZnO nanoparticles shows higher efficiency on Gram Positive bacteria *S. aureus* than that of Gram negative bacteria *E. coli* as shown in the Fig. 6. Thus, these Bi doped ZnO nanoparticles have a good biocidal effect and shows a good efficacy in destroying the bacterial growth, which may lead to the valuable inventions and can be used in antimicrobial systems as well as medical devices.

4 Conclusion

A soft chemical method was employed for the synthesis of undoped and Bi doped ZnO nanoparticles. The structural, morphological, photoluminescence and antibacterial activities are studied and reported. It has been found the crystalline quality and size of the crystallite size increase with the increase in the Bi doping level. The FESEM images shows a good hexagonal wurtzite structure indicating that there is no

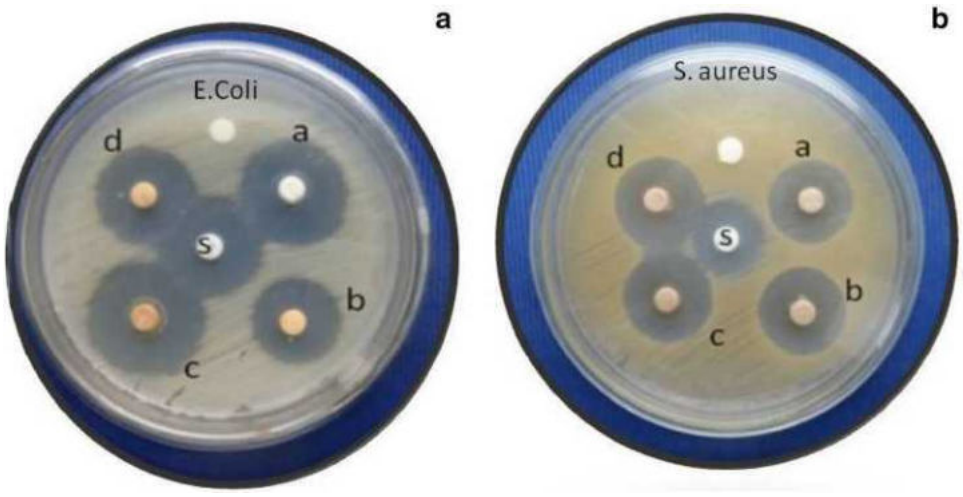

Fig. 5 The variation of inhibition exhibited by Bi:ZnO nanoparticles against **a** *E. coli*, **b** *S. aureus*

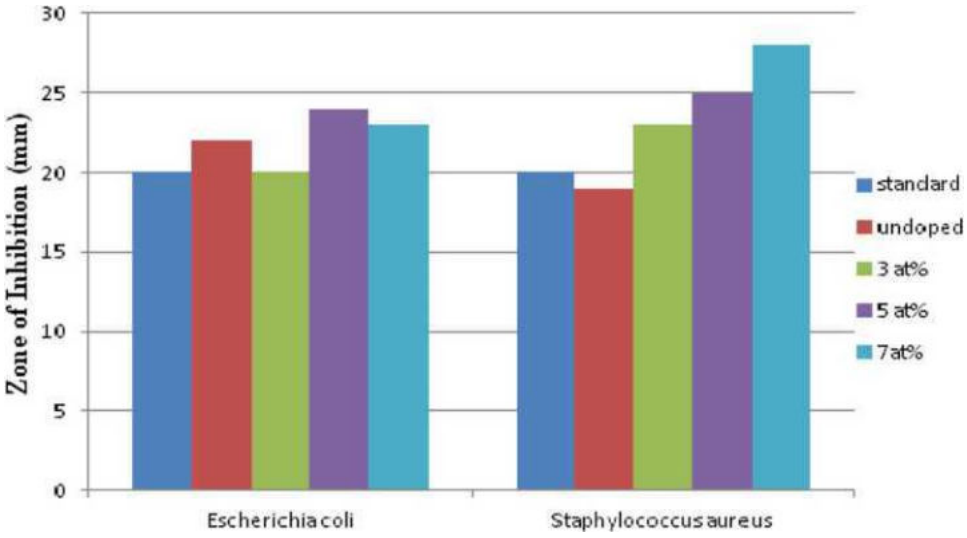

Fig. 6 Graphical representation of the inhibition zones caused by undoped and Bi doped ZnO nanoparticles against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) organisms

change with respect to Bi doping and the grain size increases with the increase of Bi content. The PL spectra confirm the proper substitutional incorporation of Bi^{2+} into the O^{2-} sites of the ZnO structure and emission of violet light. The antibacterial studies reveal that the higher concentration of Bi doping level is found to be significantly higher for *S. aureus* when compared with *E. coli* micro-organisms.

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Growth, Structural, Optical, Thermal and Mechanical properties of Copper Glutamate Dihydrate Single crystal

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Abstract: *Semiorganic nonlinear optical single crystals of copper glutamate dihydrate ($CuC_5H_7NO_4.2H_2O$) were grown by slow evaporation technique at room temperature. Single crystal X - ray diffraction analysis reveals that the grown crystal belongs to orthorhombic system with space group $P2_12_12_1$. The crystallinity of the grown crystals was studied by powder X - ray diffraction analysis and their diffraction pattern was indexed using AUTOX 93 software. Functional groups of synthesized material was identified using Fourier transform infrared (FT – IR) spectroscopic analysis. The optical transmission percentage of grown CLGD crystal was ascertained by UV – Vis – NIR spectrum. The photoluminescence spectrum shows an emission peak at 555 nm using the excitation wavelength of 275 nm. The mechanical strength of the grown crystal was determined using Vickers microhardness tester. Electrical properties were analyzed by dielectric measurement at different temperatures. Thermal stability of the grown crystal was studied by thermogravimetric, differential thermal analysis and differential scanning calorimetry. Etching study was carried out to assess the perfection of the grown crystals. The second harmonic generation efficiency was calculated by Kurtz and Perry powder technique.*

Keywords: *Crystal growth, Mechanical strength, Thermal properties, Optical properties.*

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I. Introduction

L-glutamic acid is a dicarboxylic amino acid and is a significant constituent in proteins. It also plays an important role in the metabolism of sugar and fats. L-glutamic acid crystallizes in two polymorphs one a metastable α and a stable β which has different lattice parameters of the same space group of the orthorhombic $P2_12_12_1$. The α form of L - glutamic acid structure was published by Bernal [1] and the β polymorph was reported by Hirokawa [2]. The kinetics of polymorphic transformation between α and β forms of L glutamic acid was observed [3]. The metastable α form is easily grown and poor conformational discrimination at the (111) faces favours surface nucleation of β form. Crystals of α form are rhombic whereas the β polymorph forms needle like crystals [4]. Crystal structures of L - glutamic acid hydrochloride [5], DL glutamic acid hydrochloride [6], anhydrous DL glutamic acid [7] and bis L - glutamic acid sulphate hemihydrate [8] have been reported. Due to the inherent limitations of organic and inorganic single crystal researchers developed a new hybrid crystals containing organic and metals. With the aim of growing efficient NLO crystals various groups have published several salts and mixed salts of L – glutamic acid [9 - 12]. The crystal structure of copper L - glutamate dihydrate was first reported by Gramaccioli and Marsh [13]. Orthorhombic crystals of CLGD crystallizes in a noncentrosymmetric structure with lattice dimensions a = 11084 Å, b = 10.350 Å and c = 7.235Å. In this study we report the results of single crystal growth of copper L - glutamate dihydrate and characterization studies of its linear and nonlinear optical, spectroscopic, photoluminescence, mechanical, dielectric and thermal stability.

II. Experimental Procedure

2.1 Synthesis

Copper L glutamate dihydrate salt was synthesized by mixing L – Glutamic acid 99% purity and copper (II) hydroxide carbonate purchased from Merck were taken in 1:1 equimolar ratio. L - Glutamic acid was dissolved completely at 35 ºC in double distilled water then Copper (II) hydroxide carbonate is mixed. The solution was thoroughly stirred and few drops of HNO_3 are added for complete dissolution. The prepared solution was constantly stirred about 3 hours using magnetic stirrer to obtain homogeneous mixture over the

entire volume. The salt was obtained after a week by slow evaporation. To ensure high purity, the material was purified by successive recrystallization. The single crystal growth was achieved by dissolving the synthesized polycrystalline salts in double distilled water to form saturation solution. The solution was filtered twice to remove the impurities using Whatman filter paper and kept in a borosil beaker covered with porous paper to facilitate the evaporation of the solvent. The crystals of optimum size (6×6×3) mm^3 were obtained after a period of 15 days. The photograph of grown crystals of copper L-glutamate dihydrate is shown in Fig. 1.

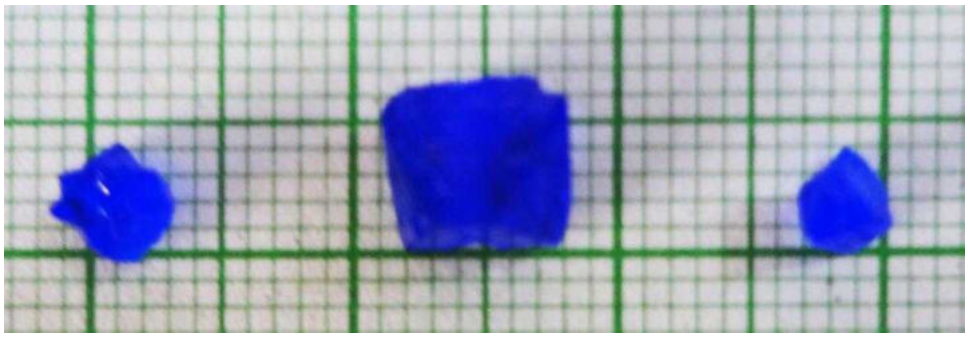

Fig. 1 As grown single crystals of CLGD

III. Results And Discussion

3.1 Single crystal X – ray diffraction

The structure of the grown single crystal was confirmed by single crystal X-ray diffraction analysis using ENRAF CAD4 diffractometer with MoKα radiation. The structure was solved by direct method and refined by full matrix least squares refinements using SHELXL program. CLGD crystallizes in orthorhombic system with noncentrosymmetric space group $P2_12_12_1$. The lattice parameters obtained from single crystal X – ray diffraction analysis are presented in Table 1. Fig. 2 shows the molecular ORTEP diagram of CLGD. The coordination of copper atom is approximately square planar, the square comprising of two oxygen atoms and a nitrogen atom of glutamate groups and a water molecule. The average distance from the copper atom to these four ligands is 2.056 Å. The nitrogen atom is tetra coordinated and the Cu – O and Cu – N distances range from 1.9656 to 1.9946 Å.

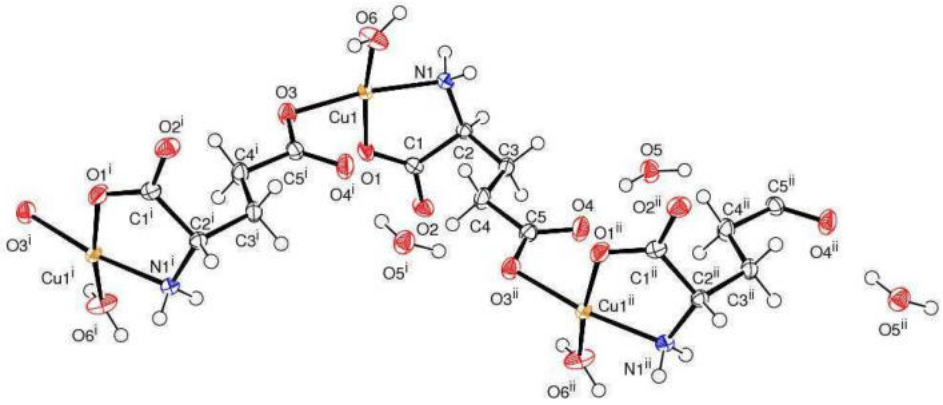

Fig. 2 ORTEP diagram of CLGD

TABLE 1 Crystal Data and Structure Refinement for CLGD

Empirical formula	$C_5 H_{11} Cu N O_6$
Formula weight	244.69
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 7.2248(3) Å α = 90 deg. b = 10.2992(5) Å β = 90 deg c = 11.0453(5) Å γ = 90 deg.
Volume	821.88(6) A^3
Z, Calculated density	4, 1.977 Mg/m^3
Absorption coefficient	2.657 mm^-1
F (000)	500
Crystal size	0.35 x 0.32 x 0.30 mm

Theta range for data collection	2.70 to 26.96 deg.
Limiting indices	-9<=h<=8, -13<=k<=13, -14<=l<=14
Reflections collected / unique	13523 / 1787 [R(int) = 0.0302]
Completeness to theta = 26.96	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5096 and 0.4514
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1787 / 9 / 143
Goodness-of-fit on F^2	1.141
Final R indices [I>2 sigma (I)]	R1 = 0.0133, wR2 = 0.0363
R indices (all data)	R1 = 0.0140, wR2 = 0.0367
Absolute structure parameter	-0.008(9)
Extinction coefficient	0.0405(14)
Largest diff. peak and hole	0.239 and -0.249 e.A^-3

3.2 Powder X - ray diffraction analysis

Finely crushed grown crystals have been subjected to powder X - ray diffraction using XPERT - PRO diffractometer employing Cu k_α radiations (λ=1.5406 Å). The specimen in the form of a thin film was scanned over 2θ range 10 to 90º at the scan rate of 1º/min. The sharp peaks indicate the crystalline nature and all the diffraction planes were indexed using software AUTOX 93. Fig. 3 represents the indexed powder diffraction pattern of grown CLGD crystal.

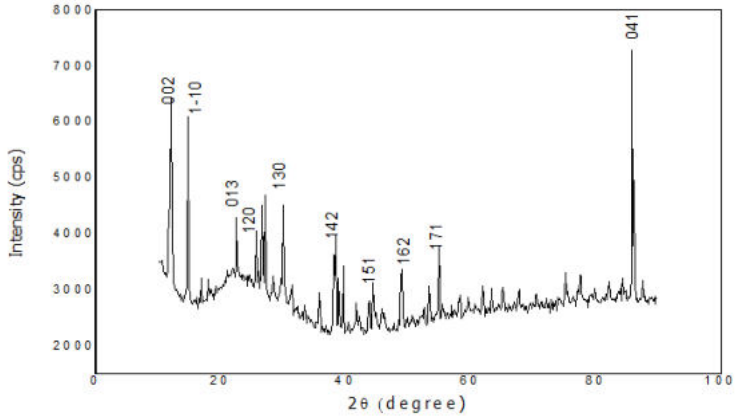

Fig. 3 Powder X – ray diffraction of CLGD

3.3. FT - IR spectral analysis

The FT - IR spectrum of Copper L - Glutamate dihydrate was recorded in the range of 450 - 4000 $cm^{-1}$by Perkin Elmer FT - IR spectrometer to identify presence of various functional groups and it is shown in Figure 4. The observed wavenumbers and assignments are presented in Table 1. The band observed at 483 cm^{-1} is due to the COO^- rocking. The peaks observed at 1131 and 567 cm^{-1} are due to NH_3 rocking and NH_3 torsion modes respectively. C = O bending and asymmetric stretching mode occurs at 1611 and 633 cm^{-1} . C-C-O deformation mode of vibration appears at 758 cm^{-1}. Asymmetric and symmetric stretching modes of C - N are observed at 1395 and 1265 cm^{-1}. Broad peak observed at 3398 and 2322 cm^{-1} was due to OH asymmetric and symmetric stretching vibrations. The N - H bending appeared at the wavenumber 1572 cm^{-1}.

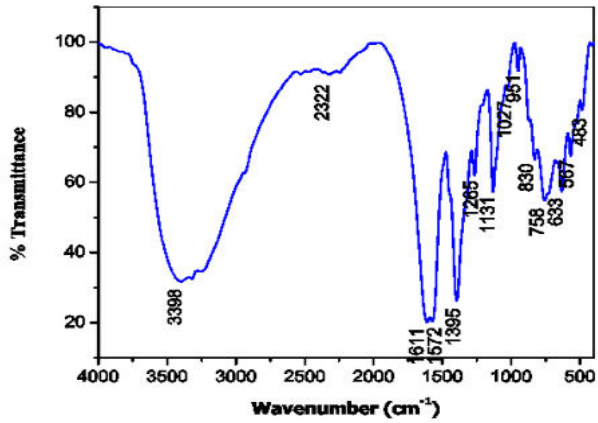

Fig. 4 FT IR spectrum of CLGD

TABLE 2 FT - IR frequency assignments of CLGD single crystal.

FT- IR	Assignment of vibrations
3398	O – H asymmetric stretching
2322	O – H symmetric stretching
1611	C = O asymmetric stretching
1572	N – H bending
1395	C – N asymmetric stretching
1265	C – N symmetric stretching
1131	NH_3 rocking
1027	C – C – N asymmetric stretching
951	C – C stretching
830	C – C symmetric stretching
758	C – C – O deformation
633	C = O bending
567	NH_3 torsion
483	COO rocking

3.4 UV – Vis – NIR Spectral studies

UV-Vis-NIR transmittance and absorption studies have been carried out by using Perkin-Elmer Lambda 35 UV-Vis spectrometer in the spectral region 190 and 1100nm. Optically polished single crystal of thickness 2mm was used to record the spectrum. Figure 5 shows the transmittance and absorbance spectrum of CLGD. The transparency of the crystal is 98% and displays no absorption in the entire UV visible region. The cut-off wavelength of CLGD crystal is observed at 200nm and this is an advantage of amino acid complexes where the absence of strongly conjugated bonds leads to broad transparency range [14]. Knowledge of the optical band gap and extinction coefficient of materials is important parameter for selection of material. The optical absorption coefficient (α) is calculated from the relation $\alpha = (1/t) \log (1/T)$, where T is the transmittance and t is the thickness of the crystal.

The direct band gap of the crystal can be obtained from the absorption coefficient (α) using the relation $\alpha h\gamma = A(h\gamma - Eg)^{1/2}$, where Eg is the optical band gap energy of the crystal, h is the Plank's constant, γ is the frequency and A is a constant. Fig. 6 depicts the variation of $(\alpha h\gamma)^2$ versus photon energy hγ. The band gap was estimated by extrapolating the linear portion near the onset of absorption edge. The band gap energy of CLGD is 5.21eV. The absorption coefficient (α) is related to the extinction coefficient K by the relation $K = \alpha\lambda/(4\pi)$. Figure 7 shows the variation of extinction coefficient of the grown crystal. The extinction coefficient sharply decreases and saturates at 300 nm.

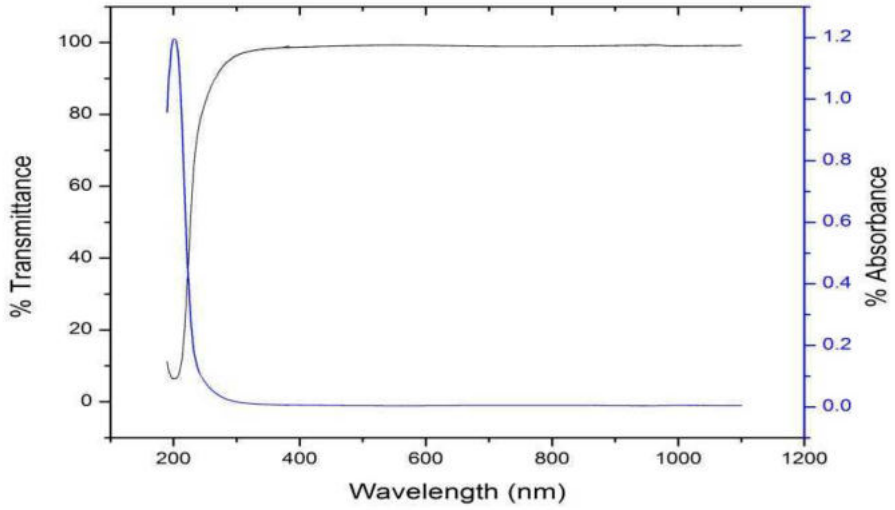

Fig. 5 UV- Vis - NIR spectrum of CLGD.

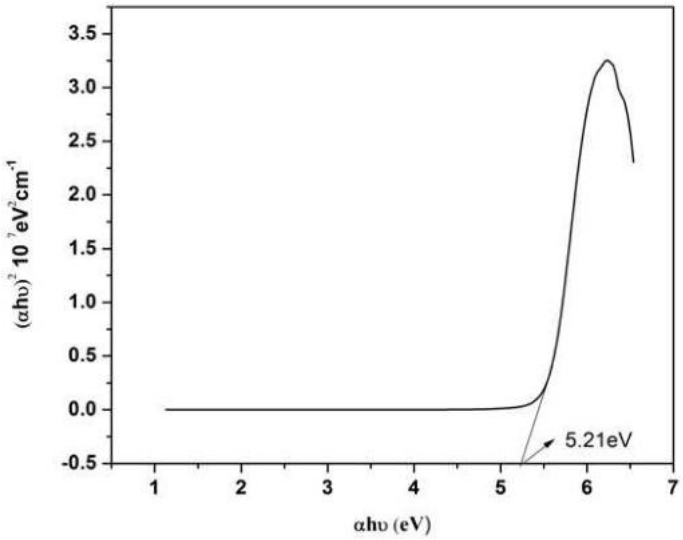

Fig. 6 Energy band gap of CLGD

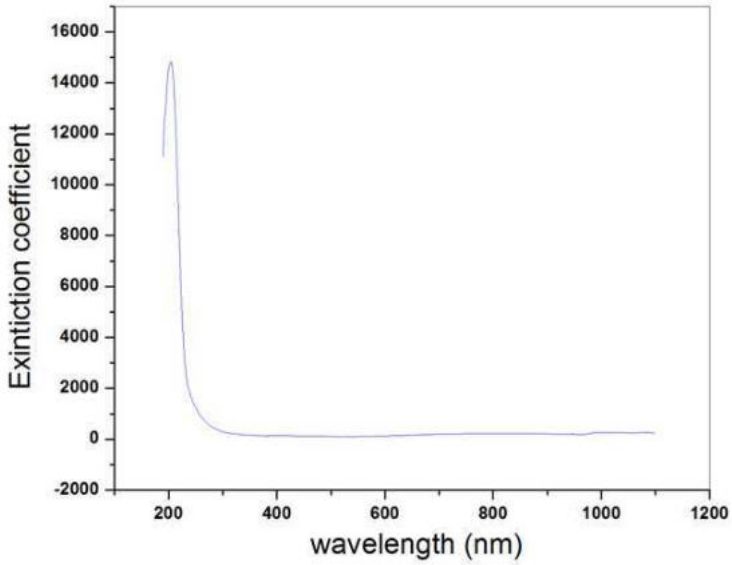

Fig. 7 Extinction coefficient Vs wavelength for CLGD

3.5 Photoluminescence Analysis

Photoluminescence is an elegant tool for characterizing defects, vacancies and other imperfections in the grown crystal. Photoluminescence spectrum was recorded in the wavelength range from 500nm to 600nm using Jasco PL spectrometer. On applying the excitation wavelength 275 nm (4.517 eV) the electronic emission started at 2.91eV and ends at 2.311eV. Hence total energy is emitted with an emission period $0.122X10^{-12}$ s. Photoluminescence emission spectra of CLGD is shown in Fig. 8. The emission peak observed at 553.55 nm (2.244 eV) which is in green region in the electromagnetic spectrum. The band width of this emission spectrum is $2377.21X10^{10}$ Hz. This low bandwidth with sharp peak is the characteristics of radiation transitions at deep neutral defects and good crystalline nature. The relaxation time of CLGD crystal is $1.6\ X10^{-14}$s. The energy band gap of CLGD crystal was calculated using the formula $Eg = 1240/\lambda_{max}$ (eV) where λ is the emission peak wavelength. The energy gap (Eg) of the crystal is 2.378 eV, hence CLGD will be used as insulating material.

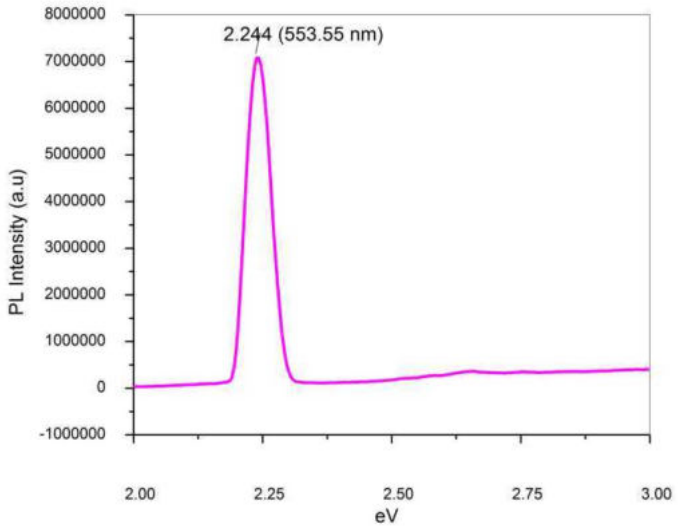

Fig. 8 Photoluminescence spectrum of CLGD

3.6 Dielectric properties

Dielectric constant (ε_r) and dielectric loss (tan δ) are the basic electrical properties of the solids. The single crystal of CLGD of dimensions (4x4) mm^2 in surface area and 2mm thickness of the crystal was smoothly polished using alumina. The opposite faces of the sample were coated with silver paste. A two terminal copper electrode was used as sample holder and the sample was held between the electrodes. Hence the parallel plate capacitor was formed. Hioki LCR dielectric meter working in the range of 10 – 8MHz and a microprocessor supported furnace fitted with a temperature controller was used for dielectric measurements. The variation of capacitance with reference to varying frequencies and dielectric loss measurements were made in the frequency range 50 – 5000 kHz at different temperature. Four type of polarization usually contribute to the dielectric polarization of any ferroelectric material. They are electronic, ionic, dipolar and space charge polarization ($\alpha_t = \alpha_i + \alpha_e + \alpha_o + \alpha_s$). The space charge contribution depends on the purity and perfection of the grown crystals. The contribution of space charge polarization at lower temperature and higher frequencies are negligible. However it is significant at low frequencies. Electronic polarization occurs at very high frequencies. Space charge and dipolar polarization are relaxation processes and are strongly temperature dependent while as ionic and electronic polarization are resonance process and are temperature independent. The dielectric constant is calculated using the relation $\varepsilon_r = Cd / (A\varepsilon_o)$. Where C is the capacitance (F), t the thickness, A the area (m^2) and ε_o the absolute permittivity in the free space having the value of 8.854×10^{-12}F/m. The variation of dielectric constant with frequency of the applied a.c. field is shown in figure 9. In the lower frequency region (0 - 1000Hz) the dielectric constant decreases as the frequency increases. In the higher frequency region the dielectric constant attains saturation. In the higher frequency range the dielectric constant almost remains unaffected by input a.c field. It is clear from this curve that the dielectric constant and dielectric loss of the material strongly dependent on both temperature as well as frequency. Figure 10 shows the dependency of the dielectric loss on frequency. The dielectric loss decreases with increase in frequency.

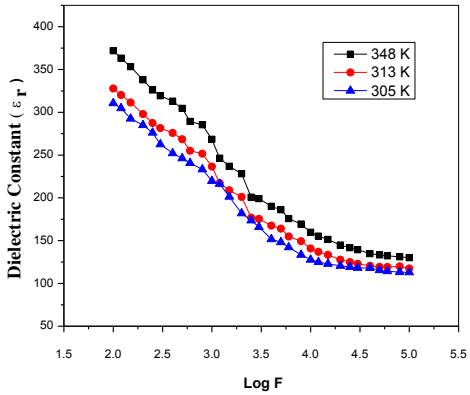

Fig. 9 Dielectric constant as a function of log frequency

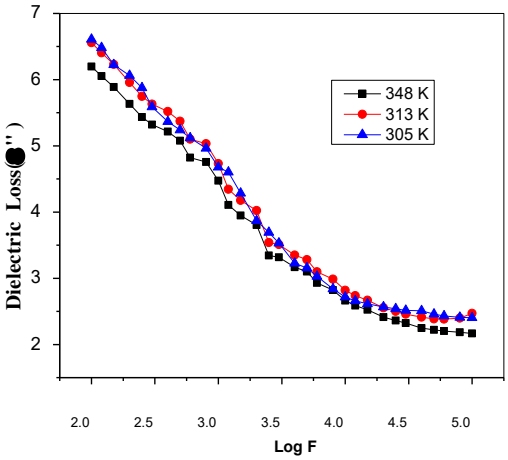

Fig. 10 Dielectric loss versus frequency

The variation of dielectric constant with temperature at four different frequencies 50 kHz to 150 kHz is shown in Figure11.

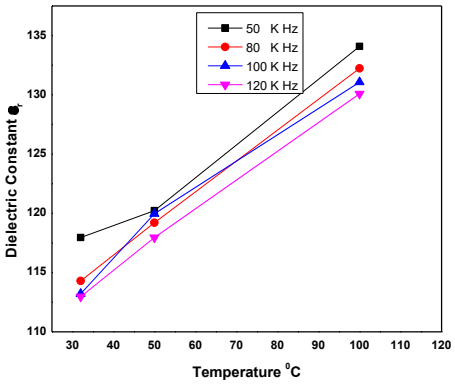

Fig. 11 Temperature vs dielectric constant

The dielectric constant increases as the temperature increases. The rate of variation of dielectric loss with temperature is shown in Figure 12 at four different frequencies. Dielectric loss also exhibits similar behavior as the frequency of the applied field increases. The relaxation time is the time taken by the electron from disturbed position to equilibrium position in the presence of an electric field. Also the decrease of dielectric constant and dielectric loss with increase in frequency suggests that the grown crystal seems to contain molecules of varying relaxation times. At higher frequencies relaxation time is large, hence molecules not able to respond with frequency so the dielectric constant and dielectric loss were low.

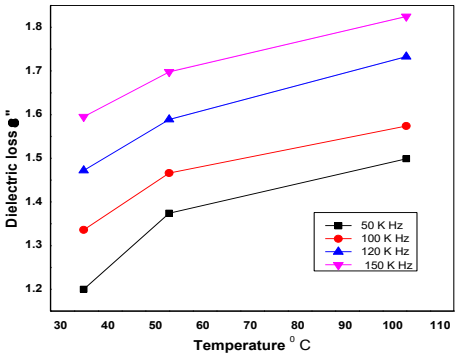

Fig. 12 Temperature vs dielectric loss

3.6 Thermal analysis

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) are very important characteristic techniques is used to reveal the thermal stability of the crystal. TG/DTG and DTA curves (Fig. 13) were recorded for copper L - glutamate dihydrate crystal using Perkin Elmer thermal analyzer in the range of temperature from 25 ºC to 1000 ºC at a heating rate of 10 ºC/min in nitrogen atmosphere. Ceramic crucible was used for heating the sample. The initial mass of the material subjected to analysis was 9.9290 mg. Two weight losses were observed in the TGA curve. The material was stable up to 80.58 °C and then weight loss takes place. The first step of weight loss takes place between the temperature 80.58 ºC and 184.02 ºC. In this stage hydroxide group is removed. Second step of decomposition is observed between the temperature 220.57 ºC and 1000 ºC. During this stage L-glutamic acid is removed. The DTA curve clearly follows the TG curve with two peaks. The sharp and well resolved endothermic peaks were observed at 167.58 ºC and 226.38 ºC. The endothermic peak corresponds to the loss of hydroxyl group and L-Glutamic acid.

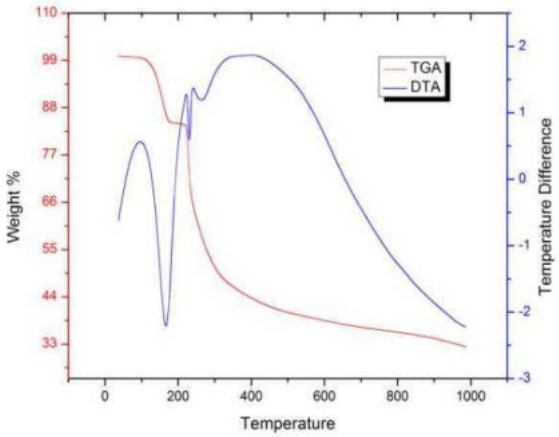

Fig. 13 TGA/DTA spectrum of CLGD

3.7 Differential Scanning Calorimetry

Differential Scanning calorimetric study (DSC) was carried out on a Perkin Elmer DSC 7 Calorimeter with heating rate of 10 ºC / min in nitrogen atmosphere. For this, a small piece of crystal weighting 9.92g was taken. The sample was scanned over the temperature range from 25 to 1000 ºC. The DSC plot shows a sharp peak at 167.58 ºC and highest peak of exothermic at 536.4 ºC. This well-marked endothermic peak is due to the melting point of the compound.

3.8 Microhardness studies

Crystal hardness is a measure of the resistance to the local deformation [15]. The knowledge of hardness is very important and it plays a vital role in device fabrication. Vickers microhardness values were estimated by employing Shimadzu microhardness tester for different loads. The Vickers pyramidal indenter is attached to a microscope with an adopted video camera in order to measure the indentations on a monitor. The dwell time of indentation was kept at 3s. Two indentations were made and the mean values of the two diagonal lengths used for hardness calculation. Vickers microhardness number (H_v) was calculated using the relation $H_v = 1.8544(P/d^2)$ kg/mm^2 where P is the indenter load (kg) and d is the diagonal length of the impression (mm). Fig. 14 shows the variation of Vickers hardness values with applied load. The value increases up to a load of 100g. Cracks develop around the indentation mark above the load of 100g. It is observed from the figure that hardness value is load depending and the value of the hardness increases with increasing load. This phenomenon is called reverse indentation size effect (RISE). To analyze the RISE curve fitting the data according to Meyers [16] law $P = Ad^n$, which correlate the applied load P and its corresponding indentation size d. A is the constant for a given material and n is the Meyers work hardening co-efficient. Figure 15 obtained by plotting log P against log d, the slope of this fit gives "n". The value of n is equal to 2 which means the crystal is soft material characteristic nature according to Onitsch [17]. Since Meyers law is simply an empirical relation, Li and Bradt [18 - 20] proposed a model called Proportional Specimen Resistance (PSR) to explore indentation size effect. To describe the indentation size effect regime we applied the proportional specimen resistance model.

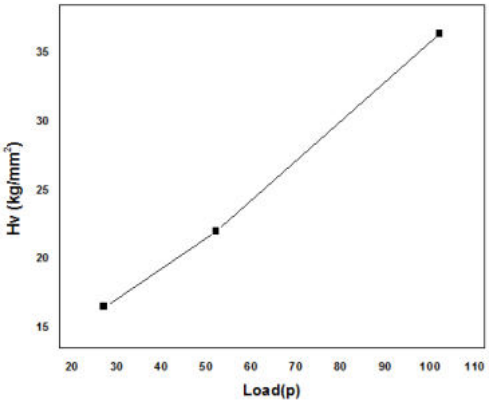

Fig. 14 Hardness behavior of CLGD single crystal.

In the PSR model of Li and Bradt, microhardness can be described by two components, the first term represents the indentation load dependent part and second term represents the load independent part. The indentation test load P is related to the indentation size d as follows.

$$\frac{P}{d} = a_1 + \left(\frac{P_s}{d_s^2}\right) d$$

In the above equation a_1 is the contribution of PSR to the apparent microhardness and a_2 dis the coefficient related to the load dependent microhardness. A plot of P/d against d gives a straight line. The slope of which gives the value of load independent microhardness. Linear regression of P/d versus d confirms the ISE regime. Figure 16 illustrates the load independent part and load dependent part. The slope gives the value of P/d^2 which when multiplied by the Vickers conversion factor 1.8544 gives load independent microhardness. The load independent microhardness value is calculated to be 22.25 g/mm^2. Elastic stiffness constant was computed by Wooster's [21] empirical relation $C_{11} = H_v^{\frac{7}{4}}$. The elastic stiffness increases with increase of load. The calculated stiffness constant for different loads is shown in Table 3.

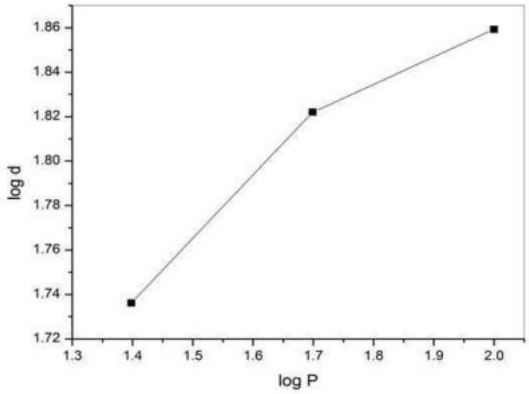

Fig. 15 A plot of log P vs log d.

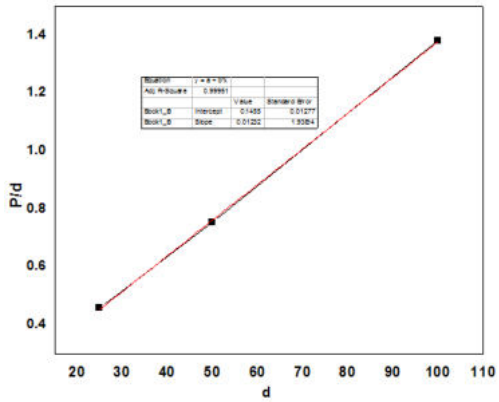

Fig. 16 P/d vs d

TABLE 3 Stiffness Constant of CLGD Crystal

H_v (g/mm^2)	$C_{11} \times 10^{14}$ (N/m^2)
15.5	2.078×10^{14}
20.7	3.44×10^{14}
35.2	8.73×10^{14}

3.9 Etching studies

Etching is a technique which is used to reveal the defects in crystals like dislocations, growth bands, twin boundaries and point defects. Normally when the crystal is dissolved in the solvent, well defined etch pits are formed. The formation of the etch pits are assumed to be the reverse of growth process. The etching features observed on the grown crystal was recorded by high resolution optical polarization microscope. The surface of the crystal was polished well before the etching process. The crystal was dipped in double distilled water and wiped using tissue paper. The etch patterns were recorded using polarization microscope fitted with Motic camera. The photographs were taken with a maximum etching time of 5 seconds. Figure 17 shows the etch patterns observed on the CLGD single crystal. Etch pits and cracks were observed.

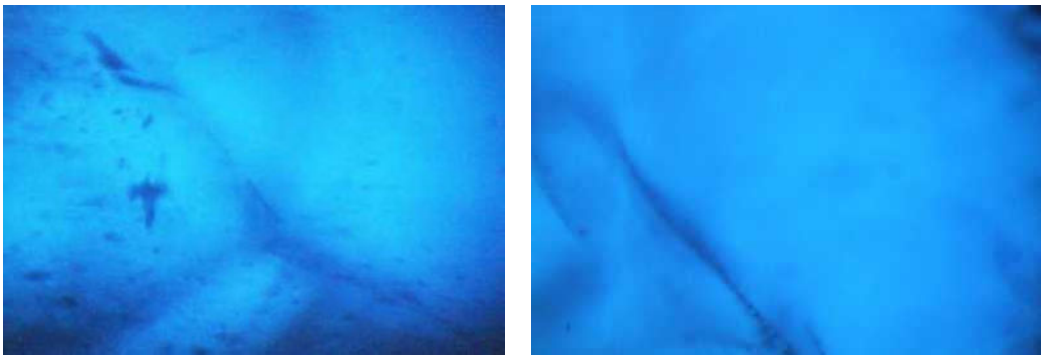

Fig. 17 Etch patterns of CLGD

3.10 SHG Efficiency

The quadratic NLO property was checked and the SHG relative efficiency in the powder material was measured by Kurtz and Perry method [22]. KDP crystal was powdered to the identical size and used as a reference material in the SHG measurement. The crystal was grained into the powder and densely packed in 1.5mm diameter micro capillary tube. The laser energy of 7mJ was applied on the sample there was absence of green radiation energy (532 nm) and SHG signal was very low. So CLGD could not be used in the fabrication of NLO devices.

IV. Figures And Tables

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V. Conclusion

CLGD crystals were grown from aqueous solution by slow evaporation method. The crystal structure was elucidated using standard crystallographic procedures. FT-IR spectra revealed the presence of the various functional groups. UV-Vis-NIR study shows that the crystal transparent for the fundamental and second harmonic of Nd:YAG (λ=1064 nm) laser. Thermal analysis reveals that CLGD is thermally stable up to 80 ºC. From Vickers microhardness it was observed that the microhardness values increases with increase of load. The work hardening coefficient n>2 indicates that the crystal belongs to soft material category. The elastic stiffness constant gives an idea of tightness of bonding between the neighboring ions. The dielectric constant and dielectric loss of CLGD crystals dependent on frequency of the applied electric field at different temperature. In the low frequency region both the dielectric constant and dielectric loss decreases sharply.

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Uniform and Well-Dispersed ZnO:Fe Nanoparticles with High Photoluminescence and Antibacterial Properties Prepared by Soft Chemical Route

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Abstract Fe doped ZnO nanoparticles were synthesized using simple soft chemical route by varying the Fe doping level (5, 10 and 15 at.%). The obtained samples were characterized for their structural, optical, surface morphological and antibacterial properties. XRD profiles confirmed that the synthesized material is nanocrystalline ZnO with hexagonal wurtzite structure. The XRD studies reveal that the crystalline size of Fe doped ZnO nanoparticles are range from 56 to 24 nm. The size of the particle decreases gradually as Fe content is increased. The surface morphological studies confirmed the nanosize of the obtained particles. The FESEM and TEM images show that the particle size reduces after doping. The EDAX profiles confirmed the presence of expected elements in the final product. The Photoluminescence studies showed the occurrence of energy transition from ZnO to dopant site. The antibacterial activity of Fe doped ZnO nanoparticles against *Staphylococcus aureus* (Gram-positive) were found to be significantly higher than that against the *Bacillus subtilis* (Gram-positive) micro-organism.

Keywords Nanoparticles · ZnO · Soft chemical route · TEM · Photoluminescence and antibacterial activity

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1 Introduction

The transparent host matrix has recently generated increasing interest as advanced technological materials because of their unique optical, mechanical, electronic and structural [1–4] properties of composite metal nanoparticles. Such nanomaterials can be used as promising materials for novel functional applications in optoelectronics, medicine and magnetic [5–7] etc. ZnO with a wide energy band-gap (3.37 eV) in bulk is one of the II–VI semiconductor materials, making it attractive for the nano-electronic and photonic applications [8]. Recent studies have demonstrated that specially formulated metal oxide nanoparticles have good antibacterial activity [9, 10] antimicrobial formulations compressing nanoparticles could be effective bacterial materials [11, 12]. Interestingly, ZnO nanoparticles (NPs) are reported several studies on non-toxic to human cells [13], this aspect necessitated their usage as antibacterial agents noxious to micro-organisms and hold good biocompatibility to human cells [14]. Investigations of antibacterial nanomaterials, mostly ZnO NPs, would enhance the research area of nanomaterials, and the mechanism behind nanostructured materials.

The properties of nanostructured ZnO can be tailored by doping selective elements like Al, Mg, Mn, F, Zr, Ag, and Ni [15–21]. Iron doped ZnO nanoparticles synthesized by Jagannatha Reddy et al., suggested that the optical properties of the material were modified due to the dopant iron Fe^{3+}, which created new additional levels nearer to the absorption edges. Many reports have been proposed to synthesize nanostructured ZnO is using well-established methods like hydrothermal, wet chemical, soft chemical route, polyol method, microwave irradiation method [21–26], etc. Of these methods, soft chemical synthesis route offers several advantages. It's very fascinated, simple, facile and

inexpensive method which is suitable to grow a lot of nanostructured materials.

Here, we have successfully prepared undoped and iron (Fe) doped ZnO nanoparticles by simple soft chemical route. Even though, to our best knowledge, there are few reports of Fe doped ZnO nanoparticles, the study of the combined antibacterial and photoluminescence properties of Fe doped ZnO is not so far. In this present work the structural, optical, morphological and antibacterial activities of Bi doped ZnO nanoparticles prepared by soft chemical route were examined.

2 Materials and Methods

2.1 Synthesis Process

Fe doped ZnO nanoparticles were synthesized by a simple soft chemical route. 0.2 M of zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] is dissolved in deionized water and is treated the starting solution. An undoped and three sets of doped nanoparticles samples are synthesized from starting solution having $Fe(NO_3)_3$ doping level 5, 10 and 15 at.%. The required amount of NaOH (0.5 M) solution is added to maintain the pH value of the starting solution at 7. The obtained mixture was then magnetically stirred for 2 h at 85 °C. After the completion of the stirring process, the precipitate formed was separated carefully by filtration and washed several times with a mixture of ethanol and water kept in the ratio 1:3. Finally, it was calcined at 550 °C for 3 h in muffle furnace to obtain the final product.

2.2 Characterization Techniques

The crystalline structure of the synthesized nanoparticles was analyzed using an X-ray powder diffraction technique (PANalytical-PW 340/60 X' pert pro) using Cu-Kα radiation (λ = 1.5406 Å), Photoluminescence (PL) spectra were recorded using Spectro-fluorometer (Jobin Yvon_FLUROLOG-FL3-11) with xenon lamp (450 W) as the excitation source, of wavelength 325 nm. The Surface morphological studies of the products are investigated using Field Effect Scanning Electron microscopy (FESEM, Hitachi SU8000), Transition Electron Microscopy (TEM, Hitachi H-7100) and the elemental composition analysis was made using energy dispersive X-ray analysis (EDAX) (Model: JEOL-JSM 6390 with attachment INCA-penta FETX3 OXFORD).

2.3 Evaluation of Antibacterial Activity

The antibacterial activity of the synthesized ZnO nanoparticles was tested against *Bacillus subtilis, Staphylococcus aureus* (Gram-positive) bacteria using well diffusion method. The nutrient agar medium was prepared and sterilized by autoclave at 121 °C for 15 min. the medium was poured into the sterile petri plates and allowed to solidify. The bacterial broth culture was swapped on the agar plates using sterile buds and three wells were made by the well cutter. In each well, 200 µL/mL of the stock solution was loaded and the agar plates were incubated at 37 °C for 24 h. After incubation, the plates were observed in the formation of a clear inhibition zone around the well. The zone of inhibition was noted by measuring the diameter of the inhibition zone around the well.

3 Results and Discussion

3.1 Structural Studies

Figure 1 shows the XRD patterns of synthesized undoped and Fe doped ZnO nanoparticles. All the diffraction peaks are the reflection of samples indexed to the hexagonal wurtzite structure of ZnO. It is matched well with the standard data of JCPDS card 36-1451. In the case of undoped and Fe doped ZnO, the (101) diffraction peak is predominant to over all other diffraction peaks. No diffraction peaks of the other possible impurity phase are found, indicating the successful preparation of ZnO nanoparticles.

The average crystallite size (D) of the particles is estimated using the Scherrer's formula [27]

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

where λ is the wavelength, β is the peak width half maximum and θ is the Bragg's angle.

The lattice constant 'a' and 'c' are calculated using the formula [28]

$$1/d^2 = \left(4/3\left(h^2 + hk + k^2\right)/a^2\right) + \left(k^2/c^2\right) \quad (2)$$

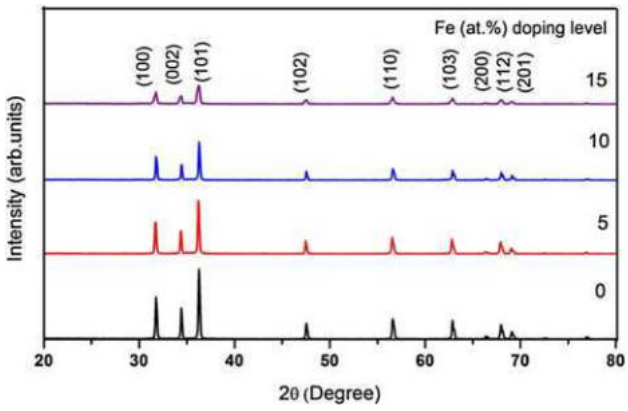

Fig. 1 XRD patterns of undoped and Fe doped ZnO nanoparticles

where d is the interplanar spacing and h, k and l are the Miller indices.

The Micro strain (ε) along the c-axis calculated the formula [29]

$$\varepsilon = \left(c - c_0\right)/c_0 \quad (3)$$

where c is calculated and c_0 is standard lattice constant values.

The calculated structural parameters are shown in Table 1. The crystallite size decreases (56 to 24 nm) as the concentration of Fe increases from 0 to 15 at.%. The decrease in the crystallite size can be explained on the basis of the Zener pinning effect. In the present work, the variation is well pronounced at the higher doping level. Due to zener pinning effect, the growth of the grain is restricted, as the retarding force generated by the lattice defects (electrostatic interaction of the incorporated Fe^{3+} ions) is greater than the driving force that causes the outward movement of the grain boundaries [30]. The calculated lattice parameters 'a' and 'c' decreases as the doping level increases which indicate the substitution of Fe^{3+} ions into the ZnO lattice. The calculated strain values show that the Fe doped ZnO nanoparticles exhibit tensile strain, whereas, as the Fe level increases to 10 at.%, the material exhibits a compressive strain. The transition from the tensile strain to the compressive strain may be due to the substitutions/interstitial incorporation of the number of Fe^{3+} ions in the ZnO lattice.

Table 1 Structural parameters of undoped and Fe doped ZnO nanoparticles

Fe doping level (at.%)	Crystallite size D (nm)	Lattice constant (Å)		Strain $\varepsilon \times 10^{-4}$
		a	c	
0	56	3.270	5.211	9.604
5	48	3.251	5.209	5.762
10	36	3.248	5.205	−1.92
15	24	3.230	5.202	−7.68

Standard value: a = 3.24982, c = 5.20661

3.2 Morphological and Compositional Analysis

The FESEM images of undoped and Fe doped ZnO nanoparticles are shown in the Fig. 2. The images show that the samples have well-defined grains with hexagonal wurtzite structure. The decrease in the grain size with Fe doping may be due to the fact of building up of some of the doped Fe at crystalline boundaries to enhance of crystalline

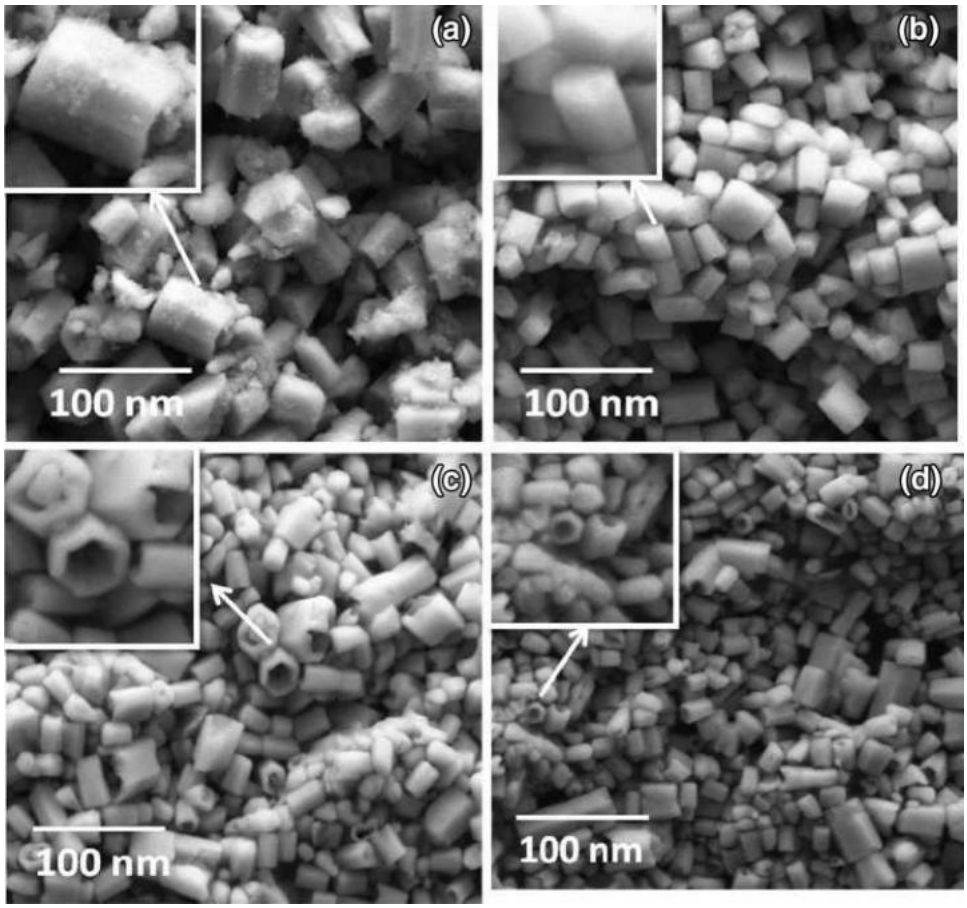

Fig. 2 FESEM images of undoped and Fe doped ZnO nanoparticles (a) undoped, (b) 5 at.%,(c) 10 at.% and (d) 15 at.%

forming larger grains than compared to that of undoped ZnO, whereas Fe (15 at.%) doped ZnO nanoparticles show reduced particle size in the range of around 24 nm. Figure 3b shows the TEM image of undoped ZnO nanoparticles. The figure depicts the morphology and size distribution of ZnO nanoparticles in the ZnO nanoparticles. The size of the particles was in the range 5–10 nm. The chemical composition of the synthesized nanoparticles is analyzed using the EDAX profile and show in Fig. 3a. The EDAX results clearly show the presence of Zn, O and Fe atoms that are very much expected in the system.

3.3 Photoluminescence (PL) Studies

The PL intensity of the undoped and Fe doped ZnO nanoparticles (Fig. 4). The PL intensity of ZnO nanoparticles with Fe increase with increasing Fe concentration from 5, 10, and 15 at.%. The PL enhances for the Fe concentrations of 5, 10, and 15 at.% in ZnO nanoparticles, at the wavelength of 420 nm has been observed at an excitation wavelength in the range of 360–370 nm. Majority donors for the luminescence in the visible region can be attributed to structural defects such as (Zn_i & O_i), vacancies (V_o & V_{zn}) and surface traps of the ZnO nanoparticles [31, 32]. The broad emission peak at 396 nm in the UV region is associated with near-band-edge emission (NBE) of ZnO results in due to band to band transition [33]. The stronger blue emission at 467 nm is excess surface defects leads to the formation of hydroxyl radicals [34]. This OH^- ion plays the role for the improvement of the efficiency of antibacterial agents [35].

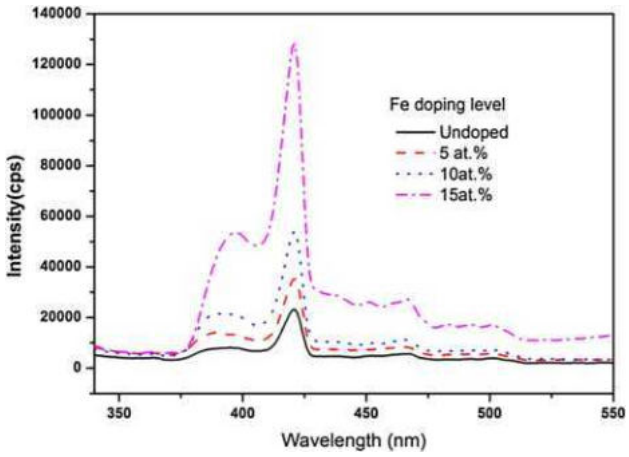

Fig. 4 Photoluminescence spectra of undoped and Fe doped ZnO nanoparticles

3.4 Antibacterial Studies

The antibacterial activity of undoped and Fe doped ZnO nanoparticles with different concentrations of stock solutions was investigated against *Bacillus subtilis, Staphylococcus aureus* (Gram-positive) strains of bacteria using the well diffusion method as shown Fig. 5. From the result (Fig. 5), it's observed that the no zone of inhibition around the control. It is observed that doped ZnO nanoparticles exhibit higher antibacterial activity than that of undoped ZnO nanoparticles. The zone of inhibition is increased as increase the Fe concentration. The efficiency of antibacterial activity of undoped and Fe doped ZnO nanoparticles

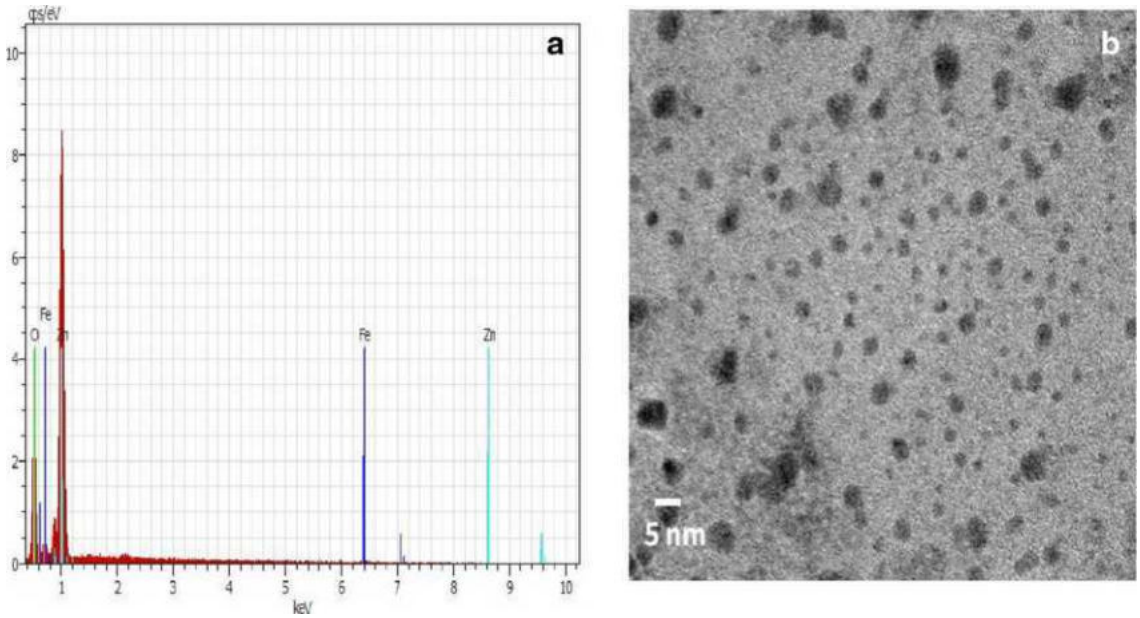

Fig. 3 **a** EDAX profile of Fe (15 at.%) doped ZnO nanoparticles and **b** TEM micrograph of undoped ZnO nanoparticle

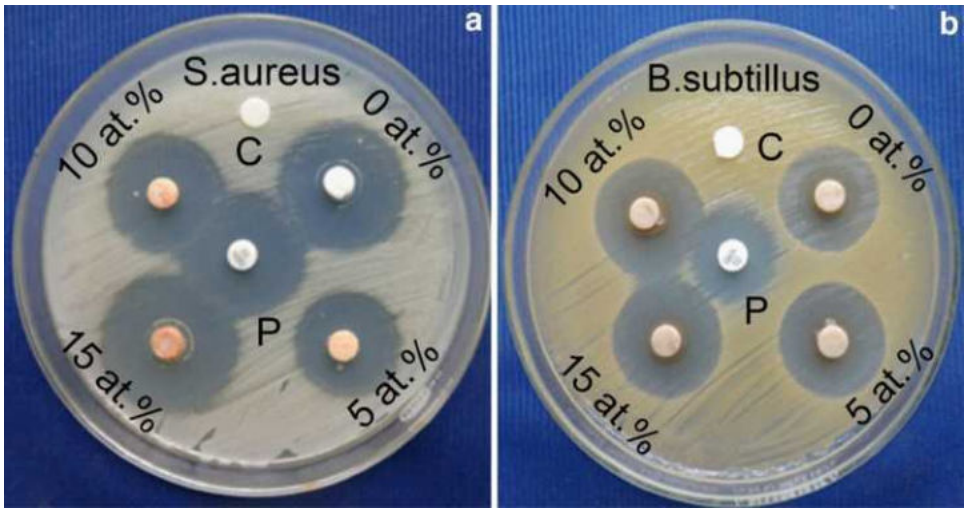

Fig. 5 Variation of zone of inhibition exhibited by Fe:ZnO nanoparticles against **a** *Staphylococcus aureus* and **b** *Bacillus subtilis*

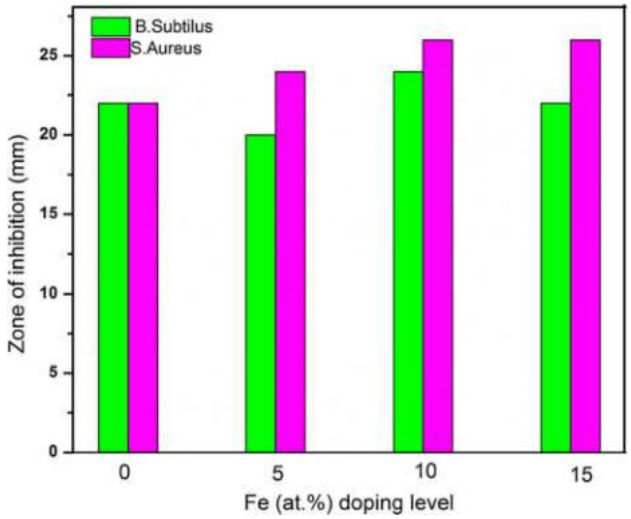

Fig. 6 Variation in the zone of Inhibition caused by ZnO + Fe nanoparticles

against *S. aureus* higher than *B. subtilis* bacteria. For comparison, the variation in the diameter of zone of inhibition is plotted as bar diagram (Fig. 6) for undoped and Fe doped ZnO nanoparticles for all two micro-organisms. It is seen that the Fe doped ZnO nanoparticles has a stronger antibacterial efficiency on gram positive bacteria which can be explained as follows: *Bacillus subtilis* and *Staphylococcus aureus* have a thick wall consisting of a large number of mucopeptides, murein, and lipoteichoic acids [36]. The factors responsible for the antibacterial activity of ZnO nanoparticles are as follows: (i) reduced size of the grains (ii) release of Zn^{2+} ions and (iii) generation of reactive oxygen species (ROS). These three factors may lead to the rupture of cell membranes, leakage of cellular contents and subsequent cell death [37]. This smaller size of the particles more readily enables them to penetrate and interact with an interior of the bacteria thereby destroying it [38]. The electron and hole pairs generated in the system result in the generation of ROS such as hydroxyl radicals (OH^-), the superoxide anions (O_2^-) and hydrogen peroxide (H_2O_2). These oxidizing species play a crucial role in the antibacterial activity of synthesized ZnO nanoparticles [39, 40]. The major origins for the generation of the electron–hole pairs are singly ionized oxygen vacancies and Zn interstitials.

The increase in the generation of ROS is due to the substitution of the Fe^{3+} ions in the Zn^{2+} sites in the ZnO lattice which causes the generation of the free carriers in the system. These free carriers play a crucial role in the generation of ROS. The generation mechanism can be written as follows [41]:

$$ZnO + h\nu \rightarrow h^+ + e^-$$
$$H^+ + H_2O \rightarrow OH^\bullet + H^+$$
$$O_2 + e^- \rightarrow O_2^{\bullet -}$$
$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$$
$$H^+ + HO_2^\bullet + e^- \rightarrow H_2O_2$$
$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^\bullet + O_2 + OH^-$$

The penetration of ROS into the cell membrane of micro-organism leads to the damage of the DNA, cell membrane and cellular protein and consequently to death of the bacteria. It is well known that these ROS have an ability to rupture the cell membrane and destroy the bacteria. It is clear that the hydroxyl radicals and superoxide anions are negatively charged. Hence, they cannot penetrate into the cell membrane, but they can cause damage to the surface of the bacteria, whereas, the H_2O_2 can penetrate directly into the cell wall and cause the destruction of the bacteria [42]. As a result, holes are generated in the valence band which can react with hydroxyl groups and absorbed water to create hydroxyl radicals (OH^-). The electrons in the conduction band can be trapped by the presence of O_2 to produce

superoxide radical anions (O_2^-) which in turn can react with hydrogen ions to form HO_2 radicals. The H_2O_2 can be generated by the combination of hydrogen ions and electrons. The decrease in the particle size enhances the penetration of the nanoparticles into the bacteria is more effective [43]. The smaller particle size, having more number of zinc interstitial and oxygen vacancies are responsible for the generation of singlet oxygen that shows good antibacterial activity against the bacterial strain which can be used in the biomedical application.

4 Conclusion

Undoped and Fe doped ZnO nanoparticles prepared using simple soft chemical route are found to exhibit good optical and antibacterial properties. The structural studies through X-ray diffraction technique clearly establish the purity of the ZnO crystal surface as no phase other than the hexagonal wurtzite ZnO is observed. The FESEM micrographs of the samples indicate that the decrease of grain size increases with the increase of Fe content in the ZnO lattice. The average crystallite size has been estimated using XRD found to be in 56 to 24 nm ranges. The photoluminescence studies are well agreed with the optical studies. It has been found that the ZnO nanoparticles doped with 15 at.% of Fe exhibit higher antibacterial efficacy compared with the undoped ZnO sample.

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Enhancing the structural, optical and magnetic properties of Cu_2O films deposited using a SILAR technique through Fe-doping

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Abstract

Undoped and Ferrous (Fe)-doped Cu_2O thin films were deposited onto glass substrates using successive ionic layer adsorption and reaction method. The variation in the concentration of Fe has significant impact on the final film properties, Fe doping with 5 wt% exhibited major property improvements compared with undoped and Fe doped films. The structural, optical, morphological, magnetic properties and atomic force microscope of the films were systematically investigated. The X-ray diffraction analysis showed that all the films had good crystalline quality and the preferential orientation along (111) plane. Optical studies show that the transmittance and optical band-gap values are maximum (2.5 eV) for the Fe doping level of 5 wt%. The relative errors are calculated for crystallite size and optical energy band gap values. The photoluminescence study confirms the presence of various defects in the Cu_2O matrix. The Fourier transform infrared results confirmed the presence of expected compounds in the samples. The field emission-scanning electron microscope images indicate that there is a gradual decrease in the grain-size with increase in the Fe doping level and a flower-like structure is obtained in the maximum doping level of Fe. The high resolution transition electron microscope reveals single-crystal nature. Magnetic measurements showed that undoped Cu_2O films exhibit diamagnetic behavior and at the maximum (5 wt%) Fe doping level, the films behave as anti-ferromagnetic material. The atomic force microscope reveals that the smoothness of the film surface increases at the maximum doping of Fe concentration.

1 Introduction

Metal oxide materials have a modifications in all fields because of their unique physical and chemical properties. Especially nano structured metal oxide materials are versatile in the applications. Cu_2O is one of the p-type semiconducting metal oxide materials with a direct band gap value of approximately 2.17 eV [1] and it is makes at a promising material for photo-catalytic and solar-cell application. Recently, metal oxide oxide materials have been found applicable in all fields, in their pure and doping films. Cu_2O behaves as the parent compound in many p-type transparent conducting oxides (TCOs: $CuAO_2$—Al, Cr, Ga, etc.,) [2]. The magnetic materials doped with Cu_2O (such as Fe, Ni, Co and Mn) increases the magnetic properties of the semiconducting materials [3]. In Fe-doped Cu_2O delafossite thin films iron is used in layer-quantities and serves as the important transition-element. Cu_2O is a suitable candidate for Bose–Einstein condensation because of its higher binding energy. The material can be used in a wide range applications such as gas sensors [4], Solar energy [5, 6], lithium–ion batteries [7], photo catalyst [8], dilute magnetic

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semiconducting materials [9], transparent conductors [10] and water splitting under visible light irradiation [11]. Copper oxide thin films have been deposited by several methods, like chemical vapour deposition [12], reactive sputtering [13], chemical bath deposition [14], spray pyrolysis [15] or pulsed laser deposition [16].

The present work reports the deposition of Fe-doped Cu_2O thin film using successive ionic layer adsorption and reaction (SILAR) technique. Another name for this method is solution based atomic layer deposition (SALD) or Modified chemical bath deposition (M-CBD) technique. This method has many advantages compared with another methods like low cost, simplicity, mild reaction conditions, good control over the deposition process and feasibility for large area deposition.

2 Experimental procedure

Substrate cleaning is one of the important steps in the deposition of thin films. Glass slides of 26 mm × 76 mm × 1 mm dimensions were used as substrates. These substrates were boiled in concentrated chromic acid for 2 h, then cleaned with double distilled water and finally rinsed with acetone before the deposition of the films. Many trials were carried out for optimizing the quality of copper oxide thin films for study in undoped and Fe-doped Cu_2O formats (1, 2 and 5 wt%). These thin films were deposited on glass substrates using SILAR technique. High purity chemicals (> 99%) such as copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$), sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), Ferrous sulphate ($FeSO_4$), and sodium hydroxide (NaOH) were used as precursor solutions without further purifications. Initially, 1 M NaOH solution was prepared with deionized water and maintained at 80 °C throughout the experiment. Then, the precursor solutions of ($CuSO_4 \cdot 5H_2O$) and ($Na_2S_2O_3 \cdot 5H_2O$) were prepared and the required concentration of 0.1 M was constantly stirred. Then 1, 2 and 5 wt% of $FeSO_4$ were added to the precursors and mixed systematically using a magnetic stirrer. The deposition-cycle of the thin film formations consists of three steps. (1) First, on cleaned glass substrate were immersed in hot NaOH solution at 80 °C for 20 s. (2) Secondly, the substrates were immersed in copper thiosulphate complex solution for 20 s. (3) Thirdly, the substrate was rinsed with ample amounts of deionized water for 10 s to remove loosely-bound particles from the substrate. The process was repeated up to 30 cycles, to obtain good quality of undoped and Fe-doped Cu_2O thin films. The deposited films were characterized extensively using the following instruments. X-ray diffraction pattern of the films was obtained using X'pert PRO (PANalytical) diffractometer with CuKα radiation (k = 0.15405 nm) in steps of 0.1 over the 2θ range of 15°–75°. The formation of copper oxide was further confirmed by Fourier transform infrared (FTIR) Spectroscopy (Model: Spectrum RXI, Make: Perkin Elmer). In order to determine the band gap energy of the films, the optical-transmission was recorded using Perkin Elmer Lambda 35 spectrophotometer. Photoluminescence (PL) spectra were studied using spectro-flurometer (JobinYvon_FLUROLOG-FL3-11). The morphological examination of the films was done using Hitachi (S-3000H) scanning electron microscope. High resolution transition electron microscope (HRTEM) images and electron diffraction patterns for the film layers were measured using the JEOL JEM 2100, 200 KV operating voltage. The atomic force microscope (AFM) studies were carried out using the instrument of (Veeco-di CP II). The room-temperature magnetic properties were obtained using a vibrating sample magnetometer (VSM, Lake Shore-7400, USA).

3 Results and discussion

3.1 Structural analysis

The XRD patterns of undoped and Fe doped Cu_2O thin films are shown in the Fig. 1. All the XRD patterns exhibit the preferential orientation along (111) plane because it has the lowest surface energy. In but, the undoped and doped films (1, 2 and 5 wt%) the crystallinity of the films is observed. No additional peaks are present. In Fe doped Cu_2O film with 1% the intensity increases, this may be caused by the compensation of oxygen vacancies by the incorporated Fe ions. In the doping level of (2 wt%), the additional peaks reveal the diffraction peak position at (39.62°) with a corresponding plane at (306). The intensity of the diffraction peak, corresponding to the preferential orientation is found drastically increased

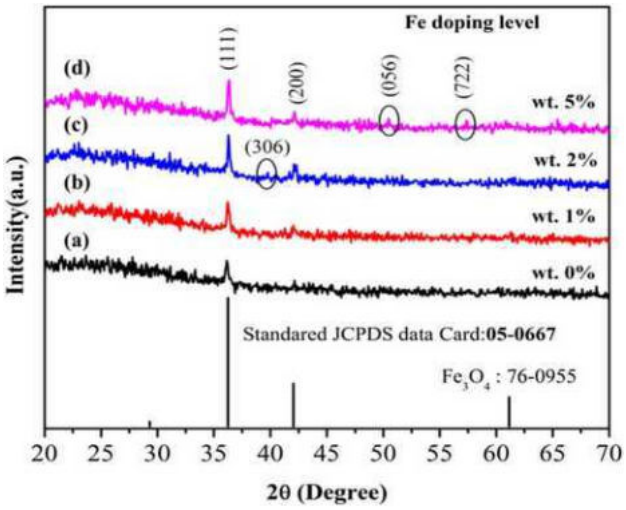

Fig. 1 XRD patterns of Fe-doped Cu_2O thin films with (*a*) 0%, (*b*) 1%, (*c*) 2% and (*d*) 5% of Fe doping concentrations

with the increase in the doping of Fe ions. For the maximum doping concentrations (5 wt%) of Fe ions, two additional peaks are induced nearly at 2θ = (50.47°) and (57.37°) for the corresponding planes at (056) and (722). It is simultaneously low when the peak at (306) plane disappears, because the radius of Fe^{3+} ions (63 pm) is lower when to compared with Cu^{2+} ions (77 pm). The other peak exhibited in Copper Oxide, may be attributed to the incorporation of Fe on to Cu_2O. At this doping level (5 wt%), the intensity of the preferential orientation peak decreases, which may be due to the interstitial incorporation of excess Fe ions in to the Cu_2O matrix. The interstitial incorporation induces a different growth pattern, which has been shown by the XRD patterns for the sample with 5 wt% of Fe. The XRD patterns are exactly matched with the standard value in JCPDS (Card No: 05-0667). The crystallinity of the film increases with increases of Fe doping concentration and it is evidenced by the gradual decrease in the full width half maximum (FWHM) value and the resultant enhancement of the crystallite size. From the Debye–Scherrer's formula (Eq. 1) [17], the crystalline size can be calculated,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where k is a constant (k = 0.9), β is the full width at half maximum (FWHM), λ is the wavelength of the X-ray, θ is the diffraction angle. The cubic system of lattice constant 'a' (Eq. 2) and dislocation density (Eq. 3) can be calculated using the formula [18] and the calculated values are tabulated in Table 1.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{2}$$

$$\delta = \frac{1}{D^2} \tag{3}$$

3.2 Optical properties

Optical transmittance spectra of undoped and Fe-doped films with different concentrations were recorded from ranges of 450 to 1100 cm^{-1} as shown in inset Fig. 2. The transmission percentage of the film gradually decreased when the doped material increased. Due to, the very high transmittance in the visible region, these materials are used as aesthetic window glass. On varying the concentration of doping, the energy band gap value also increased. The fundamental absorption can be used to determine the band-gap of the films. Figure 2 shows the band gap of the films as estimated from the Tauc's plot relation of absorption co-efficient (α) and the photon energy (hν) as [19] showing the following Eq. (4).

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right) \tag{4}$$

3.3 The relative error measurement

The undoped and Fe doped Cu_2O thin films are deposited on to a glass substrate with different concentration. In this part, we have studied the correlation between the crystallite size and optical energy band gap values with the different doping concentration of Fe ions. The calculation of relative error is measured using the formula [20], and these results are

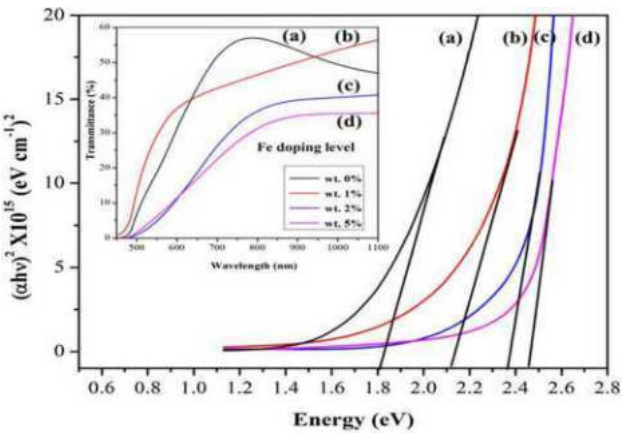

Fig. 2 The plot for calculated band gap for Fe-doped Cu_2O thin films with (*a*) 0%, (*b*) 1%, (*c*) 2% and (*d*) 5% of Fe doping concentrations and optical transmittance (inset). (Color figure online)

Table 1 Structural and optical parameters of undoped and Fe-doped Cu_2O thin films

Doping concentration	Crystallite size (D) nm	Crystallite size (Dc) nm	ε (%)	Dislocation density (δ) (lines/m^2)	a[a] (Å)	Energy band gap ($E_{g\text{-}Exp}$) (eV)	Energy band gap ($E_{g\text{-}Corr}$) (eV)	ε (%)
Undoped	62.83	30.00	52.25	2.53	2.4844	1.80	2.50	30.00
Fe 1%	59.80	26.00	56.52	3.52	2.4728	2.10	2.30	9.52
Fe 2%	41.83	22.00	47.40	4.26	2.4710	2.36	2.20	6.77
Fe 5%	36.40	28.00	23.07	6.49	2.4706	2.45	2.30	6.12

D—experimental value of crystallite size, Dc—correlated value of crystallite size, $E_{g\text{-}Exp}$—experimental values of optical band gap energy, $E_{g\text{-}Corr}$—Correlated values of optical band gap energy, ε—relative error

[a]Standard data: a = 2.4650 Å (JCPDS Card No: 05-0667)

reported in Table 1. Figures 3 and 4 shows the evaluation of Fe doping levels of Cu_2O thin films calculated of crystallite size and optical energy band gap values respectively. From the Fig. 3, the undoped film was found to be the maximum enhancement of crystallite size and maximum doping (5%) level the film was found to be a minimum relative error. Based on the experimental and correlation values for the crystallite size that were developed, good agreement was found between the calculated and experimental values. From Fig. 4, the relative error of optical energy band gap value is calculated between the experimental and correlated values. For the undoped film, the relative error is maximum, further increases the doping level the relative error are reached very smaller compare than the undoped film. The decrease in the relative error of undoped to Fe doped films can be explained by the enhancement of good optical properties which can be observed in fewer defects and fewer disorders.

$$\varepsilon = \left[\frac{\left(E_{g\text{-}Exp}\right) - \left(E_{g\text{-}Corr}\right)}{E_{g\text{-}Exp}} \right] \times 100\% \quad (5)$$

Figure 5 shows the FTIR spectrum of undoped and Fe-doped films. The FTIR is a key indicated of chemical bonding in the respective material. The spectra for related to un-hydrogenated and hydrogenated Cu, Fe-doped nanocrystalline films. The peak around the wavenumber 2442–2445 cm^{-1} is due to the exatance of the CO_2 molecule in air. Asymmetric and symmetric stretching of the carboxyl group (C=O) are exhibited around the peaks 1645–1722 cm^{-1} and 1387–1384 cm^{-1} and the stretching vibrations of O–H groups are observed approximately at 3559 cm^{-1}. The Cu–O stretching vibrations are see around 524 cm^{-1} [21]. It is strong evidence at the presence of CuO. The absorption peaks are observed nearly at 612 cm^{-1} for the respective Cu_2O compound [22]. The

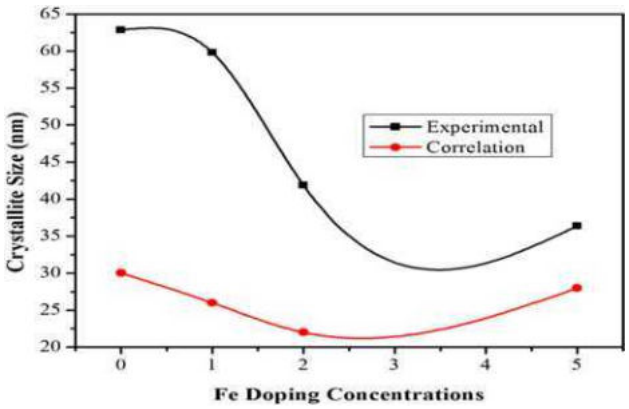

Fig. 3 Experimental Crystallite size and correlation Crystallite size of undoped and Fe doped Cu_2O thin films

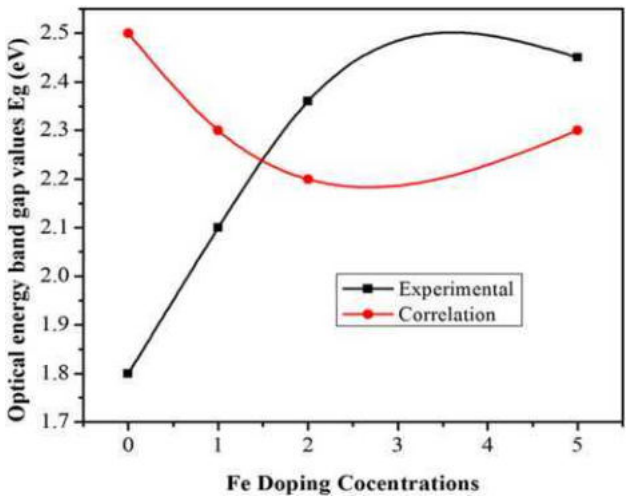

Fig. 4 The variation of optical energy band gap values for experimental and correlation of undoped and Fe doped Cu_2O thin films

unknown functional frequencies are detected using FT-Raman spectra as shown in Fig. 6.

Figure 7 shows the photoluminescence (PL) spectra of undoped and Fe-doped Cu_2O films measured at room temperature for the range between 525 and 800 nm. The intensity of the peaks increases with increase in Fe doping in Cu_2O, 1, 2 and 5 wt%. The intensity of the PL indicates the electron–hole scattering and recombination in the process. The near band energy (NBE) is seen at 611 cm^{-1} [23].

3.4 FESEM, HRTEM and AFM

Figure 8 shows the field emission-scanning electron microscope (FE-SEM) images of undoped and Fe doped Cu_2O

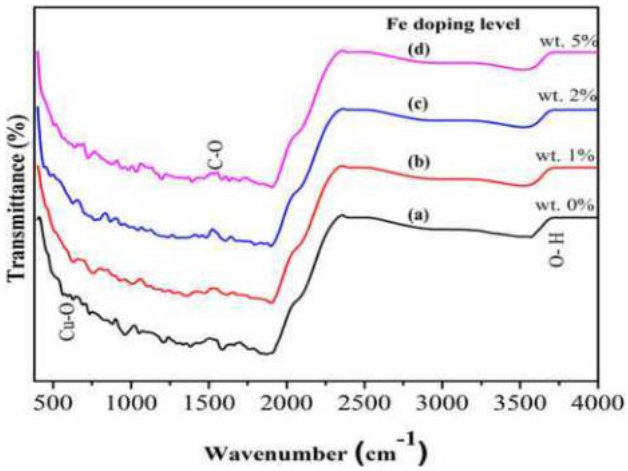

Fig. 5 FTIR spectrum of Fe-doped Cu_2O thin films with (*a*) 0%, (*b*) 1%, (*c*) 2% and (*d*) 5% of Fe doping concentrations

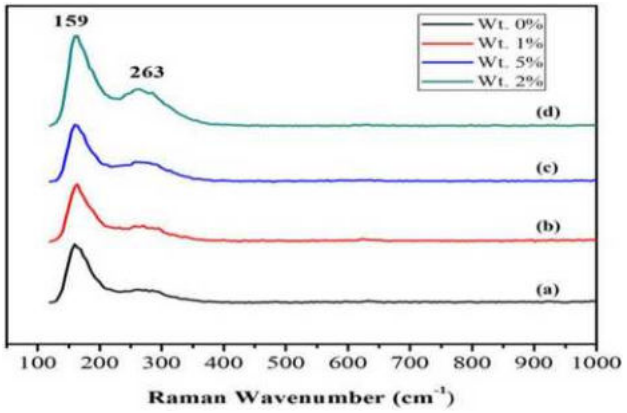

Fig. 6 FT-Raman spectra of Fe-doped Cu_2O thin films with (*a*) 0%, (*b*) 1%, (*c*) 2% and (*d*) 5% of Fe doping concentrations. (Color figure online)

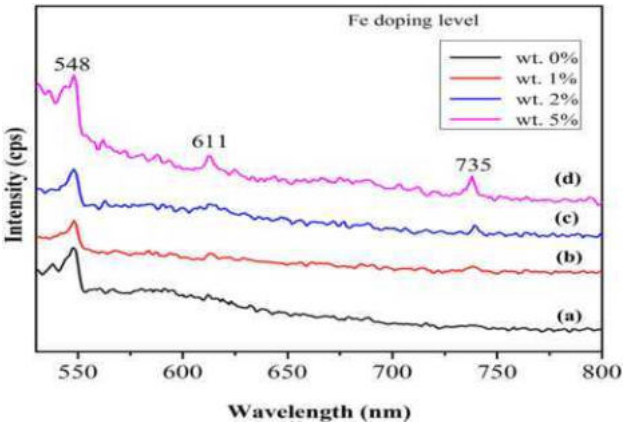

Fig. 7 Photoluminescence (PL) spectrum of Fe-doped Cu_2O thin films with (*a*) 0%, (*b*) 1%, (*c*) 2% and (*d*) 5% of Fe doping concentrations. (Color figure online)

thin films. In the case of undoped film, the surface shows a number of small grains which combine to form larger grains. The large grains are uniformly distributed in the surface. After doping of Fe concentration, the film shows remarkable changes in the surface morphology. For 1% of Fe-doping level, it is seen that well defined nanorods form on the undoped film. For the 2 wt% of Fe doping level, the nanorods are clearly indicated and the diameter of the rods decrease but simultaneously the length of the rods increases. Additionally the surface of the film exhibits a flower-like structure. But it is not clearly visualized. The Cu atoms (minority) are replaced by Fe atoms in the crystalline matrix and the secondary phase of Fe atoms are exhibited. This results in good agreement with the XRD result, as evidenced from the secondary peak (Fe_2O_4 at the plane of 306) are the near absence of other peaks. When the doping level increases, the nanorods disappear and the flower-like structure is uniformly exhibited on the surface of the film. The inset figure of Fig. 8d shows well defined flower-like structure for the maximum Fe-doped film. This result correlate with those of XRD studies.

Figure 9 shows the TEM and HR-TEM images of undoped and Fe-doped Cu_2O thin films for 5 wt% respectively. The TEM images are found to be consistent with the SEM results. The HR-TEM images clearly depict the uniform growth of the film along (111) plane as the lattice-fringes are found to be regularly arranged with the interplanar spacing of 0.247 nm. The magnification of HR-TEM are insets in the bottom right corner of TEM images. It is well known that the 'd' spacing corresponding to the (111) plane of cubic structure of Cu_2O is 0.247 nm (JCPDS Card No: 05-0667). The pattern well matches with the cubic structure of the Cu_2O. This result is in good agreement with the XRD observations.

This is clearly confirmed by the AFM image Fig. 10. The surface properties are found to be greater in the 5 wt% of Fe doped film. For example, the surface smoothness and Fe doping level are uniformly distributed. This enhances the packing density which is very high when compared with that in other films. These results may be attributable to the reduction in the oxygen deficiency and are well supported by XRD, FESEM and HRTEM results.

3.5 Magnetic behavior

Figure 11 shows the magnetic behaviour of undoped and Fe-doped Cu_2O thin films studies observed using a vibrating sample magnetometer. These films were investigated at room temperature. No impurity phase peaks were evident in the X-ray diffraction patterns. The films showed good crystallinity. Pure Cu_2O is diamagnetic in nature. At 305 K the 1% Fe-doped Cu_2O film showed diamagnetic property. Increased Fe-doping (2 wt%), slightly changed the diamagnetic property because of the increased hole-concentrations with the doping of Fe ions (5 wt%), the film exhibits anti-ferromagnetic behaviour. With increases of Fe concentration both the number of Fe^{3+}–Cu^{2+} pairs and the hole concentrations increased and so the crystallite size decreased.

4 Conclusion

Undoped and Fe doped thin films were deposited using a low-cost SILAR technique. It is found that the film doped with 5% of Fe concentration possessed good crystalline quality, better optical transmittance, and enhanced optical energy band gap. The relative errors of crystallite size and optical energy band gap values are decreased for maximum doping level compare than undoped film. The FESEM studies showed that the Fe (5%) doping caused drastic changes

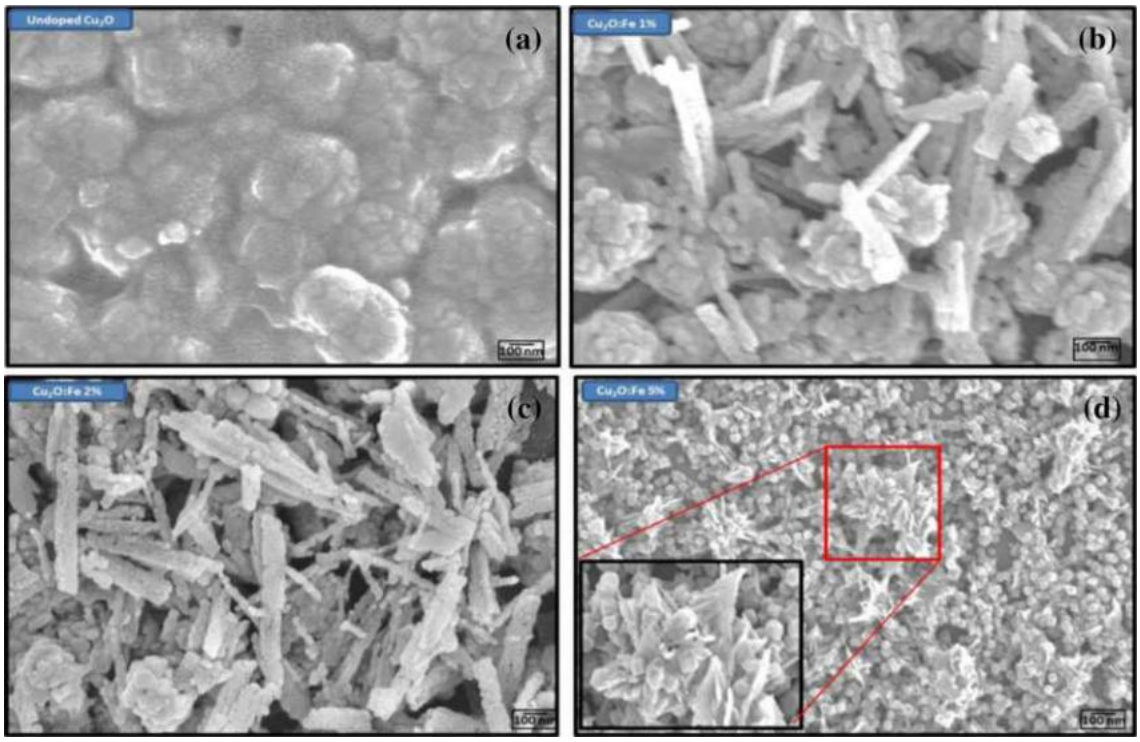

Fig. 8 FESEM images of Fe-doped Cu_2O thin films with (**a**) 0%, (**b**) 1%, (**c**) 2% and (**d**) 5% of Fe doping concentrations

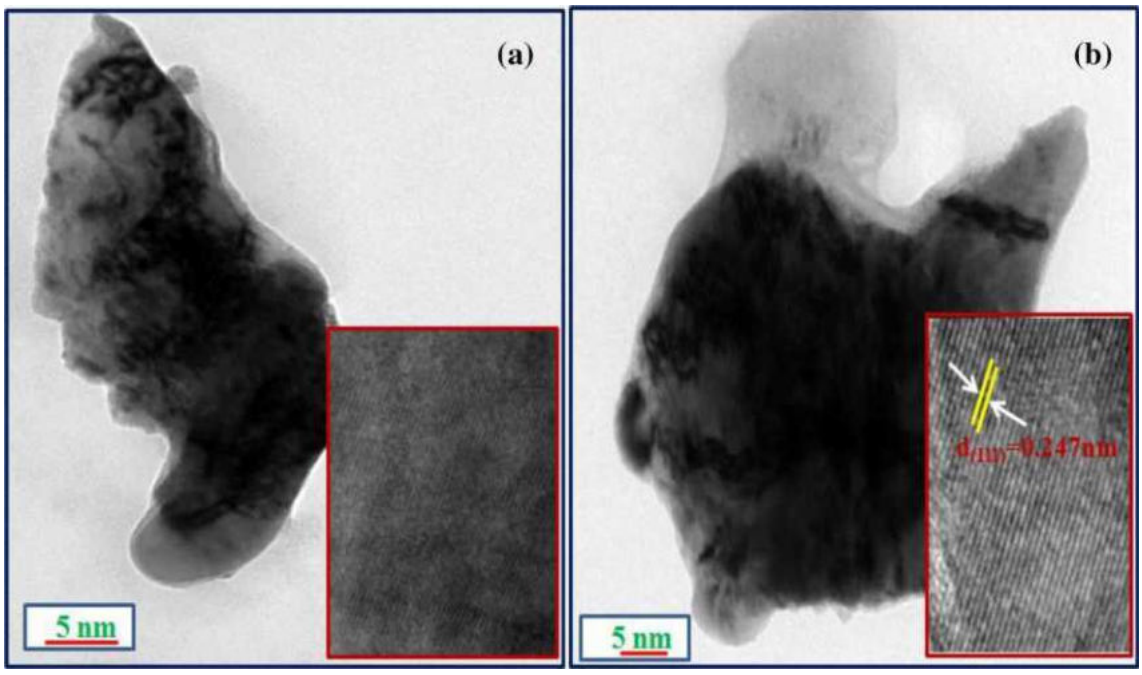

Fig. 9 TEM and HRTEM (inset) images of **a** undoped and **b** Fe-doped with 5% of Cu_2O films

in the surface morphology of the films. From the HRTEM studies revealed that the undoped and Fe doped Cu_2O films are predominantly exposed (111) orientation plane. From AFM and VSM studies, the smoothness of the film increased and the anti-ferromagnetic behavior achieved for the maximum doping level of Fe 5%.

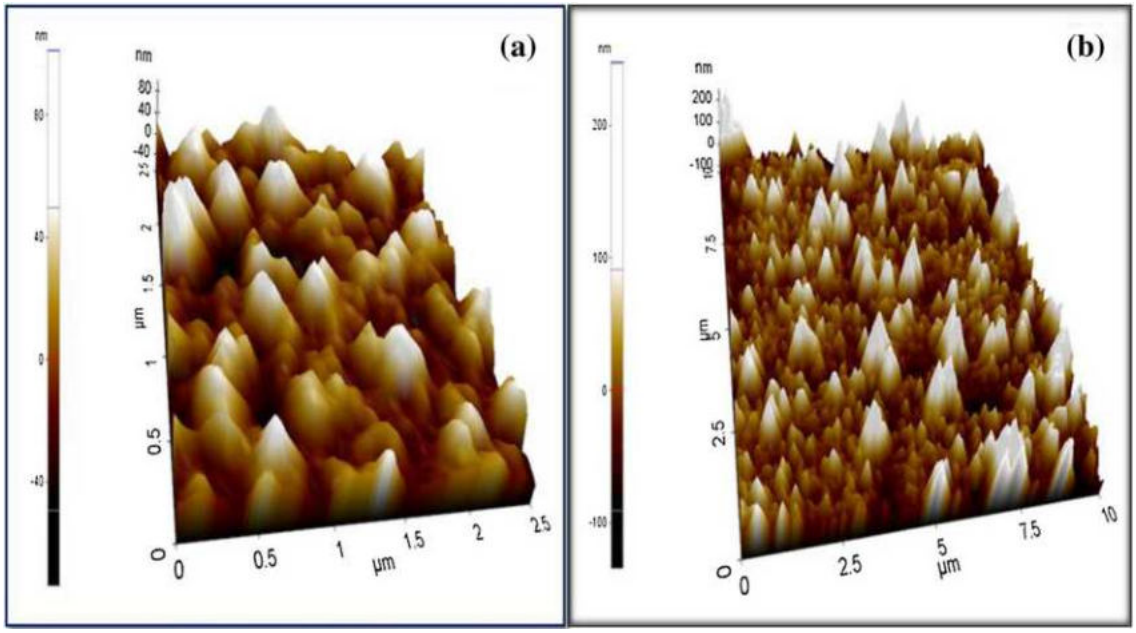

Fig. 10 AFM images of (**a**) undoped and (**b**) Fe-doped with 5% of Cu_2O thin films. (Color figure online)

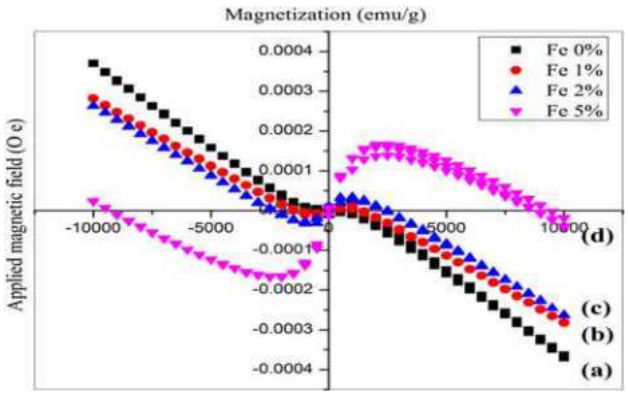

Fig. 11 Magnetic behavior of Fe-doped Cu_2O thin films with (*a*) 0%, (*b*) 1%, (*c*) 2% and (*d*) 5% of Fe doping concentrations

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GROWTH AND CHARACTERIZATION OF ZTS SINGLE CRYSTAL AND ITS ANALYSIS OF OPTICAL, STRUCTURAL, MECHANICAL, THERMAL AND DIELECTRIC STUDIES

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ABSTRACT: The growth of Zinc Thiourea Sulphate (ZTS) Single Crystals is analysed in this study. The crystals were grown by slow evaporation technique. The X-Ray diffractions study indicates that the prepared grown crystals confirm the crystal structure for ZTS crystal. In Good quality crystals of size 12x5x7mm^3 single crystals were grown. The presence of Sulfur- to- Zinc bonds in the complex has been revealed by Fourier transform infrared analysis. The optical characterization shows that the grown crystal having ZTS crystal has low UV cutoff of 220nm and has a good transparency in the visible region. The thermal analysis shows that the Zinc Thiourea Sulphate can be expoliated up to 240°C of ZTS Single Crystal. The Vicker's microhardness number was found to increase ZTS crystal which studies the mechanical stability of the grown crystal. The dielectric properties of dielectric constant as function of frequencies 80KHz room temperature for electro optic modulators of ZTS Single crystal.

Key word: FTIR, UV-Visible, Micro hardness test, Powder XRD, Thermal analysis, electrical studies.

1.INTRODUCTION:

Zinc thiourea sulphate (ZTS) is a semi organic nonlinear optical material (NLO) [1-2]. In semi organic nonlinear optical materials, metal complexes of thiourea which have low UV cutoff wavelengths, and high power frequency conversion [3]. ZTS crystals have thermal stability is less and more over nlo efficiency is high. In inorganic crystals, NLO composition is very low but thermal stability is high [4]. In semi organic nlo material non-linearity is very high and it has laser induced damage, low angular sensitivity and good mechanical hardness. The ZTS possess is 1.2 times more SHG efficiency than KDP [5]. Nonlinear optical crystals has a significant impact on laser technology. Optical communication and electro optical modulation [6]. The grown crystal has been characterization by carrying out FTIR,UV-Visible spectrometer, Vickers hardness test, thermo gravimetric (TG/DTA), powder X-Ray diffraction, and dielectric measurements.

2.MATERIALS AND METHODS:

The compound is synthesized from purified zinc thiourea sulphate in the stoichimetric ratio 1:3. By recrystallization process the synthesized material is purified using water as a solvent.

$$ZnSO_4+3[CS(NH_2)_2]\rightarrow Zn[CS(NH_2)_2]_3.O_4$$

Purified compound is dissolved in double distilled water to obtain a homogenous solution. The solution is kept under a constant temperature to obtain seed crystals by spontaneous nucleation. The temperature was reduced at a rate of 0.05-0.5^{0}C/day growth progressed. The seeds obtained from slow evaporation were employed for the growth. The period of growth ranged from 40-60 days. Good quality crystals of size 12x5x7mm^3 were grown single crystal.

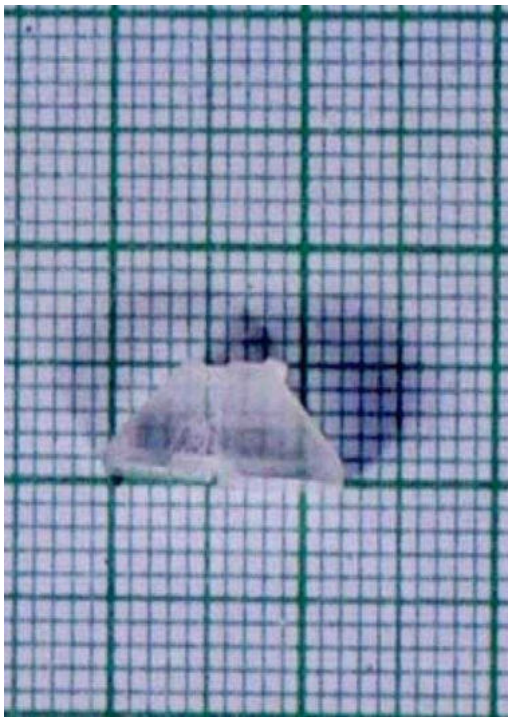

Fig1. The Photograph of ZTS single crystal.

3. CHARACTERIZATION:

3.1 Powder X-Ray Diffraction:

The powder X-Ray diffraction analysis of pure ZTS was subjected. The samples were scanned over the range 11 to 52 (2θ). The recorded X-ray spectra of pure ZTS is shown in figure 2(a). The interplaner d spacing was calculated using bragg's equation. Using the value of d, the hkl values for all the reflections were obtained. The experimental and calculated d-values along with the hkl indices of the corresponding reflecting planes for pure ZTS crystals are tabulated respectively. All the peaks could be indexed to the orthorhombic structure and cell parameters for ZTS crystal are a=11.12Å, b=7.773Å, c=15.49Å for ZTS crystal.

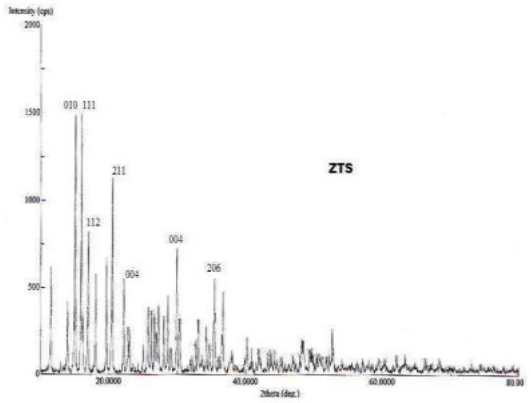

Fig 2(a) Powder X-Ray spectrum of ZTS

3.2 Uv-Visible Transmittance Study:

The UV-Visible spectrum of pure ZTS crystals were recorded in the range of 190nm-1100nm using LAMBDA-35 uv-visible spectrophotometer. The optical transmission spectra shown in fig 2(b) of ZTS has a good transparency in between 200 and 1100nm. The lower cutoff frequency of pure ZTS crystals occur 220nm. The ZTS crystals has minimum of 55% transmission increasing transparency in visible region for pure ZTS single crystal.

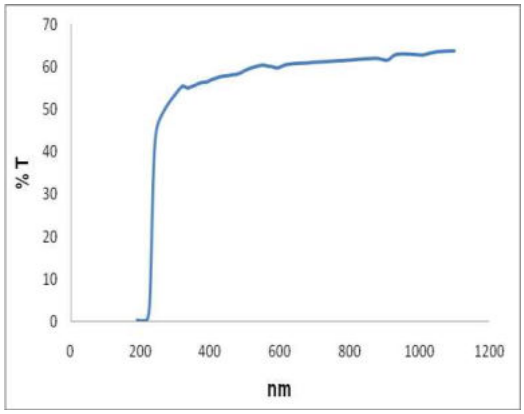

Fig 2(b) UV-Vis spectrum of ZTS

3.3 FTIR Analysis:

The presence of ZTS crystal was analyzed from the FTIR spectra of the grown crystals and compared with each other. The figure 2(c) shows that the FTIR spectra of pure ZTS crystals. The spectrum was recorded using KBr pellet technique in the frequency region 400 - 4000cm^{-1} using PERKIN ELMER fourier transform infarad spectrometer. The FTIR spectrum contains the bands corresponding to different molecular groups present in the sample. The ZTS show a broad envelope lying in between 2712cm^{-1} and 3585 cm^{-1} arising the symmetric and asymmetric modes of the NH_2 group of Zinc coordinated thiourea. The absorption band at around 1626cm^{-1} in the spectra of NH_2 bending vibration. The absorption observed at around 1508cm^{-1} corresponds to the N-C-N stretching vibration. The absorption band at about 1400cm^{-1},1030cm^{-1},948cm^{-1},746cm^{-1}corresponds to the N-H stretching vibration. The presence of sulphate ion in the coordination sphere of pure ZTS from the peaks FTIR spectrum in the frequency region.

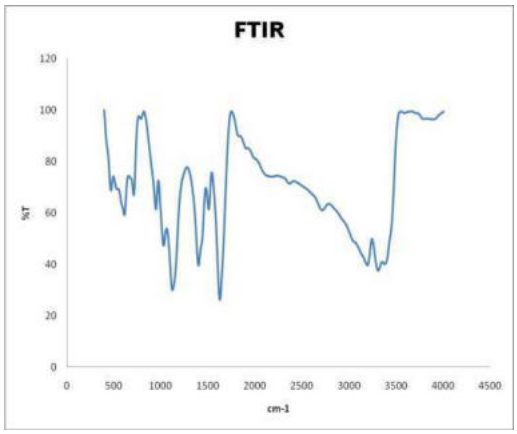

Fig 2(c) FTIR Spectrum of ZTS

Table1: Wavenumber for FTIR Spectrum of ZTS

Thiourea	Pure ZTS	Assignment
3585	2712	NH_2 stretching
1626	1508	Asymmetric N-C-N stretching
1400	1030	N-H stretching
948	746	N-H stretching

3.4 Microhardness Measurement:

Microhardness testing is performed on single crystals to evaluate the mechanical properties to the suitability of the material by measuring the resistance of the lattice was applied load. The hardness measured using the leitz - wetzler hardness tester. The ZTS crystal shown in fig 2(d) grown and load P was varied between 25g to 100g by the

time of constant (10s) for the all trials and the diagonal length was measured.

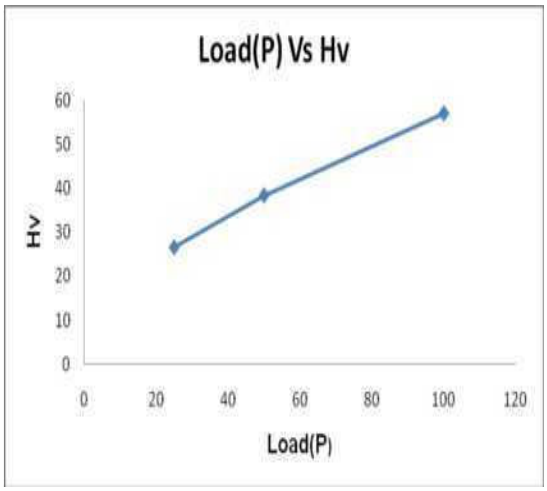

Fig 2(d) Microhardness test of ZTS

3.5 THERMAL ANALYSIS OF ZTS:

The thermo gravimetric analysis of pure ZTS crystals were analyzed of SDT Q600. In TGA/DSC figure 2(e) shows that the sample pure ZTS crystals are carried and between 25°C is stable till 240°C in nitrogen atmosphere at a heating rate 10°C/min with 37.78% weight loss of observed from second endothermic peak is increasing to 347.84°C. this ZTS crystal due to the sulphur of thiourea from zinc coordination in thermo gravimetric analysis.

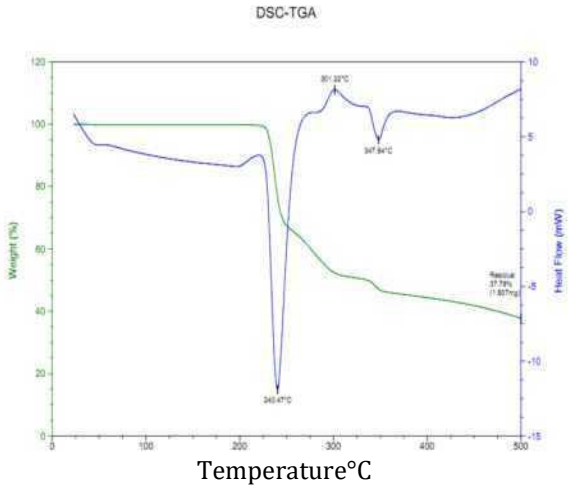

Fig 2(e) TGA-DSC crystal of ZTS

3.6 Dielectric Properties:

Dielectric properties are correlated with electro-optic property of the crystal. The figure 2(f) shows that the relative dielectric constant (ε_r) for ZTS crystals. The room temperature values of ε_r gradually decreases as the frequency increases ε_r decreases upto 80 KHz with respect to the room temperature. These values are low frequencies the dipolar contribution decreases the electronic contribution increases at high frequencies to the total polarizability of ZTS temperature increases.

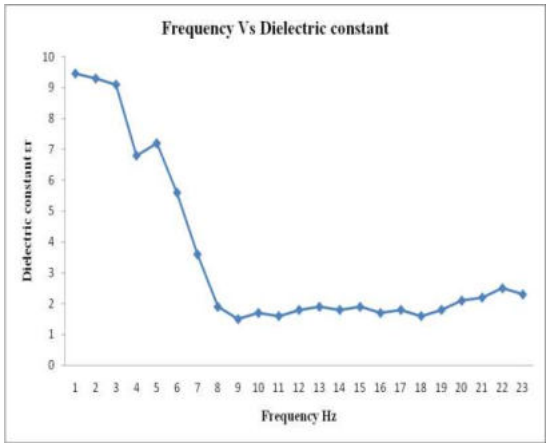

Fig 2(f) dielectric studies of ZTS

CONCLUSION:

The growth and characterization of pure ZTS crystals were grown by slow evaporation method. The crystal is confirmed with X-Ray diffraction were determined to the orthorhombic system for PC2a1. The FTIR spectra revealed all the characteristic bands corresponding to different molecular groups present in the sample. The transmission spectra revealed that the crystals have an extended transparency down to UV-Visible spectrometer. The thermo gravimetric (TGA/DSC) analysis shows that the thermodynamically more stable than pure ZTS crystal. The mechanical property of the grown crystal has been studied by microhardness number values is increased. The frequency of variation dielectric constant at room temperature and above shows the decrease with increase in frequency 80 KHz is a characteristic of a normal dielectric in ZTS single crystal.

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ACOUSTICAL STUDIES OF ZINC ACETATE AND ITS STATISTICAL INTERPRETATION

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ABSTRACT

The structure of liquids are less well established than that of gases or solids. Despite a great deal of research in this area, we still do not have a clear picture of the way in which molecules are arranged in even the most common liquid, water. We do, however, have a reasonably detailed knowledge of the average distances between atoms or molecules in a liquid. Moreover, we can estimate with considerable accuracy the magnitude of the forces between particles in a liquid. Since the molecules in a liquid are much closer together than those in a gas, attractive forces between molecules are considerably stronger.

The Scientist A. PASSYANSKI gave the Signal Acquisition in Ultrasonic systems. Compressibility is explained by assuming that the molecules are fully compressed. The compressibility of the solution is mainly due to free solvent molecules. this was given by S.BARNARTT. W.SCHAFF HAS been engaged on the study of importance of Molecular interaction between the acceptor and the Donor molecules.

In India V.A.TABHANE worked on the Acoustical study of organic materials. The internal pressure and free volume analysis for Aqueous solution of Pinacol was given by S.Sekar and A.Dhanalakshmi. The Molecular interaction studies on liquids by Viscometric / Ultrasonic techniques was given by J.B.THAKARE, D.T.DONGRE & DEOGANKAR. The measurement of Experimental Ultrasonic velocity of organic substances was given by S.JAYAKUMAR, V.KANNAPPAN, S.SUBRAMANIAN and others. The study of Molecular interactions has inspired many researchers and extensive investigations have been carried out in aqueous solutions.

Introduction:

The energy of perfect gas is the sum of the internal energies and the transactional kinetic energies of the individual molecules, the intermolecular potential energy being zero. The inter-atomic or vibrations have low potential energies. However in this case also an adequate partition function can be obtained. In a liquid Cohesive forces are not strong enough to present a considerable transactional energy to individual molecules. A liquid shows short range ordering in space. Ultrasonic studies of electrolytic solutions yield valuable information about the nature and strength of molecular interactions. The estimation of ultrasonic velocity helps to evaluate the internal pressure and free volume of solutions.

Internal pressure of liquids provides a wealth of information about the state of liquid. It explains many of the properties of liquids and solutions. Internal pressure though a single factor appears to vary due to all the internal interactions such as hydration of solute solvent interactions.

The effect of temperature and concentration on internal pressure and free volume are studied and quantitative relationships are established. The dependence of internal pressure and free volume on each other is also checked.

Experimental studies:

The aqueous solutions of Ammonium and calcium sulphate (AR Grade) is dissolved in double distilled water for making up different concentrations under study. A Mittal type fixed frequency Interferometer (2 MHz) is used for the determination of Ultrasonic velocity. A 10 ml specific gravity bottle& cannon Fenske Viscometer was used for determining both density & viscosity of the solutions respectively. A circulating thermostat to maintain the temperature of the system constant for temperature variation studies.

Mathematical formulas:

Intermolecular free length (L_f): $L_f = \left(\frac{K}{U_\beta^{1/2}}\right) = K(\beta_{ad})^{1/2}$

Ultrasonic Velocity (U) =λ x f

λ = wavelength f=frequency

Where λ=2d/n

Relaxation time (ι) = 4η/ (3ρU^2)

Rao's Constant (R)= $R = \frac{M}{\rho} \bullet u^{1/3}$

Wada's Constant(W)= $\left[\frac{M}{\rho}\right](\beta_{ad})^{-1/7}$

Results and Discussion

The experimentally determined values of ultrasonic velocity for Zinc Acetate at temperatures 303K, 313K and 323K are summarized in the table.

The measurement of ultrasonic velocity is an important tool to study the physical & chemical properties of the liquid. Ultrasonic velocity and allied temperatures are presented graphically in figures.

The parameters derived from ultrasonic measurements such as adiabatic compressibility, acoustical relaxation time, intermolecular free length, specific acoustic parameters for Ammonium and calcium sulphate for various concentrations, at different impedance, molar sound velocity and molar compressibility prove a better insight into molecular environment in liquid mixtures and solutions.

In this the ultrasonic velocity increases with increase in both temperature and concentration.

The plots between the ultrasonic velocity and concentration potential shows that the ultrasonic velocity is found to linearly increase with temperatures. This linear increase suggests that there are strong solute-solvent interactions in the liquid solution. These interactions are both concentration and temperature dependent. The effects of temperature on the interactions are more than that of concentration. At low concentrations, the number of hydrogen bonds formed may be less and at higher concentrations, it may be more due to solute-solute interactions **[Graph1]**.

The intermolecular free length of the liquid systems decreases with increase in concentration. The free length is the distance between the surfaces of the neighboring molecules. It indicates significant interactions between the solute and solvent molecules, due to which the structural arrangement in the neighborhood of constituent solute particles is considerably affected. At lower concentrations, the molecules are not closer and then the intermolecular free length will be high **[Graph 2]**.

The variations of molar sound velocity (Rao's constant) and molar compressibility (Wada's constant) show both trend with the variation of temperatures as expected **[Graphs 4,5]**. Any modifications induced by the solute on the local structure of the solvent generate changes in the solutions and therefore it can be used to characterize solvated properties of solute in dilute solutions.

Acoustical relaxation time of all the systems studied here, is found to decrease with increase in temperatures. It is directly proportional to adiabatic compressibility and viscosity. These changes with respect to concentrations are not similar to those found in adiabatic compressibility. These changes in acoustical relaxation time with respect to concentrations and temperatures are

similar to those found in viscosity[4]. This supports the view that viscous forces play a dominant role in the relaxation processes **[Graph 3]**.

From the statistical Interpretation the values of R^2 for ultrasonic velocity agrees with the results of ultrasonic studies.

The values of R^2 For the intermolecular Free length, Free volume also agrees better with the Results of ultrasonic studies.

***Velocity* (U) (m/s)**

Mol/Temp	303k	313k	323k
0.1	1519	1618	1652
0.2	1570	1624	1663
0.3	1585	1613	1664

Intermolecular free length (L_f)mt

303k	313k	323k
0.006605	0.005709	0.005616
0.005864	0.005688	0.005578
0.005761	0.005498	0.005352

Relaxation Time (10^{-13}sec)

Mol/Temp	303k	313k	323k
0.1	6.864	3.62	3.14
0.2	8.959	3.59	3.01
0.3	9.276	4.68	3.25

Rao's Constant

303k	313k	323k
932.143	914.235	937.378
884.042	917.609	943.620
885.203	874.938	906.421

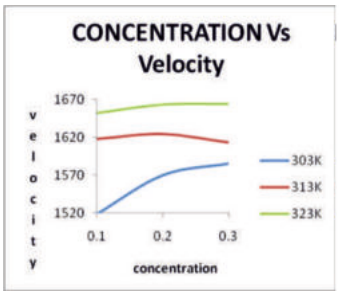
Wada's constant (W)

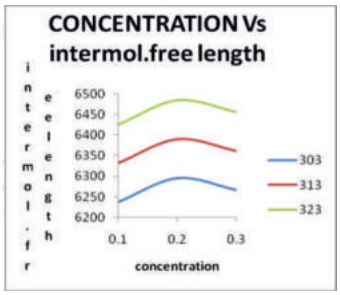
Mol/Temp	303k	313k	323k
0.1	330.32	362.50	372.10
0.2	348.90	364.23	375.29
0.3	353.61	363.17	377.77

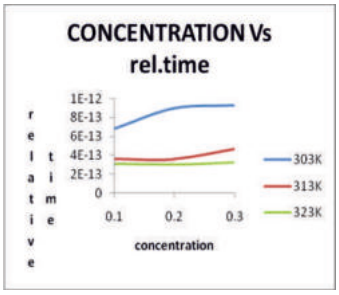
Free volume (V_f)(mt):

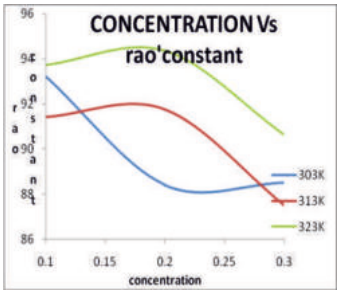
303k	313k	323k
0.1146	0.1665	0.1697
0.2293	0.1721	0.1704
0.3440	0.1738	0.1692

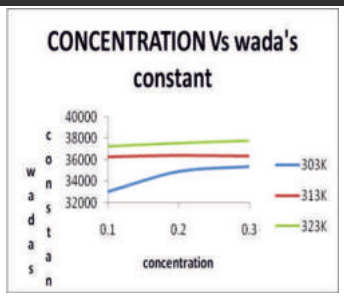
Graph

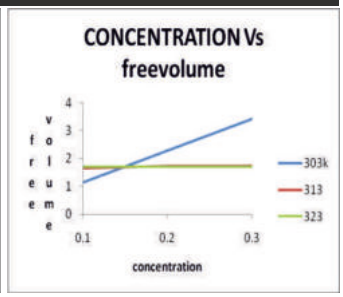












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Growth ,Thermal, Mechanical, Structural Properties and Surface Morphology of Manganese Chloride Diammonium Phosphate Mixed Crystal

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ABSTRACT

The inorganic compounds often consist of relatively small number of broad bands compared with the spectra of organic compounds. The metal halogen absorption band is dependent on the strength of the bond, the mass of the metal atom and the valence state of the metal atom. A number of crystalline ammonium compounds undergo characteristic phase transitions, resulting in dramatic changes in a variety of physical properties as their temperature is changed. In the report on Mn doping on barium tartrate identifies few extra peaks and the intensity of the prominent peak is found to be decreased . In this paper we report the thermal,mechanical, structural properties and surface morphology of manganese chloride diammonium hydrogen phosphate mixed crystal .

1. Introduction

Diammonium Hydrogen Phosphate (DAHP) is one of the series of water soluble ammonium phosphate salts that can be used as a corrosion inhibitor and fertilizer. It increases soil pH. It lowers combustion temperature of material, decreases maximum weight loss rates. This is also used in the manufacturing of important materials, such as fire-proofing textiles, paperwood, and vegetable fibres. The applications of diammonium hydrogen phosphate crystals are discussed in many literature[1-7].There is no literature reporting the change in the physical and chemical properties of DAHP crystals by the addition of manganese chloride. In this article the change in mechanical, thermal and structural properties of DAHP due to addition of manganese chloride is discussed.

2 Growth Procedure

The commercially available AR grade sample of DAHP and manganese chloride were the parent materials. 1M DAHP solution was prepared by constant stirring. IM $MnCl_2$ solution was also prepared. Both the solutions were mixed and stirred for 10 hours using magnetic stirrer. Super saturated conditions were confirmed by the formation of precipitate. The solution was filtered and kept undisturbed. Single crystals of manganese chloride diammonium hydrogen phosphate mixed crystals[MCDAHP] were grown by solution method after a period of 30 days. The crystals of high quality can be obtained by purification of starting material. The grown crystals are shown in the Figure 1.

3 Results and Discussions

3.1Thermo gravimetry analysis (TGA)

TGA was carried cut in the nitrogen atmosphere at 20ml/min using Perkin-Elmer make at the rate of 30 deg/min between the temperature range 35°C-900°C.

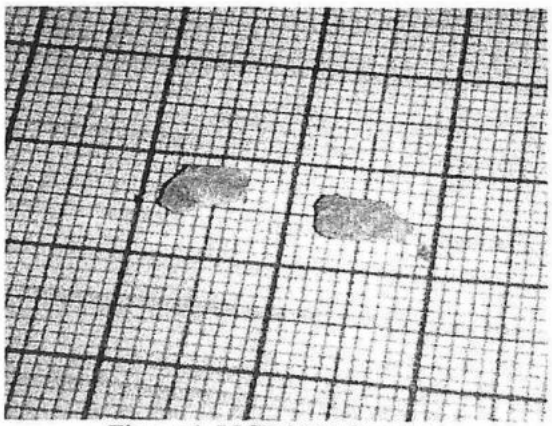

Figure 1. MCDAHP Crystals.

The trace is shown in the Figure2. Pure DAHP decomposes in a complex manner.The mass loss is due to sublimation of P_2O_5 with maximum rate at 625°C. This is confirmed from crystal transition of diammonium hydrogen phosphate reported **[8,9]**. It was reported that strontium doped Barium hydrogen Phosphate crystal has more thermal stability than pure Barium Hydrogen Phosphate (BHP) crystal and it may be due to increase in bond energy caused by the incorporation of Sr^{2+} ions in the lattice of the doped BHP Crystals**[10]**. Similarly the manganese chloride mixed diammonium hydrogen phosphate crystal has higher thermal stability than DAHP. From the thermal study of a variety of phosphate crystals, it was concluded that the thermal decomposition is a complex process with the release of ammonia gas and yields pyrophosphate**[11]**.

In the present study the maximum weight loss of about 95% occurs in the range 200°C - 350°C which is due to the decomposition of the sample

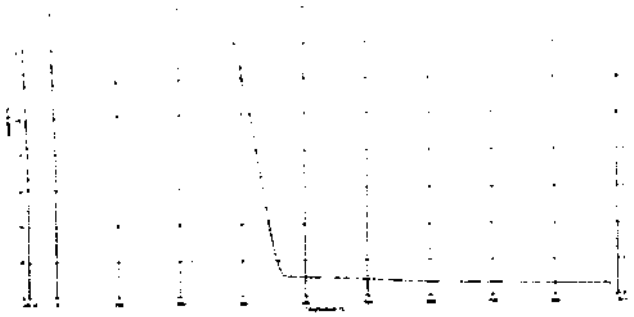

Figure 2. TGA of MCDAHP.

3.2. Differential Thermal Analysis

The DTA curve of MCDAHP is given in the Figure 3. It shows a sharp endothermic peak at 326.32°C. This value can be attributed to the decomposition or melting point of the crystal. From the DTA result it may be interpreted that MCDAHP crystal has more thermal stability than DAHP crystal.The absence of endothermic peak around 100°C shows that there is no inclusion of water molecules in the same.

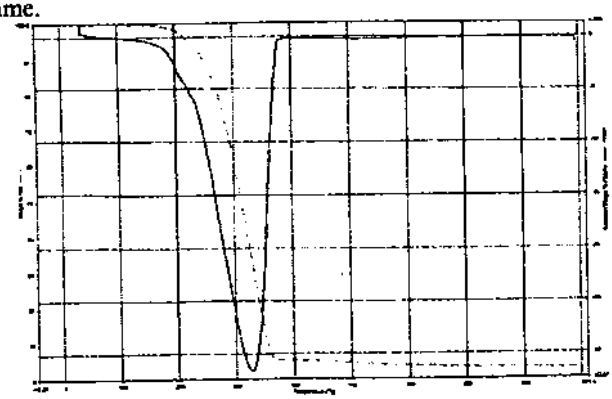

Figure 3. DTA of MCDAHP.

3.3 Differential Scanning Calorimetry (DSC)

DSC was carried cut in the nitrogen atmosphere at 20ml/ml using Perkin-Elmer make at the rate of 30 deg/min between the temperature range 35°C-400°C.The DSC curve of MCDAHP is shown in the Fig 4.It has two endothermic peaks. The peak around 340°C is due to decomposition of MCDAHP.The DSC curve has similar profiles, verifying the endothermic and exothermic transitions, in agreement with the DTA and TGA results.

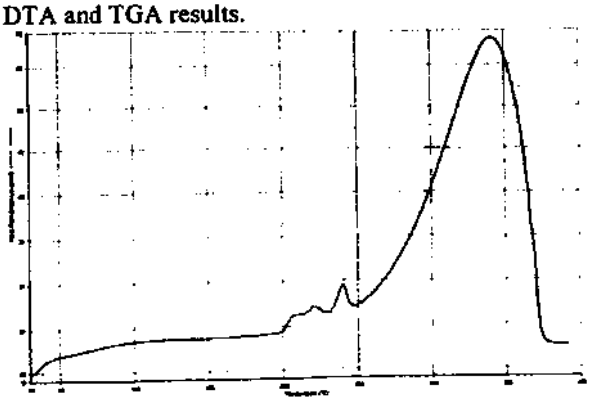

Figure4. DSC of MCDAHP.

3.4. Vicker's Microhardness Test

The mechanical strength of the grown crystal is studied using Shimadzu model HMV-2T. The hardness of the material is a measure of its resistance to applied load. The response for low loads is observed. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed.

The variations of micro hardness number with load applied is given in the Figure 5. The Hardness number H_v increases with applied load. The hardening coefficient is calculated from the plot [Figure 6] between log d and log p. The crystals come under soft material category. The stiffness constant C_{11} is also measured from the formula.

$$C_{11} = H_v^{7/4} \text{ and}$$

C_{11} gives the idea of toughness of bonding between neighbouring atoms. Table -1 gives the C_{11} corresponding to H_v values.

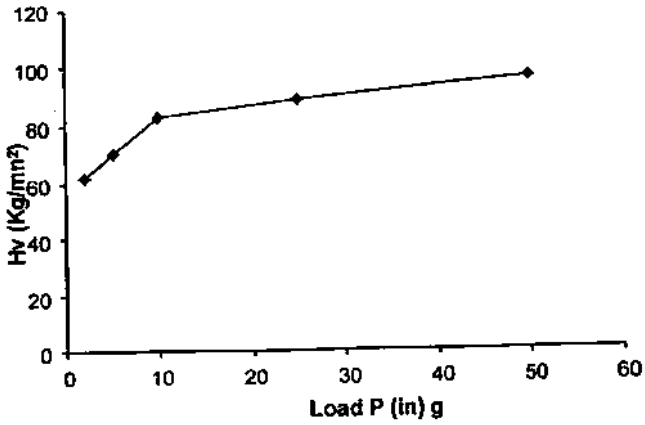

Figure 5.Variation of Vicker's micro hardness number Hv with load.

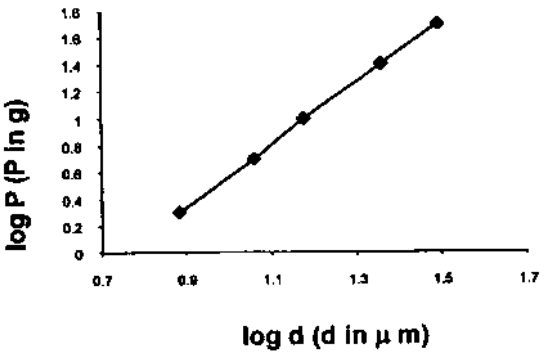

Figure 6. log P vs log d.

Table 1. Stiffness Constant for Various Load

Load 10^{-3} Kg	H_vKg/mm^2	$C_{11}10^{14}$Pa
2	62	13.7
5	70.3	17.06
10	82.6	22.63
25	88.4	25.48
50	95.7	29.28

3.5 Structural Analysis

3.5.1 Single Crystal X-ray Diffraction Analysis

The Single Crystal X-ray diffraction has been carried out using Bruker Kappa APEX II diffractometer with Mo K_α(0.71073A°) radiation as the source. The crystallographic parameters of the grown crystal is given in Table 2.The crystal belongs to tetrogonal system. The unit cell parameters,crystal system and hence the volume of unit cell of MCDAHP differ from pure DAHP crystal.

Table 2. Crystallographic Parameters.

Parameters	MCDAHP
a Å	7.528
bÅ	7.528
cÅ	7.586
Crystal system	tetrogonal
Space group	P4
Volume($Å^3$)	429.8

3.5.2 Structural Analysis from Powder X-ray diffraction

To confirm the crystal structure of the grown crystals , powder XRD has been performed at room temperature using Rigaku Ultima 3 diffractometer. The diffraction pattern shows sharp peaks.The well defined peaks at specific 2θvalues prove the high crystallinity of the grown crystals.

The diffraction pattern is shown in Figure 7. The reflections of the PXRD pattern was analysed using chekcell and expo 2014 software**[12,13]**. The d spacing, FWHM and relative intensity corresponding to 2θ values are given in Table -3. The indices of the six major peaks are presented in Table -4. The grain size is calculated from the formula

$D = 0.9\lambda / \beta\cos\theta$ as7.266Å

The analysis of different diffraction peaks indicate the formation of tetrogonal system. The indices of the major peaks of MCDAHP are (022), (004), (332),(002) and (331) respectively in the decreasing order of intensities.

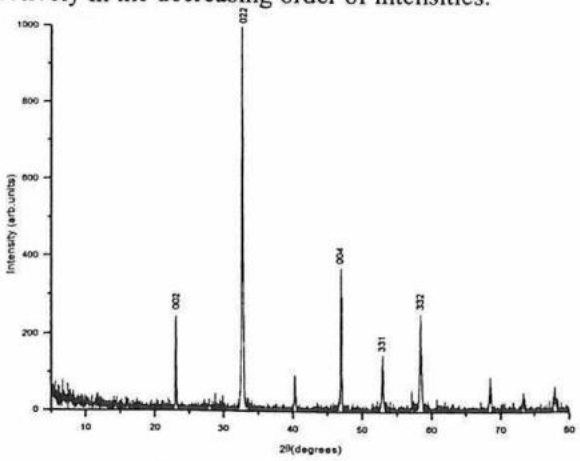

Figure 7. Powder XRD of MCDAHP.

Table 3. d spacing, FWHM and relative intensity corresponding to 2θ values.

S.No	2theta	d	FWHM	100. *I/I_{max}
1)	7.2886	12.118	0.2406	3.98
2)	7.5600	11.6841	0.2051	4.98
3)	7.7800	11.3542	0.4196	5.47
4)	8.2000	10.7735	0.2379	4.98
5)	8.9200	9.9055	0.3880	3.98
6)	9.3600	9.4408	0.2597	3.98
7)	10.1400	8.7163	0.3607	3.48
8)	10.8800	8.1250	0.2511	3.48
9)	11.0631	7.9910	0.1857	1.99
10)	11.7597	7.5191	0.3395	4.48
11)	12.3994	7.1326	0.3427	2.99
12)	12.6412	6.9967	0.4389	2.99
13)	12.6910	6.8248	0.2786	2.49
14)	14.5161	6.0969	0.7550	3.48
15)	17.6221	5.0287	0.1895	2.49
16)	17.9763	4.9304	0.2813	2.49
17)	18.5441	4.7807	0.1789	1.49
18)	19.5205	4.5437	0.1688	2.49
19)	21.6094	4.1090	0.1587	1.99
20)	21.9609	4.0440	0.1211	2.99
21)	22.2217	3.9971	0.2643	2.49
22)	23.0203	3.8602	0.1468	24.38
23)	27.9646	3.1879	0.3067	2.99
24)	32.5800	2.7461	0.1988	100.00
25)	33.1400	2.7010	0.3372	3.48
26)	33.6445	2.6616	0.1875	2.99
27)	34.2350	2.6170	0.1548	1.99
28)	34.2088	2.6190	0.1496	1.99
29)	36.4170	2.4651	0.1283	1.99
30)	40.2627	2.2381	0.2164	9.45
31)	46.8615	1.9371	0.1608	36.82
32)	51.6000	1.7698	0.1789	1.99
33)	52.1200	1.7534	0.2786	2.99
34)	52.9000	1.7293	0.2328	14.93
35)	53.5635	1.7095	0.1559	2.49
36)	55.6074	1.6514	0.1730	1.99
37)	56.3798	1.6306	0.2437	1.99
38)	56.5621	1.6258	0.1832	1.99
39)	57.1056	1.6116	0.2437	5.97
40)	57.4803	1.6020	0.1303	2.99
41)	58.3201	1.5809	0.2210	25.37
42)	67.0990	1.3938	0.1052	2.99
43)	68.4776	1.3690	0.1866	8.96
44)	68.6213	1.3665	0.1966	6.47
45)	69.6553	1.3487	0.1812	1.49
46)	70.5696	1.3335	0.1438	2.49
47)	71.2922	1.3217	0.2372	1.99
48)	73.2143	1.2917	0.2746	4.98
49)	73.4495	1.2882	0.2638	3.48
50)	77.1793	1.2349	0.1141	2.99
51)	77.6409	1.2287	0.1653	3.98
52)	77.9401	1.2248	0.2560	6.47

Table 4. hkl indexing.

S.No	2θ	Relative intensity	hkl index
1	32.58	100	022
2	46.8615	36.82	004
3	58.32	25.37	332
4	23.02	24.38	002
5	52.9	14.93	331

3.6 SEM Analysis

The SEM analysis was performed using Vega 3 instrument. The SEM micrographs are shown in Figure 4.10. SEM acceleration voltage was 5.0 kV. Sample was kept in highly vacuum state 18.16 nm work distance was maintained and monochromatic colour modes were employed. SEM shows homogeneous distribution of the material with plate, triangular, tetragonal and pentagonal structures.

Figure 8. SEM Images of MCDAHP.

4. Conclusions

The title compound has been synthesized and the characterization studies are carried out to know the change in mechanical, thermal and structural properties .

The TGA Analysis confirms that there is no water molecules present in the grown crystal . Due to inclusion of manganese chloride in DAHP crystal, there is variation in melting point of MCDAHP which is observed from DSC curve .Vicker's hardness study shows that the crystal has a high hardness value .This reveals the reasonable mechanical strength of the material. The crystals belong to soft material category. The unit cell parameters of the mixed crystal varies from pure DAHP crystal. The MCDAHP crystal belong to tetragonal system whereas DAHP crystal belong to monoclinic system.

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Ethyl 6-(4-chlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-pyran-5-carboxylate

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Ethyl 6-(4-chlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-pyran-5-carboxylate

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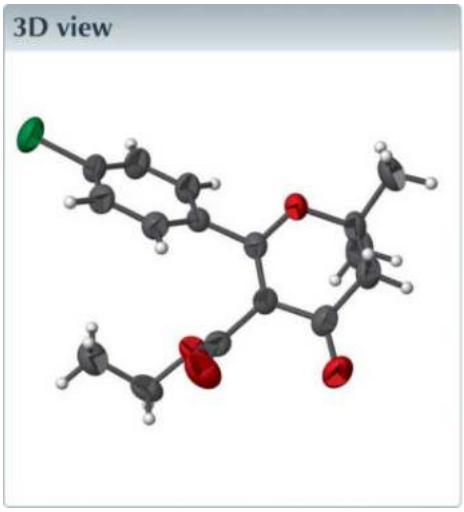
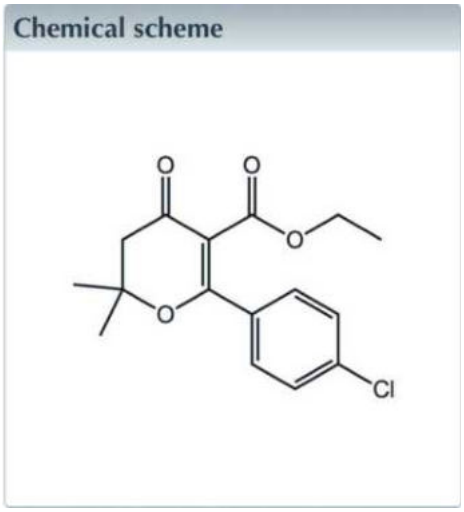
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{16}H_{17}ClO_4$, is a derivative of 3,4-dihydro-2*H*-pyran-4-one in which the root moiety forms a dihedral angle of 49.36 (5)° with the pendent chlorobenzene ring. The crystal structure features weak methyl-C—H···O(ring carbonyl) contacts, leading to an $R_2^2(12)$ ring motif, and benzene-C—H···O(ester) interactions, leading to a supramolecular chain along the *b* axis, to form a three-dimensional network.





Structure description

4*H*-Pyran-4-ones and their various derivatives are known for their significant biological and pharmacological activities, and are structurally similar to biologically active 1,4-dihydropyridines (1,4-DHPs) (Zonouz *et al.*, 2014). They act as calcium antagonists (Súarez *et al.*, 2002) and serve as potent apoptosis inducers (Zhang *et al.*, 2005). As a continuation of structural investigations of a series of 4*H*-pyran-4-one derivatives, we report herein on the crystal structure determination and the geometry optimization of the title compound, (I).

A perspective view of (I) with the atomic numbering scheme is illustrated in Fig. 1. The 3,4-dihydro-2*H*-pyran-4-one moiety (C7–C11/O1/O2) forms a dihedral angle of 49.36 (5)° with the benzene ring. The bond distances and angles are essentially equivalent compared to those in the previously reported structure ethyl 2,2-dimethyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (II) (Sharmila *et al.*, 2016). However, the benzene group has rotated about the C6—C7 bond as evident from the change in torsion angles namely, C1—C6—C7—C11 and C5—C6—C7—C11 of −133.37 (15) and 50.56 (19)°, respectively, *cf.* 138.6 (2) and −43.3 (3)° in (II). Also, a fragment overlay

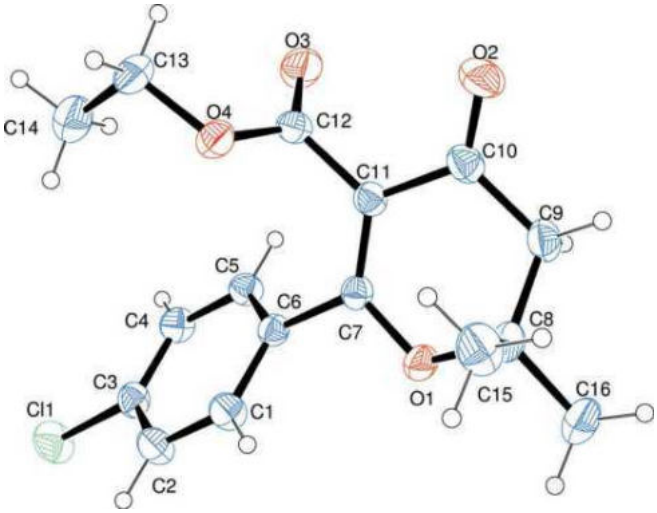


Figure 1
The molecular structure of (I), with displacement ellipsoids for the non-H atoms drawn at the 30% probability level.

(Gans & Shalloway, 2001) analysis of (I) with (II) gives an r.m.s. deviation of 2.91 Å (Fig. 2). These observations indicate that the structural changes could be attributed to the substitution of the heavier Cl atom at C3 and the involvement of C2 in making a hydrogen bond with O4 *via* H2 (Table 1). Another superposition analysis of (I) but, with 4-(4-fluorophenyl)-6-methylamino-5-nitro-2-phenyl-4*H*-pyran-3- carbonitrile (III) (Vishnupriya *et al.*, 2013) gives an r.m.s. deviation of 1.57 Å, which confirms the effect of relatively heavier Cl substitution at C3 resulting in the small conformational changes in the molecule.

The pyran ring of (I) is puckered (puckering parameters: Q = 0.4539 (16) Å, $q2$ = 0.378 (15) Å, $q3$ = −0.2512 (15) Å, θ = 123.61 (19)° and φ = 91.6 (2)°, with atom C8 showing the maximum deviation of 0.2946 (16) Å from the plane defined by O1/C7/C11–C8.

Table 1
Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O4^{i}	0.93	2.66	3.3694 (18)	134
C15—H15*B*···O2^{ii}	0.96	2.66	3.553 (2)	156
C13—H13*B*···*Cg*^{iii}	0.97	2.96	3.6463 (17)	129

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+2, -y+1, -z+1$; (iii) $x, y+1, z$.

Theoretical calculations of the molecular structure were performed using MOPAC2016′s PM7 geometry optimization algorithm (Stewart, 2016). This shows satisfactory agreement with the results of the X-ray crystal structure analysis. The HOMO and LUMO energy levels were found to be −9.829 and −1.127 eV, respectively. The total energy and dipole moment values of (I) are −3643.34886 eV and 5.235 Debye, respectively. In the geometry optimized structure of (I), a decrease in bond distances seems to be observed for the bonds O1—C8 (1.46 Å) and C6—C7 (1.47 Å) when compared to those in the crystal, *i.e.* 1.4732 (16) and 1.4832 (16) Å. The O1—C7—C6 bond angle decreased from 110.78 (11) to 110.2°, and the O1—C8—C9 bond angle increased from 108.65 (11) to 110.5°. The relative conformation about the bond joining the 3,4-dihydro-2*H*-pyran-4-one moiety with the chlorobenzene group of (I) is defined by the torsion angles C1—C6—C7—O1 and C5—C6—C7—O1 of 47.68 (17) and −128.38 (13)° in the crystal, *i.e.* show (+) *syn*-clinal and (−) *anti*-clinal conformations, respectively, and compare with 49.9 and −130.8° in the optimized structure. A superimposed fit of (I) with its energy-minimized molecule gives an r.m.s. deviation of 0.152 Å (Fig. 3).

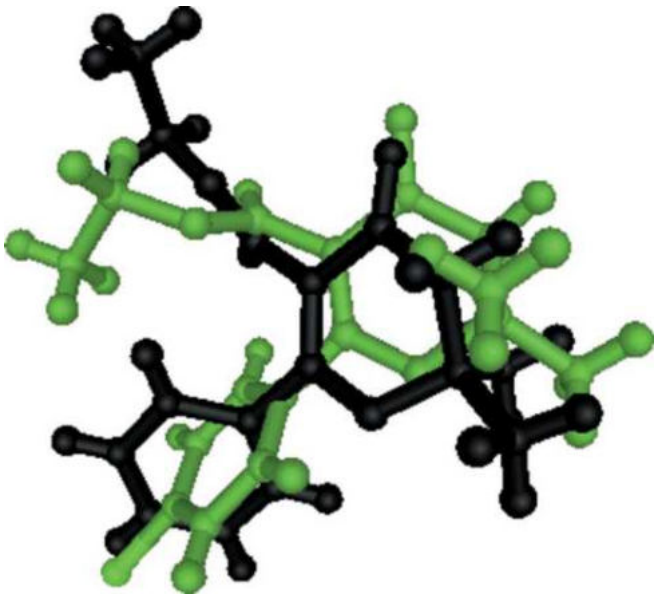


Figure 2
A superimposed fit of (I) (green) and related structure (II) (black).

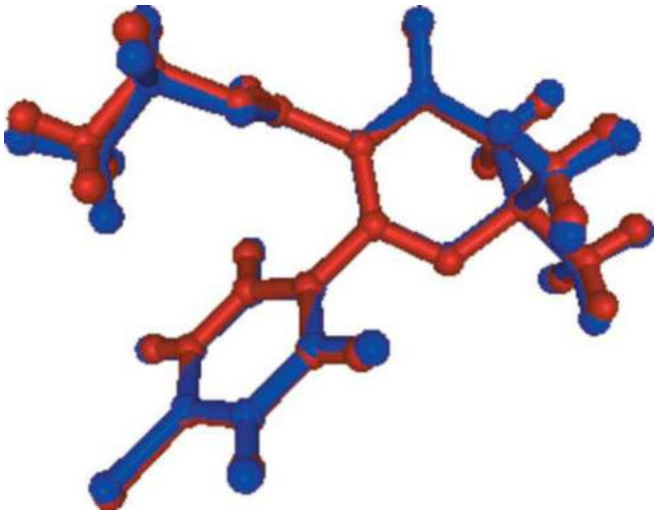


Figure 3
A superimposed fit of (I) (red) and its energy-minimized counterpart (blue).

One of the methyl carbons, C15, is involved in hydrogen bond with O2 of a symmetry-related molecule *via* H15*B* to form a $R_2^2(12)$ ring motif. The phenyl carbon C2 is involved in an interaction with O4 of a symmetry-related molecule *via* H2 to form a chain along the *b* axis (Table 1 and Fig. 4). These combine to give a three-dimensional architecture. Further, a weak C—H$\cdots\pi$ interaction between C13 and the centroid (*Cg*) of the C1–C6 ring *via* H13*B*, provides additional stabilization to the crystal (Table 1).

Synthesis and crystallization

To a solution of ethyl 3-(4-chlorophenyl)-3-oxopropanoate (226 mg, 1.0 mmol), $CaCl_2$ (11 mg, 0.1 mmol), triethylamine (278 µ*L*, 2.0 mmol) and 3-methylbut-2-enoyl chloride (112 µ*L*, 1.0 mmol), dichloromethane (4 ml) was added at ambient temperature. After completion of the addition, the reaction mixture was subjected to stirring at room temperature for 3 h. The progress of the reaction was monitored by thin-layer chromatography. The organic layer was separated, filtered and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/hexane = 2:8 *v*/*v* as eluent). The product was a colourless solid (yield 90%, 277 mg) and was crystallized in hexane/EtOAc (6:4 *v*/*v* (m.p. 354–356 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{17}ClO_4$
M_r	308.74
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, *b*, *c* (Å)	10.4412 (3), 7.6959 (2), 20.2651 (5)
β (°)	102.311 (2)
V (Å^3)	1590.94 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	0.25 × 0.17 × 0.12
Data collection	
Diffractometer	Bruker Smart CCD Area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.746, 0.845
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15125, 3995, 2978
R_{int}	0.018
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.037, 0.108, 1.03
No. of reflections	3995
No. of parameters	193
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.26

Computer programs: *SMART* and *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *QMOL* (Gans & Shalloway, 2001), *Mercury* (Macrae *et al.*, 2008), *ORTEPIII* (Burnett & Johnson, 1996), *WinGX* publication routines (Farrugia, 2012) and *PLATON* (Spek, 2009).

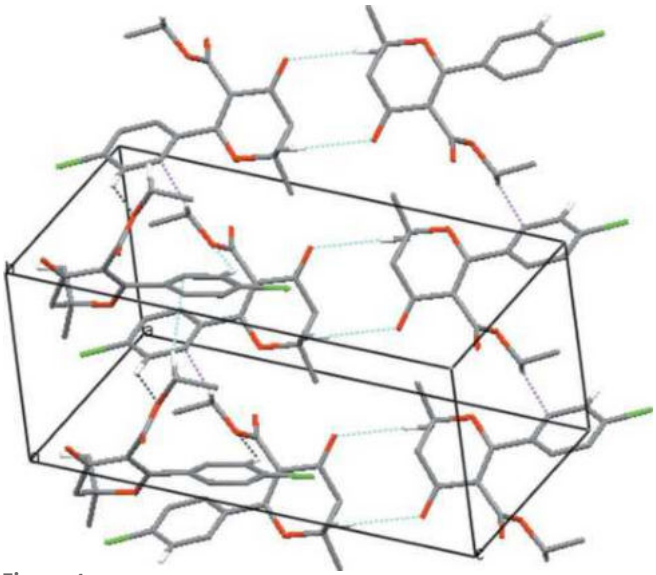


Figure 4
Molecular packing of (I), showing the C—H$\cdots$O interactions as dashed lines. Other H-atoms are omitted for clarity.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170034 [https://doi.org/10.1107/S2414314617000347]

Ethyl 6-(4-chlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-pyran-5-carboxylate

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Ethyl 2,2-dimethyl-4-oxo-6-phenyl-2,3-dihydro-4H-pyran-5-carboxylate

Crystal data

$C_{16}H_{17}ClO_4$
M_r = 308.74
Monoclinic, $P2_1/c$
a = 10.4412 (3) Å
b = 7.6959 (2) Å
c = 20.2651 (5) Å
β = 102.311 (2)°
V = 1590.94 (7) Å^3
Z = 4
$F(000)$ = 648
D_x = 1.289 Mg m^{-3}
Melting point: 356 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3995 reflections
θ = 2.0–28.4°
μ = 0.25 mm^{-1}
T = 296 K
Block, colourless
0.25 × 0.17 × 0.12 mm

Data collection

Bruker Smart CCD Area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.746, T_{max} = 0.845
15125 measured reflections
3995 independent reflections
2978 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 28.4°, θ_{min} = 2.0°
h = −13→13
k = −10→10
l = −24→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.108
S = 1.03
3995 reflections
193 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.3683P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.43713 (4)	0.28175 (7)	0.02231 (2)	0.06956 (16)
O1	0.76719 (10)	0.25784 (13)	0.33513 (5)	0.0475 (2)
O2	1.03226 (13)	0.63993 (19)	0.40015 (6)	0.0736 (4)
O3	0.96413 (11)	0.71077 (17)	0.24439 (7)	0.0670 (3)
O4	0.76146 (10)	0.76716 (13)	0.25811 (5)	0.0494 (3)
C1	0.56401 (14)	0.3304 (2)	0.22085 (7)	0.0476 (3)
H1	0.5298	0.3190	0.2594	0.057*
C2	0.48338 (14)	0.3058 (2)	0.15815 (7)	0.0515 (4)
H2	0.3950	0.2802	0.1541	0.062*
C3	0.53638 (14)	0.3198 (2)	0.10154 (7)	0.0451 (3)
C4	0.66627 (14)	0.3583 (2)	0.10654 (7)	0.0464 (3)
H4	0.7003	0.3669	0.0678	0.056*
C5	0.74647 (13)	0.38433 (18)	0.16963 (7)	0.0420 (3)
H5	0.8347	0.4102	0.1733	0.050*
C6	0.69542 (12)	0.37183 (17)	0.22726 (6)	0.0368 (3)
C7	0.78238 (12)	0.39149 (17)	0.29499 (6)	0.0374 (3)
C8	0.83024 (15)	0.2695 (2)	0.40731 (7)	0.0498 (4)
C9	0.96580 (15)	0.3470 (2)	0.41366 (7)	0.0524 (4)
H9A	1.0057	0.3629	0.4611	0.063*
H9B	1.0200	0.2667	0.3948	0.063*
C10	0.96159 (14)	0.5182 (2)	0.37801 (7)	0.0486 (3)
C11	0.86698 (12)	0.52417 (18)	0.31346 (6)	0.0391 (3)
C12	0.87223 (13)	0.67511 (18)	0.26829 (7)	0.0415 (3)
C13	0.75166 (17)	0.9164 (2)	0.21306 (9)	0.0601 (4)
H13A	0.8384	0.9637	0.2147	0.072*
H13B	0.6989	1.0060	0.2279	0.072*
C14	0.6913 (2)	0.8648 (3)	0.14272 (10)	0.0745 (5)
H14A	0.7470	0.7826	0.1269	0.112*
H14B	0.6805	0.9657	0.1142	0.112*
H14C	0.6072	0.8128	0.1416	0.112*
C15	0.74350 (17)	0.3815 (3)	0.44129 (8)	0.0685 (5)
H15A	0.7383	0.4966	0.4226	0.103*
H15B	0.7800	0.3869	0.4889	0.103*
H15C	0.6573	0.3319	0.4339	0.103*
C16	0.8362 (2)	0.0834 (3)	0.43209 (10)	0.0813 (6)
H16A	0.7490	0.0372	0.4255	0.122*
H16B	0.8768	0.0801	0.4793	0.122*
H16C	0.8866	0.0149	0.4072	0.122*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0693 (3)	0.0924 (4)	0.0396 (2)	−0.0122 (2)	−0.00473 (17)	−0.0057 (2)
O1	0.0577 (6)	0.0468 (6)	0.0350 (5)	−0.0092 (5)	0.0030 (4)	0.0070 (4)
O2	0.0762 (8)	0.0824 (9)	0.0531 (7)	−0.0320 (7)	−0.0067 (6)	−0.0001 (6)
O3	0.0486 (6)	0.0729 (8)	0.0846 (9)	−0.0020 (6)	0.0258 (6)	0.0254 (7)
O4	0.0498 (6)	0.0426 (5)	0.0581 (6)	0.0033 (4)	0.0169 (5)	0.0065 (5)
C1	0.0446 (7)	0.0631 (9)	0.0370 (7)	−0.0032 (6)	0.0127 (5)	0.0018 (6)
C2	0.0396 (7)	0.0701 (10)	0.0439 (7)	−0.0049 (7)	0.0067 (6)	0.0000 (7)
C3	0.0495 (7)	0.0482 (8)	0.0343 (6)	−0.0006 (6)	0.0015 (5)	−0.0007 (6)
C4	0.0531 (8)	0.0531 (8)	0.0347 (6)	−0.0021 (6)	0.0137 (6)	−0.0010 (6)
C5	0.0416 (7)	0.0468 (8)	0.0391 (7)	−0.0037 (6)	0.0120 (5)	−0.0007 (6)
C6	0.0403 (6)	0.0359 (6)	0.0338 (6)	−0.0003 (5)	0.0067 (5)	0.0016 (5)
C7	0.0396 (6)	0.0408 (7)	0.0326 (6)	0.0016 (5)	0.0095 (5)	0.0020 (5)
C8	0.0545 (8)	0.0584 (9)	0.0336 (7)	−0.0035 (7)	0.0025 (6)	0.0105 (6)
C9	0.0478 (8)	0.0663 (10)	0.0393 (7)	0.0017 (7)	0.0009 (6)	0.0076 (7)
C10	0.0435 (7)	0.0632 (9)	0.0377 (7)	−0.0068 (7)	0.0057 (6)	−0.0012 (6)
C11	0.0382 (6)	0.0442 (7)	0.0347 (6)	−0.0014 (5)	0.0075 (5)	0.0008 (5)
C12	0.0397 (7)	0.0428 (7)	0.0416 (7)	−0.0057 (6)	0.0079 (5)	−0.0018 (6)
C13	0.0657 (10)	0.0389 (8)	0.0749 (11)	0.0025 (7)	0.0134 (8)	0.0102 (8)
C14	0.0836 (13)	0.0675 (12)	0.0673 (11)	0.0038 (10)	0.0047 (10)	0.0165 (9)
C15	0.0616 (10)	0.1026 (15)	0.0442 (8)	0.0000 (10)	0.0179 (7)	0.0050 (9)
C16	0.0993 (15)	0.0726 (13)	0.0627 (11)	−0.0121 (11)	−0.0035 (10)	0.0308 (10)

Geometric parameters (Å, º)

Cl1—C3	1.7401 (13)	C8—C9	1.516 (2)
O1—C7	1.3415 (16)	C8—C15	1.518 (2)
O1—C8	1.4732 (16)	C9—C10	1.498 (2)
O2—C10	1.2177 (19)	C9—H9A	0.9700
O3—C12	1.1954 (17)	C9—H9B	0.9700
O4—C12	1.3343 (17)	C10—C11	1.4622 (18)
O4—C13	1.4571 (18)	C11—C12	1.4871 (19)
C1—C2	1.3795 (19)	C13—C14	1.484 (3)
C1—C6	1.3876 (19)	C13—H13A	0.9700
C1—H1	0.9300	C13—H13B	0.9700
C2—C3	1.380 (2)	C14—H14A	0.9600
C2—H2	0.9300	C14—H14B	0.9600
C3—C4	1.371 (2)	C14—H14C	0.9600
C4—C5	1.3854 (18)	C15—H15A	0.9600
C4—H4	0.9300	C15—H15B	0.9600
C5—C6	1.3866 (18)	C15—H15C	0.9600
C5—H5	0.9300	C16—H16A	0.9600
C6—C7	1.4832 (16)	C16—H16B	0.9600
C7—C11	1.3498 (18)	C16—H16C	0.9600
C8—C16	1.515 (2)		

C7—O1—C8	118.01 (11)	H9A—C9—H9B	107.9
C12—O4—C13	117.26 (11)	O2—C10—C11	123.09 (14)
C2—C1—C6	120.99 (12)	O2—C10—C9	123.08 (13)
C2—C1—H1	119.5	C11—C10—C9	113.82 (13)
C6—C1—H1	119.5	C7—C11—C10	120.09 (12)
C1—C2—C3	118.74 (13)	C7—C11—C12	121.88 (11)
C1—C2—H2	120.6	C10—C11—C12	117.96 (12)
C3—C2—H2	120.6	O3—C12—O4	124.04 (13)
C4—C3—C2	121.41 (13)	O3—C12—C11	124.53 (13)
C4—C3—Cl1	119.33 (11)	O4—C12—C11	111.43 (11)
C2—C3—Cl1	119.24 (11)	O4—C13—C14	110.47 (14)
C3—C4—C5	119.57 (12)	O4—C13—H13A	109.6
C3—C4—H4	120.2	C14—C13—H13A	109.6
C5—C4—H4	120.2	O4—C13—H13B	109.6
C4—C5—C6	120.13 (12)	C14—C13—H13B	109.6
C4—C5—H5	119.9	H13A—C13—H13B	108.1
C6—C5—H5	119.9	C13—C14—H14A	109.5
C5—C6—C1	119.15 (12)	C13—C14—H14B	109.5
C5—C6—C7	120.20 (11)	H14A—C14—H14B	109.5
C1—C6—C7	120.54 (11)	C13—C14—H14C	109.5
O1—C7—C11	124.54 (11)	H14A—C14—H14C	109.5
O1—C7—C6	110.78 (11)	H14B—C14—H14C	109.5
C11—C7—C6	124.68 (11)	C8—C15—H15A	109.5
O1—C8—C16	104.45 (13)	C8—C15—H15B	109.5
O1—C8—C9	108.65 (11)	H15A—C15—H15B	109.5
C16—C8—C9	111.84 (14)	C8—C15—H15C	109.5
O1—C8—C15	107.56 (12)	H15A—C15—H15C	109.5
C16—C8—C15	111.90 (15)	H15B—C15—H15C	109.5
C9—C8—C15	112.02 (14)	C8—C16—H16A	109.5
C10—C9—C8	111.96 (12)	C8—C16—H16B	109.5
C10—C9—H9A	109.2	H16A—C16—H16B	109.5
C8—C9—H9A	109.2	C8—C16—H16C	109.5
C10—C9—H9B	109.2	H16A—C16—H16C	109.5
C8—C9—H9B	109.2	H16B—C16—H16C	109.5

C6—C1—C2—C3	1.2 (2)	C16—C8—C9—C10	169.65 (14)
C1—C2—C3—C4	−0.4 (2)	C15—C8—C9—C10	−63.80 (16)
C1—C2—C3—Cl1	177.82 (13)	C8—C9—C10—O2	141.88 (16)
C2—C3—C4—C5	−0.2 (2)	C8—C9—C10—C11	−39.47 (18)
Cl1—C3—C4—C5	−178.35 (12)	O1—C7—C11—C10	7.7 (2)
C3—C4—C5—C6	−0.2 (2)	C6—C7—C11—C10	−171.07 (12)
C4—C5—C6—C1	1.0 (2)	O1—C7—C11—C12	−175.43 (12)
C4—C5—C6—C7	177.14 (13)	C6—C7—C11—C12	5.8 (2)
C2—C1—C6—C5	−1.6 (2)	O2—C10—C11—C7	−173.28 (15)
C2—C1—C6—C7	−177.69 (14)	C9—C10—C11—C7	8.07 (19)
C8—O1—C7—C11	10.50 (19)	O2—C10—C11—C12	9.8 (2)
C8—O1—C7—C6	−170.55 (11)	C9—C10—C11—C12	−168.88 (13)
C5—C6—C7—O1	−128.38 (13)	C13—O4—C12—O3	2.3 (2)

C1—C6—C7—O1	47.68 (17)	C13—O4—C12—C11	−178.24 (12)
C5—C6—C7—C11	50.56 (19)	C7—C11—C12—O3	−115.07 (17)
C1—C6—C7—C11	−133.37 (15)	C10—C11—C12—O3	61.8 (2)
C7—O1—C8—C16	−160.72 (14)	C7—C11—C12—O4	65.43 (17)
C7—O1—C8—C9	−41.22 (17)	C10—C11—C12—O4	−117.67 (13)
C7—O1—C8—C15	80.23 (16)	C12—O4—C13—C14	91.59 (17)
O1—C8—C9—C10	54.88 (17)		

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O4^{i}	0.93	2.66	3.3694 (18)	134
C15—H15*B*···O2^{ii}	0.96	2.66	3.553 (2)	156
C13—H13*B*···*Cg*^{iii}	0.97	2.96	3.6463 (17)	129

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) −*x*+2, −*y*+1, −*z*+1; (iii) *x*, *y*+1, *z*.

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Hydrogen-bonding patterns in bis(cytosinium) tartarate monohydrate

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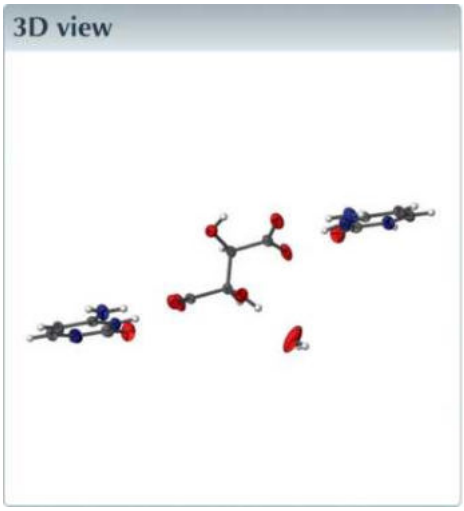
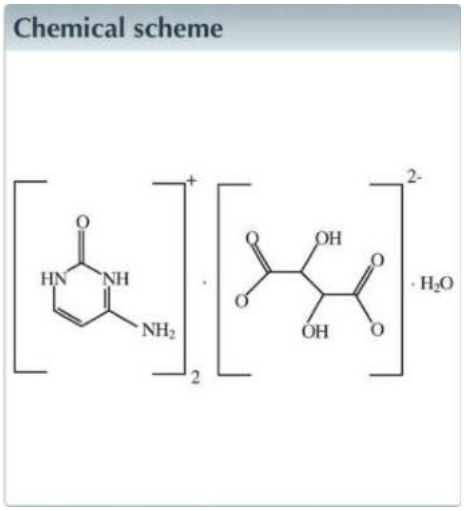
The asymmetric unit of the title cytosinium salt derivative, $2C_4H_6N_3O^+\cdot C_4H_4O_6^{2-}\cdot H_2O$, contains two cytosinium cations, one tartaric acid anion and a water molecule. The two cytosinium cations are almost planar (r.m.s. deviations of the fitted atoms are 0.0151 and 0.0213 Å). The crystal structure features C—H···O, N—H···O and O—H···O interactions. Further C—O···π and π–π interactions are observed along the *ab* plane, contributing to the crystal stability.





Structure description

Pyrimidine-based derivatives have attracted a great deal of attention in terms of their hydrogen-bonding patterns. Cytosinium is one of the naturally occurring base molecules found in DNA and RNA (Portalone *et al.*, 2009). Many cytosinium salts of organic acids have been reported previously, *viz*. cytosinium hydrogen sulfate, cytosinium perchlorate (Bensegueni *et al.*, 2009), cytosinium dihydrogen phosphite (Messai *et al.*, 2009), cytosinium hydrogen chloranilate monohydrate (Gotoh *et al.*, 2006) and cytosinium zoledronate trihydrate (Sridhar & Ravikumar, 2011). As part of our investigations on the growth and characterization of semi-organic crystals containing the nucleic acid component cytosine, we report herein the crystal structure determination and the geometry optimization of the title compound.

A perspective view of the title compound with the atomic numbering scheme is illustrated in Fig. 1. It crystallizes in the orthorhombic space group $P2_12_12_1$ with two cytosinium cations, a tartarate anion and one water molecule. The two cytosinium

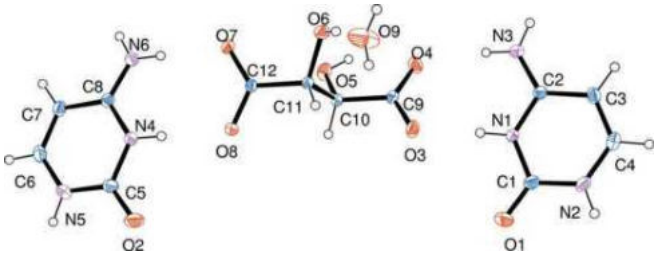


Figure 1
The molecular structure with displacement ellipsoids for the non-H atoms drawn at the 30% probability level.

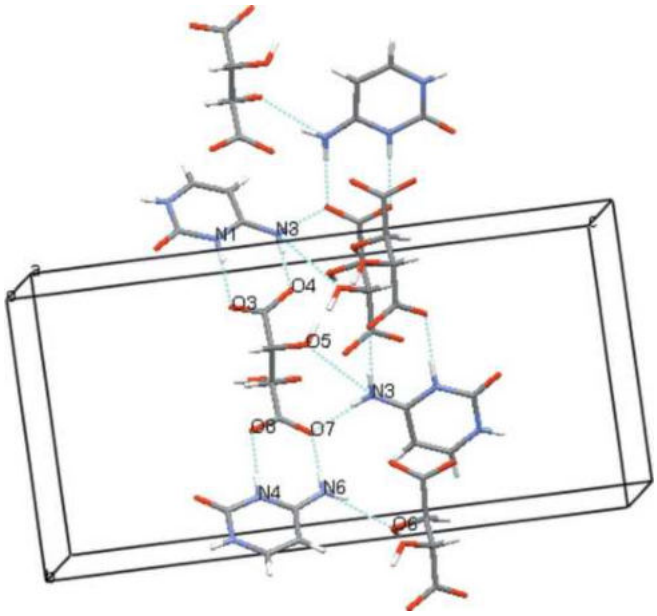


Figure 2
Crystal packing of the title compound, showing the N—H···O interactions in the $R_2^2(12)$ motif along the *c* axis and in parallel chains along the *a* and *c* axes as dashed lines. Other H atoms have been omitted for clarity.

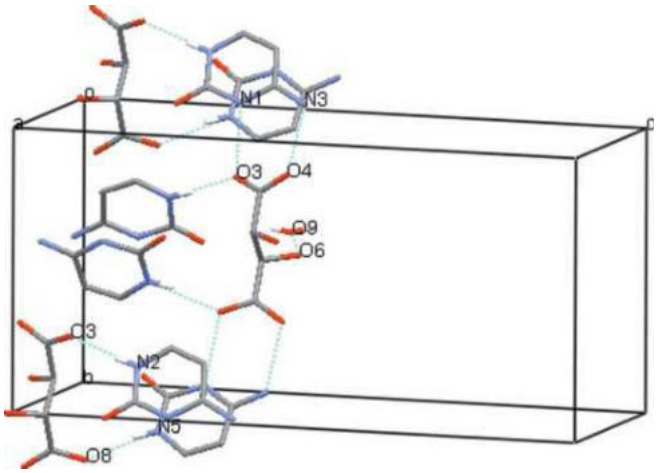


Figure 3
Crystal packing of the title compound, showing the N—H···O interactions enclosing parallel chains along the *c* and *a* axes and O—H···O interactions enclosing parallel chains along the *ab* plane, as dashed lines. Other H atoms have been omitted for clarity.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.93	2.53	3.098 (2)	120
C10—H10···O2^{ii}	0.98	2.33	3.312 (2)	175
C11—H11···O1^{iii}	0.98	2.38	3.361 (2)	179
O5—H5···O4	0.82	2.12	2.6140 (19)	118
O6—H6*A*···O9	0.82	1.87	2.688 (2)	172
N1—H1*A*···O3	0.86 (2)	1.80 (2)	2.656 (2)	171 (3)
N2—H2*A*···O3^{i}	0.86 (2)	1.91 (2)	2.768 (2)	175 (3)
N3—H3*A*···O4	0.84 (2)	2.04 (2)	2.873 (2)	171 (2)
N3—H3*B*···O7^{iv}	0.83 (2)	2.04 (2)	2.865 (2)	172 (2)
N4—H4*A*···O8	0.85 (2)	1.90 (2)	2.748 (2)	173 (3)
N5—H5*A*···O8^{v}	0.86 (2)	1.93 (2)	2.766 (2)	166 (3)
N6—H6*B*···O7	0.85 (2)	1.96 (2)	2.808 (2)	179 (3)
N6—H6*C*···O6^{vi}	0.83 (2)	2.01 (2)	2.812 (2)	163 (2)
O9—H9*A*···O2^{i}	0.83 (2)	2.24 (3)	3.040 (3)	162 (4)
O9—H9*B*···O5^{vii}	0.84 (2)	2.00 (3)	2.812 (2)	161 (3)

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (v) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (vii) $x-1, y, z$.

cations are almost planar, the r.m.s deviations of the fitted atoms C1–C4/N1–N3/O1 and C5–C8/N4–N6/O2 being 0.0151 and 0.0213 Å, respectively. An overlay analysis of the two cations gives an r.m.s. deviation of 1.128 Å. Bond distances and angles in the cations are comparable to those in the cation of cytosinium zoledronate trihydrate (Sridhar & Ravikumar, 2011).

The crystal structure features C—H···O, N—H···O and O—H···O interactions. The interaction between N4 and O8 through H4*A*, N6 and O7 through H6*B* and N1 and O3 through H1*A*, N3 and O4 through H3*A* occur alternately as chain links and form a three-dimensional network enclosing $R_2^2(8)$ ring motifs. The interaction between N3 and O7 through H3*B* and N6 and O6 through H6*C* form parallel chains along the *a*- and *c*-axis directions, respectively (Fig. 2). Similarly the interactions between N2 and O3 through H2*A* and N5 and O8 through H5*A* form infinite parallel chains along the *c*- and *a*-axis directions, respectively. The O6—H6*A*···O9 interaction encloses parallel chains along the *ab* plane (Fig. 3). Also the interactions of C4, C11 with O1 through H4, H11 form infinite parallel chains along the *b*- and *c*-axis directions, respectively (Fig. 4). The O9 interactions with O2, O5 through H9*A*, H9*B*

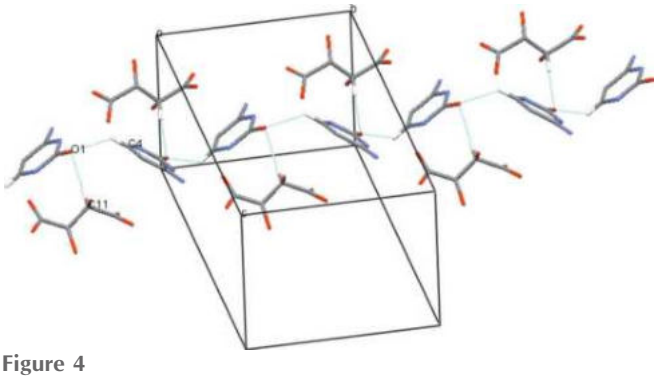


Figure 4
Crystal packing of the title compound, showing the C—H···O interactions enclosing parallel chains along the *b* and *c* axes as dashed lines. Other H atoms have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$2C_4H_6N_3O^+\cdot C_4H_4O_6^{2-}\cdot H_2O$
M_r	390.32
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, b, c (Å)	7.6932 (8), 10.1152 (8), 20.9336 (17)
V (Å^3)	1629.0 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.14
Crystal size (mm)	0.25 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.705, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22011, 4920, 4299
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.713
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.087, 1.11
No. of reflections	4920
No. of parameters	284
No. of restraints	13
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.22
Absolute structure	Flack x determined using 1669 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.1 (3)

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *XPREP* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Qmol* (Gans & Shalloway, 2001), *Mercury* (Macrae *et al.*, 2008), *ORTEPIII* (Burnett & Johnson, 1996), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

and the interaction between C10 and O2 through H10 forms an $R_3^3(7)$ ring motif along the *ab* plane (Fig. 5). A short contact is observed in the tartarate anion between atoms O4 and O5. Details are given in Table 1.

C—O$\cdots\pi$ interactions are observed along the *ab* plane [C9$\cdots$*Cg*2(x, −1 + y, z) = 3.876 (2) Å, C9—O3$\cdots$*Cg*2(x, −1 + y, z) = 15°; C12$\cdots$*Cg*1(x, 1 + y, z) = 3.497 (2) Å, C12—O8$\cdots$*Cg*1 = 2°; *Cg*1 and *Cg*2 are the centroids of the N1/C1/N2/C4/C3/C2 and N4/C5/N5/C6/C7/C8 rings, respectively]. In addition, weak π–π interactions are observed between the two symmetry-related cytosinium rings, with *Cg*1$\cdots$*Cg*2(−1 + x, −1 + y, z) = 3.401 (2) Å.

Synthesis and crystallization

A hot supersaturated water solution of cytosine (0.111 g, from Spectrochem) and tartaric acid (0.150 g, from Loba Chemie, India) were mixed in a 1:1 molar ratio and the solution was allowed to evaporate slowly, resulting in the formation of transparent plate-like crystals of cytosinium tartrate monohydrate in 15 days (m.p. 491–493 K).

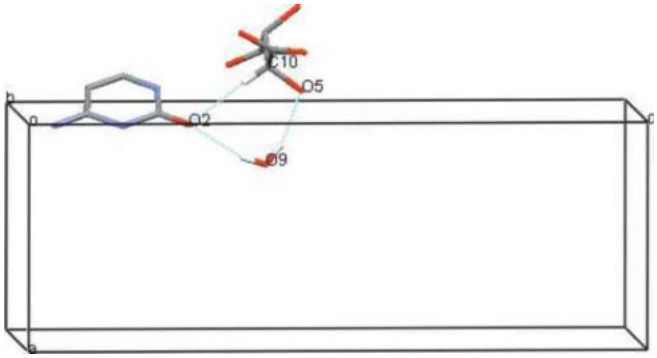


Figure 5
Crystal packing of the title compound, showing the C—H$\cdots$O and O—H$\cdots$O interactions enclosing an $R_3^3(7)$ ring motif and parallel chains along the *ab* plane as dashed lines. Other H atoms have been omitted for clarity.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Hydrogen-bonding patterns in bis(cytosinium) tartarate monohydrate

P. Jaikumar, T. V. Sundar, N. Sharmila, T. Balakrishnan and K. Ramamurthi

Bis(cystosinium) tartarate monohydrate

Crystal data

$2C_4H_6N_3O^+·C_4H_4O_6^{2-}·H_2O$
M_r = 390.32
Orthorhombic, $P2_12_12_1$
a = 7.6932 (8) Å
b = 10.1152 (8) Å
c = 20.9336 (17) Å
V = 1629.0 (3) Å^3
Z = 4
$F(000)$ = 816
D_x = 1.592 Mg m^{-3}
Melting point: 493 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7834 reflections
θ = 2.8–28.9°
μ = 0.14 mm^{-1}
T = 296 K
Plate, colourless
0.25 × 0.25 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan SADABS
T_{min} = 0.705, T_{max} = 0.746
22011 measured reflections
4920 independent reflections
4299 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 30.5°, θ_{min} = 2.2°
h = −10→10
k = −14→14
l = −29→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.087
S = 1.11
4920 reflections
284 parameters
13 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.2224P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack x determined using 1669 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.1 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5157 (3)	−0.12312 (19)	0.28216 (8)	0.0271 (4)
C2	0.4512 (2)	−0.13171 (17)	0.39524 (8)	0.0227 (3)
C3	0.3533 (3)	−0.24948 (18)	0.38552 (9)	0.0280 (4)
H3	0.3003	−0.2928	0.4195	0.034*
C4	0.3402 (3)	−0.29593 (18)	0.32550 (10)	0.0302 (4)
H4	0.2755	−0.3721	0.3182	0.036*
C5	1.0040 (3)	0.91530 (19)	0.27540 (9)	0.0282 (4)
C6	1.1517 (3)	1.09471 (19)	0.32643 (10)	0.0311 (4)
H6	1.2200	1.1700	0.3220	0.037*
C7	1.1029 (3)	1.05652 (18)	0.38512 (9)	0.0279 (4)
H7	1.1340	1.1050	0.4211	0.033*
C8	1.0018 (2)	0.93903 (17)	0.39043 (8)	0.0228 (3)
C9	0.6955 (2)	0.21335 (16)	0.40007 (8)	0.0223 (3)
C10	0.7829 (2)	0.34860 (16)	0.39920 (8)	0.0205 (3)
H10	0.8548	0.3549	0.3607	0.025*
C11	0.6476 (2)	0.45940 (16)	0.39747 (8)	0.0191 (3)
H11	0.5796	0.4511	0.3581	0.023*
C12	0.7400 (2)	0.59383 (15)	0.39722 (8)	0.0203 (3)
N1	0.5288 (2)	−0.07644 (15)	0.34392 (7)	0.0244 (3)
N2	0.4183 (3)	−0.23531 (17)	0.27525 (8)	0.0313 (4)
N3	0.4693 (3)	−0.07353 (16)	0.45057 (8)	0.0303 (4)
N4	0.9555 (2)	0.87599 (16)	0.33577 (7)	0.0245 (3)
N5	1.1043 (3)	1.02646 (17)	0.27297 (8)	0.0327 (4)
N6	0.9557 (3)	0.88801 (16)	0.44485 (8)	0.0303 (4)
O1	0.5847 (2)	−0.06662 (17)	0.23794 (7)	0.0443 (4)
O2	0.9624 (2)	0.85238 (17)	0.22833 (7)	0.0438 (4)
O3	0.6214 (2)	0.17628 (13)	0.34904 (7)	0.0366 (4)
O4	0.7027 (2)	0.14814 (14)	0.44995 (7)	0.0347 (3)
O5	0.89220 (18)	0.36252 (13)	0.45351 (7)	0.0308 (3)
H5	0.8871	0.2952	0.4752	0.046*
O6	0.53350 (18)	0.44816 (13)	0.45043 (6)	0.0276 (3)
H6A	0.4348	0.4328	0.4376	0.041*
O7	0.74807 (19)	0.65974 (12)	0.44753 (6)	0.0273 (3)
O8	0.8050 (2)	0.63023 (14)	0.34462 (6)	0.0348 (3)
O9	0.2191 (3)	0.4089 (3)	0.39776 (10)	0.0725 (8)
H1A	0.569 (4)	0.003 (2)	0.3477 (12)	0.051 (8)*
H2A	0.403 (3)	−0.258 (3)	0.2363 (9)	0.038 (7)*
H3A	0.529 (3)	−0.004 (2)	0.4530 (11)	0.037 (7)*
H3B	0.411 (3)	−0.094 (2)	0.4827 (9)	0.026 (6)*
H4A	0.902 (3)	0.802 (2)	0.3369 (11)	0.041 (7)*
H5A	1.138 (4)	1.046 (3)	0.2351 (10)	0.044 (7)*
H6B	0.895 (3)	0.8185 (19)	0.4459 (11)	0.036 (7)*
H6C	0.986 (3)	0.921 (2)	0.4795 (9)	0.037 (6)*
H9A	0.190 (5)	0.401 (4)	0.3598 (11)	0.096 (14)*
H9B	0.134 (4)	0.397 (4)	0.4223 (14)	0.088 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0325 (9)	0.0277 (8)	0.0211 (8)	0.0014 (8)	−0.0023 (7)	−0.0016 (7)
C2	0.0259 (8)	0.0190 (7)	0.0232 (7)	0.0033 (7)	0.0007 (7)	0.0005 (6)
C3	0.0308 (10)	0.0211 (8)	0.0323 (10)	−0.0018 (7)	0.0024 (8)	0.0032 (7)
C4	0.0320 (10)	0.0210 (8)	0.0377 (10)	−0.0018 (8)	−0.0044 (8)	−0.0034 (8)
C5	0.0304 (10)	0.0314 (9)	0.0227 (8)	0.0018 (8)	0.0024 (7)	0.0013 (7)
C6	0.0324 (10)	0.0222 (8)	0.0387 (10)	−0.0020 (8)	0.0023 (8)	0.0040 (8)
C7	0.0318 (10)	0.0217 (8)	0.0302 (9)	−0.0028 (8)	−0.0024 (8)	−0.0028 (7)
C8	0.0237 (8)	0.0209 (7)	0.0237 (8)	0.0025 (6)	−0.0011 (6)	0.0002 (7)
C9	0.0280 (9)	0.0174 (7)	0.0217 (8)	−0.0007 (7)	0.0011 (7)	−0.0019 (6)
C10	0.0232 (8)	0.0177 (7)	0.0205 (7)	−0.0020 (6)	0.0006 (6)	−0.0020 (6)
C11	0.0228 (8)	0.0187 (7)	0.0158 (7)	−0.0018 (6)	−0.0009 (6)	−0.0026 (6)
C12	0.0235 (8)	0.0166 (7)	0.0209 (7)	0.0004 (6)	−0.0016 (6)	0.0001 (6)
N1	0.0330 (8)	0.0200 (7)	0.0202 (7)	−0.0036 (6)	0.0005 (6)	−0.0011 (6)
N2	0.0410 (10)	0.0278 (8)	0.0250 (8)	−0.0017 (7)	−0.0048 (7)	−0.0077 (6)
N3	0.0435 (10)	0.0264 (8)	0.0210 (7)	−0.0037 (7)	0.0051 (7)	−0.0014 (6)
N4	0.0287 (8)	0.0225 (7)	0.0223 (7)	−0.0036 (6)	0.0004 (6)	−0.0009 (6)
N5	0.0414 (10)	0.0311 (8)	0.0256 (8)	−0.0027 (7)	0.0056 (7)	0.0065 (7)
N6	0.0422 (10)	0.0278 (8)	0.0210 (7)	−0.0083 (7)	−0.0002 (7)	−0.0018 (6)
O1	0.0591 (11)	0.0519 (10)	0.0219 (6)	−0.0129 (9)	0.0033 (7)	0.0021 (6)
O2	0.0543 (10)	0.0535 (10)	0.0235 (6)	−0.0138 (9)	0.0041 (7)	−0.0069 (7)
O3	0.0632 (11)	0.0226 (6)	0.0241 (6)	−0.0123 (7)	−0.0124 (7)	0.0010 (5)
O4	0.0496 (9)	0.0285 (7)	0.0261 (6)	−0.0091 (7)	−0.0056 (6)	0.0074 (6)
O5	0.0306 (7)	0.0262 (6)	0.0355 (7)	−0.0010 (6)	−0.0120 (6)	−0.0019 (6)
O6	0.0240 (6)	0.0311 (6)	0.0277 (6)	−0.0020 (6)	0.0056 (5)	−0.0044 (5)
O7	0.0398 (8)	0.0208 (6)	0.0212 (6)	−0.0040 (5)	−0.0013 (5)	−0.0042 (5)
O8	0.0563 (10)	0.0249 (6)	0.0233 (6)	−0.0100 (7)	0.0110 (6)	−0.0027 (5)
O9	0.0402 (10)	0.137 (2)	0.0409 (10)	−0.0349 (13)	0.0010 (9)	−0.0080 (13)

Geometric parameters (Å, º)

C1—O1	1.211 (2)	C9—C10	1.524 (2)
C1—N2	1.367 (3)	C10—O5	1.421 (2)
C1—N1	1.380 (2)	C10—C11	1.530 (2)
C2—N3	1.307 (2)	C10—H10	0.9800
C2—N1	1.350 (2)	C11—O6	1.419 (2)
C2—C3	1.424 (3)	C11—C12	1.534 (2)
C3—C4	1.345 (3)	C11—H11	0.9800
C3—H3	0.9300	C12—O7	1.248 (2)
C4—N2	1.358 (3)	C12—O8	1.264 (2)
C4—H4	0.9300	N1—H1A	0.86 (2)
C5—O2	1.216 (2)	N2—H2A	0.857 (18)
C5—N5	1.364 (3)	N3—H3A	0.842 (18)
C5—N4	1.377 (2)	N3—H3B	0.834 (17)
C6—C7	1.341 (3)	N4—H4A	0.854 (19)
C6—N5	1.365 (3)	N5—H5A	0.857 (19)

C6—H6	0.9300	N6—H6B	0.846 (18)
C7—C8	1.425 (3)	N6—H6C	0.833 (17)
C7—H7	0.9300	O5—H5	0.8200
C8—N6	1.300 (2)	O6—H6A	0.8200
C8—N4	1.358 (2)	O9—H9A	0.83 (2)
C9—O4	1.236 (2)	O9—H9B	0.84 (2)
C9—O3	1.267 (2)		

O1—C1—N2	123.44 (18)	C11—C10—H10	108.5
O1—C1—N1	121.52 (18)	O6—C11—C10	110.11 (14)
N2—C1—N1	115.04 (17)	O6—C11—C12	111.12 (13)
N3—C2—N1	118.14 (17)	C10—C11—C12	109.52 (14)
N3—C2—C3	124.05 (17)	O6—C11—H11	108.7
N1—C2—C3	117.81 (16)	C10—C11—H11	108.7
C4—C3—C2	117.74 (18)	C12—C11—H11	108.7
C4—C3—H3	121.1	O7—C12—O8	124.04 (15)
C2—C3—H3	121.1	O7—C12—C11	119.58 (15)
C3—C4—N2	122.18 (18)	O8—C12—C11	116.38 (15)
C3—C4—H4	118.9	C2—N1—C1	124.84 (16)
N2—C4—H4	118.9	C2—N1—H1A	118.0 (18)
O2—C5—N5	123.37 (18)	C1—N1—H1A	115.5 (18)
O2—C5—N4	121.41 (18)	C4—N2—C1	122.35 (16)
N5—C5—N4	115.20 (17)	C4—N2—H2A	123.5 (17)
C7—C6—N5	122.05 (18)	C1—N2—H2A	113.8 (17)
C7—C6—H6	119.0	C2—N3—H3A	119.2 (16)
N5—C6—H6	119.0	C2—N3—H3B	123.3 (15)
C6—C7—C8	117.66 (18)	H3A—N3—H3B	117 (2)
C6—C7—H7	121.2	C8—N4—C5	124.52 (16)
C8—C7—H7	121.2	C8—N4—H4A	121.0 (16)
N6—C8—N4	118.70 (16)	C5—N4—H4A	114.1 (16)
N6—C8—C7	123.27 (17)	C5—N5—C6	122.51 (17)
N4—C8—C7	118.01 (16)	C5—N5—H5A	113.3 (18)
O4—C9—O3	125.05 (17)	C6—N5—H5A	124.2 (18)
O4—C9—C10	117.97 (16)	C8—N6—H6B	120.2 (16)
O3—C9—C10	116.98 (15)	C8—N6—H6C	121.8 (16)
O5—C10—C9	109.89 (14)	H6B—N6—H6C	118 (2)
O5—C10—C11	110.42 (13)	C10—O5—H5	109.5
C9—C10—C11	110.95 (14)	C11—O6—H6A	109.5
O5—C10—H10	108.5	H9A—O9—H9B	111 (3)
C9—C10—H10	108.5		

N3—C2—C3—C4	177.53 (19)	O6—C11—C12—O8	−160.68 (16)
N1—C2—C3—C4	−1.9 (3)	C10—C11—C12—O8	77.45 (19)
C2—C3—C4—N2	0.9 (3)	N3—C2—N1—C1	−177.22 (18)
N5—C6—C7—C8	1.4 (3)	C3—C2—N1—C1	2.3 (3)
C6—C7—C8—N6	175.8 (2)	O1—C1—N1—C2	177.9 (2)
C6—C7—C8—N4	−2.5 (3)	N2—C1—N1—C2	−1.4 (3)
O4—C9—C10—O5	13.0 (2)	C3—C4—N2—C1	0.1 (3)

O3—C9—C10—O5	−166.62 (16)	O1—C1—N2—C4	−179.1 (2)
O4—C9—C10—C11	−109.38 (19)	N1—C1—N2—C4	0.1 (3)
O3—C9—C10—C11	71.0 (2)	N6—C8—N4—C5	−176.22 (18)
O5—C10—C11—O6	−65.06 (17)	C7—C8—N4—C5	2.2 (3)
C9—C10—C11—O6	57.03 (17)	O2—C5—N4—C8	177.85 (19)
O5—C10—C11—C12	57.41 (17)	N5—C5—N4—C8	−0.6 (3)
C9—C10—C11—C12	179.50 (14)	O2—C5—N5—C6	−179.1 (2)
O6—C11—C12—O7	19.7 (2)	N4—C5—N5—C6	−0.6 (3)
C10—C11—C12—O7	−102.17 (18)	C7—C6—N5—C5	0.2 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.93	2.53	3.098 (2)	120
C10—H10···O2^{ii}	0.98	2.33	3.312 (2)	175
C11—H11···O1^{iii}	0.98	2.38	3.361 (2)	179
O5—H5···O4	0.82	2.12	2.6140 (19)	118
O6—H6*A*···O9	0.82	1.87	2.688 (2)	172
N1—H1*A*···O3	0.86 (2)	1.80 (2)	2.656 (2)	171 (3)
N2—H2*A*···O3^{i}	0.86 (2)	1.91 (2)	2.768 (2)	175 (3)
N3—H3*A*···O4	0.84 (2)	2.04 (2)	2.873 (2)	171 (2)
N3—H3*B*···O7^{iv}	0.83 (2)	2.04 (2)	2.865 (2)	172 (2)
N4—H4*A*···O8	0.85 (2)	1.90 (2)	2.748 (2)	173 (3)
N5—H5*A*···O8^{v}	0.86 (2)	1.93 (2)	2.766 (2)	166 (3)
N6—H6*B*···O7	0.85 (2)	1.96 (2)	2.808 (2)	179 (3)
N6—H6*C*···O6^{vi}	0.83 (2)	2.01 (2)	2.812 (2)	163 (2)
O9—H9*A*···O2^{i}	0.83 (2)	2.24 (3)	3.040 (3)	162 (4)
O9—H9*B*···O5^{vii}	0.84 (2)	2.00 (3)	2.812 (2)	161 (3)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) −*x*+2, *y*−1/2, −*z*+1/2; (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) *x*−1/2, −*y*+1/2, −*z*+1; (v) −*x*+2, *y*+1/2, −*z*+1/2; (vi) *x*+1/2, −*y*+3/2, −*z*+1; (vii) *x*−1, *y*, *z*.

A Comparative Analysis of the Energy Optimized Structure of 2-Methyl Pyridinium Picrate with Its Polymorphs

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ABSTRACT-Methyl pyridinium $C_6H_8N^+$, a quaternary ammonium compound, is derived from the N-methylation of pyridine. It is found in some coffee products and is formed during roasting of coffee beans from its precursor chemical, trigonelline. It is under investigation by scientists regarding its potential anti-carcinogenic properties, particularly for its effect on colon cancer. Though the two reported polymorphs of the title compound had crystallized in the same triclinic setting with space group $P\bar{1}$, have quite different inter-axial angles. Theoretical calculations of the molecular structure has been performed using MOPAC2016's PM7 geometry optimization algorithm and structural and energy parameters corresponding to the optimum energy configuration have been computed. The dihedral angle between the methylpyridine and picrate moieties is 10.49° in the isolated molecule. The amino nitrogen the pyridine ring is involved in both N-H…N and N-H…O interactions while the ring carbon (C11) and methyl carbon (C12) make C-.H…O hydrogen bonds with the symmetry related molecule. The dipole moment of the molecule is 24.41 debye. The HOMO and LUMO energies are -9.29 eV and -2.48 eV respectively. A conductor like screening model gives the molecular area as 318.23 Å^2 and molecular volume as 336.96 Å^3. A structure overlay analysis of the isolated molecule with its energy minimized counterpart shows a root mean square deviation of 1.93 Å, indicating the effect of hydrogen bonding interactions and crystal packing effects in the solid state of the structure.

I CHEMICAL CONTEXT

Methyl pyridinium $C_6H_8N^+$, a quaternary ammonium compound, is derived from the N-methylation of pyridine. It is found in some coffee products and is formed during roasting of coffee beans from its precursor chemical, trigonelline. It is studied for its potential anti-carcinogenic [1] properties, particularly for its effect on colon cancer. Picric acid is found to form crystalline picrates of various organic molecules through ionic and hydrogen bonding and π-π interactions and the presence of phenolic OH in the picric acid favors the formation of the salts with various organic bases [2]. The formation of charge transfer complex depending on the nature of the donor-acceptor system and the orientation of anionic and cationic species facilitates the formation of expected N-H·····O hydrogen bonds between amino hydrogen and phenolic oxygen [3]. These mechanisms could be the reason for the formation of polymorphic forms of the title compound. In the light of these, the conformation and geometry of the energy minimized crystal structure of 2-methylpyridinium picrate has been studied with reference to its polymorphs in the crystalline state reported in the literature [4,5].

A. Structural Features

The chemical scheme and the geometry optimized molecular structure of 2-methylpyridinium picrate are illustrated in Figure 1 and Figure 2 respectively. Though the two reported polymorphs of the title compound had crystallized in the same triclinic setting with space group $P\bar{1}$, have quite different inter-axial angles (Table 1). The dihedral angle between the methylpyridine and picrate moieties is 10.49° in the isolated molecule. The amino nitrogen the pyridine ring is involved in both N-H…N and N-H…O interactions while the ring carbon (C11) and methyl carbon (C12) make C-.H…O hydrogen bonds with the symmetry related molecules. The structural geometry details have been obtained using PLATON [6].

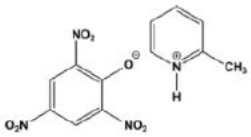

Fig. 1 Chemical scheme

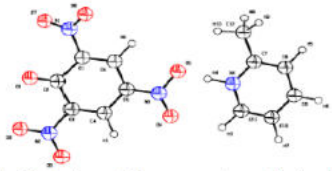

Fig. 2 A view of the geometry optimized structure of 2-methylpyridinium picrate. Hydrogen atoms are shown as small circles of arbitrary radii.

II COMPUTATION OF MULLIKEN POPULATION

The concept of atomic charge which is the net electronic and nuclear charge on each atom is often used to rationalize observed chemical behavior in the molecules

and in the structure activity studies of molecules. Though, in reality, the atomic charge of the atoms of a molecules is not a measurable physical property, a diffuse charge distribution of electrons can arbitrarily be assigned to any atomic center and quantum chemical wave functions can be used to assign atomic charges either based on the orbital occupancy or using the spatial decomposition of the overall electron distribution. The popular charge partitioning scheme is by Mulliken [7] which assign charge to an atomic center on the basis of the total electron density. The Mulliken population analysis of atomic charges to the investigated molecule using MOPAC2016 [8] gave a net charge of +0.986929 coulomb for the 2-methylpyridinium cation and -0.98693 coulomb for the picrate anion, thereby confirming the experimental observations of +1 and -1.

A. Structure Overlay Studies

A super imposed fit of the structure optimized molecule of the title compound with its energy minimized counterpart using Qmol [9] showed a root mean square deviation (r.m.s.d.) of 1.93Å (Figure 3). On the other hand on overlay of the energy minimized molecule with the unit cell components of polymorph-1 gave r.m.s.ds 3.336Å and 3.325Å respectively. A similar analysis with the unit cell components of polymorph-2 gave r.m.s.ds 3.477Å and 3.466Å respectively. These marked deviations in the overlay fit indicate the effect of packing interactions due to N-H…O and C-H…O Hydrogen bonds between the symmetry related molecules the crystalline state of the molecules.

B. Conformational Analysis

In order to explore, the conformational changes and effect of packing interaction. A semi-empirical PM7 calculation with MOPAC 2016 has been done on the structure. In the calculations the molecule was assumed to be isolated and in an absolute vacuum, therefore resulting in calculated bond length, bond angle and torsion angles that are greater than those observed experimentally. The PM7 method gives the lowest values for the HOMO & LUMO energy levels and dipole moments. No puckering was observed in the rings of the cations and anions and they maintained a planar geometry in the energy optimized structure as well as polymorphs. The total energy of the molecule is -4411.00685 eV and dipole moment is 28.93480 debye. The HOMO and LUMO energy levels are -8.805 eV and -3.084 eV respectively. A conductor like screening model gives the molecular area as 318.23Å^2 and molecular volume as 336.96Å^3.

Table 1: Crystal Data, Data Collection and Refinement

Structure Parameter	Polymorph-1 (Ref[1])	Polymorph-2 (Ref[2])
Crystal system, space group	Triclinic, P -1	Triclinic, P -1
a, b, c (Å)	8.1524 (4) 11.8809 (6) 14.6377 (9)	8.211 (3) 11.806 (4) 14.388 (4)
α,β,γ (°)	102.077 (3) 90.001 (3) 100.692 (3)	85.428 (5) 82.863 (5) 79.726 (4)

Fig.3 A structure overlay of the optimized molecule of the title compound with its energy minimized counterpart

III CONCLUSION

The geometry optimized structure and energy minimized structures of 2-methylpyridinium picrate molecule have been analyzed by semi-empirical method. The molecular conformation has been compared with its polymorphs. The protonation of the amino atom in the pyridine moiety is found to be the agent for crystal packing interactions in the form of different types of hydrogen bonds and for the structural stability of the crystal in the solid state.

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FTIR and SHG studies on STS doped KDP Crystal

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Abstract—**This Potassium Dihydrogen Phosphate (KDP) is a familiar NLO material with diverse applications. Doped crystals of KDP have been grown with sodium thiosulphate (Hypo) as dopant by slow evaporation of solvent. Hypo is an inorganic and photo sensitive material and is finding application in both photo film and photo processing. The dopant material has been incorporated into the parent compound KDP in 1 mol %. The experiment is done in order to study the photo conductivity and non-linear activity characteristics of hypo doped KDP. Here we report the preliminary results of the studies carried out as part of the investigations of elucidating photo conductive properties. This contains FTIR analysis and SHG response of the grown crystals. The FTIR spectrum confirmed the incorporation of the dopant material in to the KDP crystal. The SHG efficiency of the doped KDP crystal is found to be less than that of the pure KDP crystal.**

Keywords— NLO properties;FTIR analysis; SHG efficiency

I. Introduction

Technology is progressing at a very rapid pace in the recent times thanks to scientific advancement and the lifestyle of human beings are changing every day. Photography is one area in which the advancement in technology has really contributed a lot. The newly emerging photoconductive materials are changing the facet of image processing methods.

Photoconductivity has traditionally been playing a significant role in materials research [1]. The study of photoconductivity is one of the most effective ways to investigate the properties of solids. It is a phenomenon involving the interaction of light quanta with solids to produce free charge carriers reflecting all of the fascinating diversions encountered by an electron or hole in a solid. Thermal and hot carrier relaxation process, charge carrier statistics, effects of electrodes and several mechanisms of recombination are involved in photoconduction [2]. Photoconductivity materials find practical applications in television cameras, infrared detector, light meter, photo detectors, photo resistors etc. The other major application in which photoconductivity plays a central role is in photography processing and the vast field of electro photographic reproduction. Classic examples of photoconductive materials include the conductive polymer poly vinylcarbazole which is used extensively in photocopying (Xerography), lead sulfide used in infrared detection application and STS ($Na_2S_2O_3$) used in photographic processing etc.

Second harmonic generation (SHG) also called frequency doubling is a nonlinear optical process, in which photons interacting with a nonlinear material are effectively combined to form new photons with twice the energy. It is a special case of sum frequency generation with a non-linear optical material mediating the adding-up of two photons to form new one with twice the frequency or half the wavelength [3].

Sodium thio sulphate is used as a photographic fixer in image processing. Photographic fixer is a mixture of chemicals used in the final step of the photograph processing of film or paper. The fixer solution is a photographic waste solution of sodium or ammonium thiosulphate that converts the silver halide into water soluble silver thio sulphate complexes which diffuse from the emulsion into the fixing bath. The fixer stabilizes the image, removing the unexposed silver halide remaining on the photographic film or photographic paper, leaving behind the reduced metallic silver that forms the image to prevent the photographic chemicals from further getting dark and fix the pictures. It is much like a preservative. It prevents the pictures to be affected by further chemical oxidation. By fixation, the film or paper is insensitive to further action by light. Without fixing, the remaining silver halide would darken and cause fogging of the image or incomplete fixing can lead to sulphide staining and create havoc with subsequent toning.

In this research work $Na_2S_2O_3$ incorporated KDP crystals were grown by slow evaporation method. KDP is an inorganic material is well-studied and reported material because of the flexibility its offers in its tailoring its optical properties, physical properties and for easy synthesis. The incorporation of Na_2S_2O3 in KDP could alter its photoconductivity properties. Also this approach could be utilized in the study of photographic fixing process. Hence undoped and doped KDP

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crystals were grown and were subjected to the characterization studies namely, FTIR analysis [4] and SHG measurements.

II. Experimental method

Growth of crystal

Commercially available KDP and sodium thiosulphate of GR grade having 99.9% purity were purchased for the crystal growth process. A saturated solution of pure KDP was prepared using distilled water. The KDP was doped with sodium thiosulphate for 1 mol%. The doped solution was stirred well for about 4 hours using a magnetic stirrer to get a homogenous solution. Later the solutions were filtered with A1 quality filter paper to remove foreign particles. The doped saturated solution was taken in separate beakers and were covered with thin plastic paper. Holes were made on the cover for proper evaporation of the solvent and the solution was kept in a water bath for crystal growth. The bath temperature was maintained at a constant value of 35°C. After 28 days, nucleation was found in the beakers and single crystals of good optical quality were obtained. The obtained crystals were non-hygroscopic, transparent and free from inclusions. The grown doped KDP crystals are shown in Figure 1.

III. FT-IR analysis

In Fourier Transform Infrared (FT-IR) analysis the infrared radiation promotes transitions in a molecule between rotational and vibrational energy levels of the ground energy states. The FT-IR spectrum of Pure KDP (reference) and Doped KDP crystals (Figure 2) were recorded at room temperature in the spectral range 500- 4000 cm-1 by ATR (Attenuated Total Reflectance) mode. The recorded spectrum reveals the presence of all groups functional occurring in KDP. The spectrum of sodium thiosulphate doped KDP crystal indicates an appreciable shift of peak positions to lower and higher values suggesting incorporation of dopants in the crystal lattice. Using the characteristic frequency values and infrared structural correlation chart, the vibrational assignments were made and are shown in Table - 1.

IV. SHG studies

SHG conversion efficiency of the grown Sodium thiosulphate doped KDP crystal sample was measured by the Kurtz and Perry technique. Nd:YAG (λ = 1064 nm) laser irradiates the powder sample of KDP doped with STS kept in the triangular cell. The monochromator was set at 532 nm. NLO signal was captured by the oscilloscope through the photomultiplier tube. The Nd: YAG laser source produces nanosecond pulses (8 ns) of 1064 nm light and the energy of the laser pulse was around 1.2 mJ. The beam emerging through the sample was focused on to a Czerny–Turner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R928 photomultiplier tube. The signals were captured with an Agilent infinium digital storage oscilloscope interfaced to a computer. The generation of the second harmonic was confirmed by the emission of green light. Potassium dihydrogen phosphate (KDP) sample was used as the reference material in the SHG measurements. The SHG efficiency was obtained from the ratio of the output energy of the second harmonic to the input power of the pumping pulses. A second harmonic signal of 32mV was obtained for the doped KDP with reference to 40mV of pure KDP indicating the efficiency as 0.8.

FIGURE 1: THE GROWN CRYSTALS OF DOPED KDP

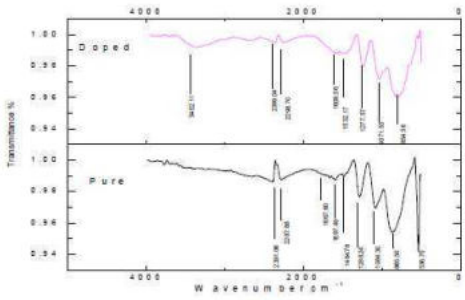

FIGURE 2: FTIR SPECTRUM OF PURE AND DOPED KDP CRYSTALS

TABLE I

PURE KDP cm^{-1}	SODIUM THIOSULPHATE DOPED KDP cm^{-1}	ASSIGNMENTS
-	3402.11	Free OH Stretching
-	2729.04	P-O-H symmetric stretching
2391.60	2399.04	P-O-H symmetric stretching
2282.88	2298.70	P-O-H Stretching
1667.60	1609.56	O=P-OH Stretching
1597.49	1532.17	O=P-OH Stretching
1484.76	-	O-H Stretching
1288.24	1277.57	P-O Stretching
1084.30	1071.55	P-O Stretching
865.58	854.56	P-OH Bending
536.70	-	HO-P-OH Bending

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V. Conclusion

Crystals of doped KDP of good quality were grown by slow evaporation solution growth technique at a constant temperature 35° C. The functional groups present in the grown crystal were confirmed from FTIR analysis. SHG activity of doped KDP was found to be slightly less than that of pure KDP crystal. As far to the knowledge of the authors concerned, no work has yet been reported in the literature on doping of KDP crystals with sodium thio sulphate. Hence, it is intended to explore the effect of hypo doping on KDP further with other characterizations.

Acknowledgment

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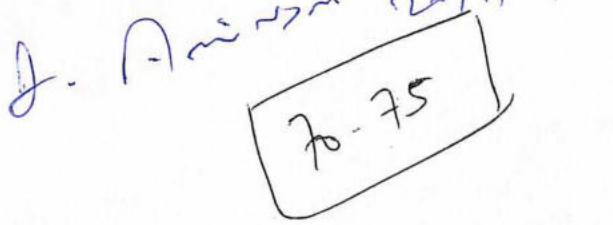
“திருக்குறள் விழுமியங்கள்”



தொகுப்பாசிரியர்

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நூல் விவரப்பட்டியல்

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தொகுப்பாசிரியர் உரை

திருக்குறள் உலகப்பொதுமறை. திருக்குறளில் காணலாகும் விழுமியங்களை இளையதலைமுறைக்கு உணர்த்த மன்னர் திருமலை நாயக்கர் கல்லூரியின் தமிழ்த்துறை விரும்பியது.

தமிழ்த்துறை கருத்தரங்கிற்கு UGC நிதி ஒதுக்கியது.

மன்னர் திருமலை நாயக்கர் கல்லூரி அன்னைதெரசா மகளிர் பல்கலைக்கழகத்துடன் இணைந்து 03.03.2017 அன்று 'திருக்குறள் விழுமியங்கள்' என்ற தலைப்பில் தேசிய அளவிலான கருத்தரங்கினை தமிழ்த்துறை நடத்துகிறது.

பல்வேறு கல்லூரிகளிலிருந்து இணைப்பேராசிரியர்கள், உதவிப் பேராசிரியர்கள், முனைவர் பட்ட ஆய்வாளர்கள் ஆர்வமுடன் கட்டுரை வழங்கினர்.

தரமான 96 கட்டுகைள் வந்து குவிந்தன. அனைத்துக் கட்டுரைகளும் தொகுக்கப்பெற்று திருக்குறள் விழுமியங்கள் என்னும் பெயரில் 524 பக்கங்கள் கொண்ட நூலாக வெளிவந்துள்ளது.

மன்னர் திருமலை நாயக்கர் கல்லூரி ஆட்சிக் குழுத்தலைவர் வி.கெங்குசாமி நாயடு, உதவித்தலைவர் பொறியாளர் எஸ். ராஜகோபால், செயலாளர் எம். விஜயராகவன், பொருளாளர் எஸ். கோவிந்தராஜன், உதவிச்செயலாளர் கே. ராஜேந்திரபாபு முதலிய நிர்வாகத்தினர் தமிழ்த்துறையின் பால் கொண்டுள்ள பாசத்திற்கும் அன்பிற்கும் உளம் கனிந்த நன்றியை உரிதாக்குகிறோம்.

இக்கருத்தரங்கிற்கு உறுதுணையாக இருந்த கல்லூரி முதல்வர் முனைவர் எஸ். நேரு அவர்களுக்கு நன்றி.

கருத்தரங்க செயல்பாட்டில் உதவிய ஆங்கிலத்துறை பேராசிரியர் முனைவர். ஆர். தனலெட்சுமி, வணிக நிர்வாகவியல் துறை பேராசிரியர் முனைவர் தை. ஆக்னஸ் நட்சத்திரம் அவர்களுக்கு நன்றி.

கருத்தரங்கம் சிறக்க என்னுடன் இணைந்து பணியாற்றிய பேராசிரியர்கள் முனைவர் நம். சீனிவாசன், முனைவர் சீ. காயத்ரிதேவி, முனைவர் க. குமரகுருபரன் ஆகியோருக்கு நன்றி

ஆய்வுக்கட்டுரை அனுப்பிச் சிறப்பித்த அறிஞர் பெருமக்கள் அனைவருக்கும் நன்றி

மிகச்சிறந்த முறையில் இந்நூலை பதிப்பித்து வெளியிட்டிருக்கும் ஷான்லாக்ஸ் நிறுவனத்திற்கு நன்றி.

தேசிய அளவிலான கருத்தரங்கம் நடைபெற நிதிஉதவி வழங்கிய பல்கலைக்கழக மானியக்குழுவிற்கு நன்றி!

மதுரை
03.03.2017

அன்புடன்,
கோ. தேவிபூமா,
கருத்தரங்க அமைப்பாளர்.

பொருளடக்கம்

13. திருக்குறள் உணர்த்தும் பன்முக ஆளுமைச் சிந்தனைகள்

முனைவர் ச. ஈஸ்வரன்

இணைப்பேராசிரியர் & தலைவர், தமிழாய்வுத்துறை, தேசியக்கல்லூரி (தன்னாட்சி), திருச்சிராப்பள்ளி - 620001.

முன்னுரை

கிரேக்கம், இலத்தீன், சீனம், வடமொழி போன்ற உலகின் தொன்மையான மொழிகளுள் தோன்றிய அறஇலக்கியங்களுடன் ஒப்பிடக்கூடிய மாண்பினைப் பெற்றது திருக்குறள். உலகின் வேறெந்த மொழிகளிலும் காணவும் பார்க்கவும் இயலாத மிகச் சிறிய அடியளவில் அரும்பெரும் கருத்துக்கள் பொதிந்துள்ள நூல் திருக்குறள். பிறமொழிகளில் அதிகமாக மொழிபெயர்க்கப்பெற்ற தமிழ்நூல் திருக்குறளே ஆகும். பிறமொழியாளர்கள் அதிகமாகச் சான்று காட்டும் நூலும் திருக்குறள்.

எவையெல்லாம் வாழ்க்கை ஒழுங்குகளைச் சிதைக்கின்றனவோ அவைகளைத் திருவள்ளுவர் கடிந்து ஒதுக்கினார். கள், கல்லாமை, பிறன்மனை நயத்தல், பரத்தமை, பொய், களவு, சூது, புறம் பேசுதல், உயிர்க்கொலை, பழிச்செயல், முயற்சியின்மை, அவா ஆகியனவற்றை முற்றிலுமாக விலக்க வேண்டும் என்று வலியுறுத்தினார். மேலும், பின்பற்றப்பெற வேண்டிய சிந்தனைகளையும் செயல்களையும் திருவள்ளுவர் அறிவுறுத்தியுள்ளார். அருளுடைமை, அழுக்காறாமை, அன்புடைமை, இடுக்கணழியாமை, இன்னாசெய்யாமை, சான்றாண்மை, நாணுடைமை, பண்புடைமை, பொறையுடைமை, மடியின்மை, வினைத்தூய்மை போன்றவை அவைகளுள் சிலவாம்.

இக்கட்டுரையில், திருக்குறள் உணர்த்தும் பன்முக ஆளுமைச் சிந்தனைகளைத் தொகுத்தறியலாம்.

1. அன்புடைமை

அன்பு இயற்கையான உணர்வு. மக்கள் எல்லோரிடத்திலும் அ·து அமைந்துள்ளது. அன்பு இல்லாதவரைக் காண்பது அறிவு. அன்பு விரைந்து பெருகும் வாய்ப்பு மக்கட் பிறவிக்கு உண்டு. அதனால் மனிதப் பிறவி விழுமியது என்று ஆன்றோரால் போற்றப் பெற்றது. அன்புவழி வாழ்க்கை வேண்டும். அவ்வழியே வளரும் வாழ்க்கை பண்பும் பயனும் உடையதாகும்.

அன்பின் வழியது உயிர்நிலை அ·துஇலார்க்கு
என்புதோல் போர்த்த உடம்பு. (80)

சதை இல்லாமல் வெறும் எலும்பும் அதன் மேல் தோலும் போர்த்தப்பட்ட உயிரற்ற உடலால் ஏதேனும் பயன் உண்டா? இல்லை. இக்காட்சியை அன்பற்றவனுக்கு உதாரணமாக வள்ளுவர் காட்டுகின்றார்.

இனிமையாகப் பேசும்போது அனைவர் உள்ளமும் இன்புறும். கடுமையாகப் பேசும்போது அனைவர் உள்ளமும் துன்பமடையும். ஆகவே இனிமையான சொற்களைப் பேச வேண்டும்.

இனிய உளவாக இன்னாத கூறல்
கனிஇருப்பக் காய் கவர்ந்தற்று (100)

2. செய்நன்றி அறிதல்

ஒருவருக்கொருவர் உதவி செய்யாவிட்டால், உலக வாழ்க்கை நடைபெறாது. அவ்வாறு உதவி செய்வோரை மறவாமல் அவர் செய்த நன்மையைப் போற்றுவது சிறந்த பண்பாகும்.

உலகத்தில் எந்தச் செயலை மறந்தாலும் தப்பித்து விடலாம். ஆனால் ஒருவன் செய்த நன்றியை மறந்த ஒருவனுக்கு உய்யும் வழியே கிடையாது.

நன்றி மறப்பது நன்றன்று: நன்றல்லது
அன்றே மறப்பது நன்று (108)

3. அடக்கமுடைமை

உலகில் வாழும் எவராக இருந்தாலும் பேசும்போது குற்றமில்லாமல் பேச வேண்டும். நா அடக்கம் வேண்டும். நா அடக்கமின்றிப் பேசுபவன் துன்பத்தில் அகப்பட்டு மிகவும் அல்லல் பட நேரிடும். ஆகவேதான் ஒருவன் எதைக் காத்திட முடியாவிட்டாலும் நாவை அடக்கிக் காத்திட வேண்டும். இல்லையேல் அவர் வாயிலிருந்து வந்த சொற்களே அவர் துன்பத்திற்குக் காரணமாக அமைந்து விடும்.

யாகாவாராயினும் நாகாக்க காவாக் கால்
சோகாப்பர் சொல் இழுக்கப்பட்டு.

எண்ணத்தாலும் பேச்சாலும் செயலாலும் அறத்தைப் போற்றி வாழ வேண்டுமானால், மனம், மொழி. மெய் என்பனவற்றை தன் ஆட்சியின் கீழ் அதாவது தன் கட்டுப்பாட்டில் வைத்திருக்கும் ஆற்றல் வேண்டும். அவ்வாறு மனம் முதலியவை அடங்கி ஒத்துழைக்கும் வாழ்வே சிறந்த வாழ்வு. ஆகவே அடக்கமாக இருக்க நம் மனத்தைப் போற்றிக் காக்க வேண்டும்.

4. ஒழுக்கமுடைமை

உயிர் எல்லாப் பொருளையும் விட உயர்வானது ஆயினும் அந்த உயிருக்கும் சிறப்புத் தரவல்லதாக இருப்பது ஒழுக்கம் விளங்குகிறது. ஆகையால் உயிரைவிட ஒழுக்கமே சிறந்ததாகக் கொண்டு காக்க வேண்டும். ஒழுக்கத்தை வருந்திப் போற்றிக்காக்க வேண்டும், ஒழுக்கத்தைக் காப்பதற்காக எவ்வளவு துன்பம் நேர்வதனாலும் வருந்தி ஏற்க வேண்டும்.

ஒழுக்கம் விழுப்பம் தரலான் ஒழுக்கம்
உயிரினும் ஓம்பப் படும். (131)

5. பிறனில் விழையாமை

ஒருவர் எவ்வளவு பெருமை உடையவராக இருந்தாலும் பயன் என்ன? எவ்வளவு சிறப்புகள் அவனைத் தேடிவந்தும் பெருமை என்ன? தினையளவும் எண்ணிப் பார்க்காமல் காமத்தால் மயங்கி பிறன் மனைவியை விரும்பினால் அந்தப் பெருமை எல்லாம் போய், சிறுமையே வந்து சேரும். தம்மை நல்லவர் என்று தெளிந்து ஐயப்படாமல் வீட்டில் இடம் கொடுத்தவரின் மனைவியிடம் நெறி தவறி நடக்கின்றவர்களை பிணம்போல் கருதி ஒதுக்க வேண்டும். பிறன் மனைவியை விரும்பி நோக்காத பேராண்மை வேண்டும். அதுவே அறநெறி நிறைந்த ஒழுக்கம் என்கிறார் வள்ளுவர்.

பிறன்மனை நோக்காத பேராண்மை சான்றோர்
அறன்ஒன்றோ ஆன்ற ஒழுக்கு (148)

6. பொறையுடைமை

பொறுமையைப் போற்றுகின்றவர் நிலத்தைப் பார்த்துக் கற்க வேண்டும். நிலம் தன்னை வெட்டித் தோண்டுகின்ற வரையும் விழாமல் தாங்குகிறது. அதனால் நிலத்தின் ஆற்றல் குறைவதில்லை. அதுபோல தம்மை இகழ்வாரைப் பொறுத்துக் கொள்வதே சிறந்த அறம். எவ்வளவு பொறுமையாக இருக்கிறோமோ அவ்வளவு ஆற்றல் வளரும் என்பது திருவள்ளுவர் கருத்து.

அகழ்வாரைத் தாங்கும் நிலம்போலத் தம்மை
இகழ்வார்ப் பொறுத்தல் தலை (151)

7. புலால் மறுத்தல்

பிற உயிர்களை உணவாக்கிக் கொள்ளலை திருவள்ளுவர் கடிந்து கூறுகிறார். தன் உடலை வளர்ப்பதற்காக வேறொரு உயிரின் உடலை வெட்டி, பக்குவப்படுத்தி உண்பவர், எப்படி, கருணை உள்ளம் கொண்டவராக இருக்க முடியும்? கொல்லுதல் அருளற்ற செயல். கொல்லாமை அருளுடைமையாகும். புலால் உண்ணாதவர்கள் பலர் இருப்பதால் பல உயிர்கள் கொல்லப்படாமல் வாழ்கின்றன. புலாலை உண்ணாதவர்கள், புலால் உண்பதற்காக உயிர்களைக் கொல்லாதவர்கள் இவர்களை எல்லா உயிரினங்களும் கைகூப்பி வணங்குமாம். ஆகவே உயிர்க்கொலை செய்து அவற்றை உணவாக்குதலை நிறுத்துங்கள் என்று திருவள்ளுவர் உலகத்தாரைக் கேட்கிறார்.

கொல்லான் புலாலை மறுத்தானைக் கைகூப்பி
எல்லா உயிருந் தொழும். (260)

8. வெகுளாமை

வலியார் மேல் சினம் பிறப்பது உண்டு. ஆனால் அப்போது அது பலிக்காது. மெலியார் மேல் சினம் பிறந்தால் அ.்.து அவர்களை வருத்தும்.

சினம் பலிக்காத வலியார் இடத்தில் மட்டும் சினம் கொள்ளாமல் காத்துக் கொள்வது போதாது. அங்கே சினம் காப்பதும் காவாமையும் ஒன்றுதான்.

செல்லா இடத்துச்சினம் தீது செல்லிடத்தும்
இல்அதனின் தீய பிற. (302)

சினத்தைவிட பெரிய பகை வேறு இல்லை. பகையிடமிருந்து ஒருவன் தன்னைத் தான் காத்துக் கொள்ள விரும்பினால் சினம் வராமல் மனத்தைக் காத்துக் கொள்ள வேண்டும். காக்கத் தவறினால் சினம் தன்னையே கொன்று விடும். சினம் என்பது ஒரு நெருப்பு. அது சேர்ந்துள்ள இடத்தையே அழித்துவிடும். ஆகவேதான் சினம் யாரிடம் உள்ளதோ அவர்களையே அழித்துவிடும் என்பது வள்ளுவர் வாக்கு.

9. கள்ளுண்ணாமை

கள் - போதை தருவது. கள்ளுண்பவர்கள் தங்களுடைய மதிப்பை இழந்து விடுவார்கள். பகைவரும் அஞ்ச மாட்டார்கள்.

சான்றோரின் உறவு போய்விடும். மற்றவர்கள் முன்பு குற்றவாளியாக நிற்க வேண்டும்.

தான் பெற்ற மகனுடைய எந்தக் குற்றமும் தாய்க்கு வெறுப்புத்தராது. ஆனால் கள்ளுண்டு மயங்குவது ஒன்று தான் தாயின் முன்பு வெறுப்புத் தருவதாகும். அந்த மகனை வெறுத்து ஒதுக்குவாள். தாயே வெறுக்கும் போது மற்ற சான்றோர்கள் அவனை எப்படிச் சகித்துக் கொள்வார்கள்.

ஈன்றாள் முகத்தேயும் இன்னாதால் என்மற்றும்
சான்றோர் முகத்துக் களி. (924)

10. வாழ்க்கைத் துணை நலம்

நற்பண்புகள் கொண்ட மனைவி அமையாத இல்வாழ்க்கை எவ்வளவு செல்வம் இருந்த போதிலும், பயனற்ற வாழ்க்கையாகவே இருக்கும். நல்ல பண்புள்ள மனைவி அமைந்த வாழ்க்கையில் எல்லாச் சிறப்புகளும் வந்து சேரும். அப்படி அமையாத வாழ்க்கையில் எதுவுமே இருக்காது.

இல்லதென் இல்லவள் மாண்பானால் உள்ளதென்
இல்லவள் மாணாக் கடை (53)

கணவனின் வருவாய்க்குத் தக்க வாழ்க்கை நடத்த வேண்டும். அத்தகையவளே வாழ்க்கை துணை. இல்லறத்திற்கு ஏற்ற பண்பு மனைவியிடத்தில் இல்லையானால் அந்த இல்வாழ்க்கை நரகமாகவே இருக்கும்.

11. மக்கட்பேறு

இல்வாழ்க்கையில் பெற வேண்டிய பேறுகள் பல உள்ளன. அவற்றுள் நல்ல மக்களைப் பெறும்பேறு ஒன்று. அறிய வேண்டியவற்றை அறிவதற்குரிய மக்களைப் பெறுவதுபோல் மற்ற பேறுகள் அவ்வளவு சிறப்புடையவை அல்ல.

பெறுமவற்றுள் யாம்அறிவது இல்லை அறிவறிந்த
மக்கட்பேறு அல்ல பிற (61)

12. புகழ்

வறியவர்க்குக் கொடுத்து உதவ வேண்டும். அதனால் புகழ்பட வாழ வேண்டும். இத்தகைய வாழ்வைத் தவிர உயிர்க்கு வேறு பயன் இல்லை.

ஈதல் இசைபட வாழ்தல் அதுஅல்லது
ஊதியம் இல்லை உயிர்க்கு (231)

வாழ்வில் ஏதாவது ஒரு துறையில் புகழோடு விளங்க வேண்டும். அத்தகைய நிலைமை இல்லாதவர்கள் அந்தத் துறையில் ஈடுபட்டுத் தோன்றுவதைவிட ஈடுபடாமல் அமைதியாக ஒதுங்கி இருப்பதே நல்லது.

தோன்றின் புகழொடு தோன்றுக அ.·.திலார்
தோன்றலின் தோன்றாமை நன்று. (236)

பிற

மிகச் சிறந்த பேச்சாளராக ஆவதற்குத் திருவள்ளுவரின், 'அவை அஞ்சாமைக்' கருத்துக்கள் பயன் தருகின்றன. நிறைமதி போன்று நாளும் வளர்வது உயர் நட்பு. தீய நட்பானது தேய்பிறை போன்றது. நட்பு, நட்பு ஆராய்தல், பழைமை (பழகிய உறவு), தீ நட்பு (தீய நட்பு), கூடா நட்பு (உதவாத நட்பு) போன்ற குறட்பாக்கள் தரும் சிந்தனைகளை மனதில் கொண்டு வாழ்தல் நலம் பயக்கும்.

'ஆசைக்கு ஓர் அளவே இல்லை' என்பர். அவற்றிற்கு முற்றுப்புள்ளி வைத்தால் நிரந்தரமான இன்பம் வாய்க்கும் என்பதை 'அவாஅறுத்தல்' வழி அறியமுடிகிறது.

'நோயற்ற வாழ்வே குறைவற்ற செல்வம்' என்பதற்கேற்ப 'மருந்து' அதிகாரத்தில் எழுதப்பெற்றுள்ள குறட்பாக்கள் விளங்குகின்றன.

'நிலையாமையை' உணர்ந்து 'மெய்யுணர்தலை'த் தெளிந்து நலமுடன் வாழ்தல் நன்றாம்.

முடிவுரை

இவ்வாறான திருக்குறள் உணர்த்தும் பன்முக ஆளுமைச் சிந்தனைகளை மனதில் ஏற்றுப் போற்றி வாழ்தல் சிறப்பானதாம்.

துணை நின்ற நூல்

திருக்குறள், கழக வெளியீடு, திருத்திய பதிப்பு, 1992.

ஆத்துமாவுக்கு ஆண்பெண் என்ற பால் வேறுபாடு கிடையாது"
ன்று விவேகனந்தர் கூறினும் ஆணும் பெண்ணும் சரியாதியான
ர்த்தநாரீஸ்வர சங்கல்ப்பங்கள் இருப்பினும் பிறப்பில் ஒன்று
னும் உறுப்பிலும் வளர்ப்பிலும் வேறுபட்டு திறக்காது என்று
தரிந்தும் தனது இருப்பைக் காட்டிக்கொள்ள, தட்டப்படும்
தவாகவும் எட்டாக்கனியாகவுமே சமத்துவமும் சுதந்திரமும்
ருக்கும்போது பெண்ணிய சிந்தனைகளும் கருத்தரங்குகளும்
ாராட்டங்களும் அவசியமானவையாகவும் இன்றியமையா
வையாகவும் மாறுகின்றன. நாகரீக நாடகங்களோ கல்வி என்ற
ர்வாழ்க்கியோ, பணம், பதவி முதலிய கண்துடைப்புகளோ
தத்துவ சன்மானம் தரப்போவதில்லை. பிறப்பில் தொடங்கி
ழர்ப்பில் வளர்ந்து இறப்பு வரை தொடரும் பாரபட்சக்
ண்ணோட்டத்தைப் பண்பென்றும், பண்பாடென்றும்,
ன்பென்றும், அடக்கம் என்றும் பாசமென்றும் தேஞ் தடவி
விட்டாமல் பெண்ணுக்கு ஊட்டும் சதிகார, சமூக
ழக்கங்களை அடிவேரோடு பிடுங்கி எறிய பெண் என்று
ல்கிறாளோ அன்று வரை இந்தச் செயல்பாடுகள் தொடர்ந்து
ானேதான் இருக்கும். அவ்வகையில் ஒரு சிறு சலனத்தை
த்துப் பத்தகமும் ஏற்படுத்தும் என்பதில் ஐயமில்லை.

முனைவர். த. விஜயலட்சுமி.

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பெண்ணியத்தின் பதிய போக்குகள்

பதிப்பாசிரியர்
முனைவர். த. விஜயலட்சுமி
முனைவர். ஹெப்சி ரோஸ்மேரி. அ

தமிழ்த்துறை
கேரளப்பல்கலைக்கழகம்

பாவேந்தரின் பெண்ணியச் சிந்தனைகள்

முனைவர் க. முருகேசன்,
உதவிப் பேராசிரியர் & தமிழ்த்துறை தலைவர்
திருச்சிராப்பள்ளி – 01. (சுயநிதி
தேசியக் கல்லூரி (தன்னாட்சி),

பெண்ணியம் என்பதற்கு ஆங்கிலத்தில் Feminism என்று பெயர். இது Femina என்ற இலத்தீன் மொழிச் சொல்லிலிருந்து உருவானதாகும். Femina என்பதற்கு 'பெண்களின் குணாதிசயங்களைக் கொண்டுள்ள' (Having the Qualities and Female) என்று பொருள். இச்சொல் முதன் முதலில் பெண்க ளின் பாலியல் குணாதிசயங்களைக் குறிப்பிடவே பயன்படுத்தப்பட்டடுள்ளது. பிறகே பெண்களின் உரிமைகளைப் பற்றிப் பேசுவதற்காக எடுத்தாளப்பட்டது. தொடக்கத்தில் பெண்களின் உரிமைப் பிரச்சனைகளையும், அதற்கான போராட்டத்தையும் உணர்த்த பயன்பட்ட 'Womanism' என்ற சொல்லின் இடத்தை 1980களில் 'Feminism' என்ற சொல் பெற்றது.

Feminism என்ற சொல்லிற்கு 1984 ஆம் ஆண்டு வெளிவந்த ஆக்ஸ்போர்டு ஆங்கில அகராதி "பெண்களின் தேவையை நிறை வேற்ற அவர்கள் சார்பாக வாதிடுவது அல்லது போராடுவது" (Advocacy of the claims of women) எனப் பொருள் தருகிறது. இருபதாம் நூற்றாண்டில் இச்சொல் பெருவழக்கில் இருந்தது. தமிழில் பெண்ணியம், பெண்நிலைவாதம், பெண்ணுரிமை ஏற்பு என இச்சொல் வழங்கிவருகிறது.

பெண்ணியத்திற்குத் தொண்டாற்றிய பலருள் பாவேந்தர் குறிப் பிடத்தக்கவர் ஆவார். பாரதிதாசனைப் புரட்சிக் கவிஞராக்கி யது அவரது சூழ்நிலையேயாகும். உருசியா ஒரு புஷ்கினையும், ஆங்கில நாடு ஒரு ஷெல்லியையும்இ பிரான்சு ஒரு ஹீகோவை யும் அமெரிக்கா ஒரு வால்ட் விட்மனையும் கண்டது போல் தமிழகமும் ஒரு பாரதிதாசனைக் கண்டடைந்தது. "மாறுவது இயற்கை" என்பது பாரதிதாசன் ஆத்திசூடி. இருக்கும் நிலை-யை மாற்றிப் புரட்சி மனப்பான்மையை ஏற்படுத்துதல், பிறர்க்கு உழைக்கும் எழுத்தாளர்களின் கடமை என்பது பாரதிதாசன்-

ின் கருத்தாகும். மதங்க ளிலும் பழைய ஆசாரங்களிலும் ஊறிக் கிடந்த மக்களிடையே இவரு டைய பாடல்கள் ஒரு பெரிய மாற்றத்தை உண்டு பண்ணியிருக்கின்றன. அடிமைப்பட்டுக் கிடந்த பெண்ணினத்தின் கல்வி, சமூக மேம்பாடு, சொத்துரிமை. நிர்வாகத்திறன், விருந்தோம்பல், குழந்தை பேணுதல் போன்ற பல தளங்களில் தம் பாட்டுப்புலமையால் பலவற்றைச் சாடி பல நிலைகளில் பெண்ணியம் மேன்மையடைய தம் பங்களிப்பைச் செவ்வனே செய்தவர் பாவேந்தர். அவருடைய பெண்ணி-யச் சிந்தனை களை ஆராய்வதே இக் கட்டுரையின் நோக்கமாகும்.

தமிழர்களின் உயர்ந்த பண்புகளில் விருந்தோம்பலும் ஒன்றாகும். விருந் தோம்பலில் பெண்ணியம் பங்களிப்பை மிகச் சிறப்பாகத் தம் 'குடும்ப விளக்கு' நூலில் சுட்டும் பாவேந்தர்,

"நற்றமிழர் சேர்ந்த புகழ்
ஞாலத்தில் என்னவெனில்
உற்ற விருந்தினரை
உயிரென்று - பெற்றுவத்தல்" (குடும்பவிளக்கு)

பெண்மையை விருந்தோம்பலின் முகமாக அடையாளப்படுத்துகிறார். மேலும்,

"கேட்டும் குறிப்பறிந்தும்
கெஞ்சியும் மிஞ்சுமன்பால்
ஊட்டுதல் வேண்டும் தாய்போல்" (குடும்பவிளக்கு)

பரிமாற வேண்டும் என்ற கருத்தையும் குறிப்பறிந்து பரிமாறும் உத்தி யையும் பெண்மை பெற்றிருத்தல் நலமென்கிறார்.

காதல் வாழ்வின் பரிசான குழந்தைப் பிறப்பாலும் ஒரு புரட்சி கூறுகிறார். குழந்தைகளின் எண்ணிக்கை அதிகமாகிப் போகாமல் இருக்க குழந்தை வேண்டாதபோது,

"சேர்கை ஒழித்துக் கருத்தடையேனும் செய்க"

என்கிறார் பாவேந்தர்.
மக்கள் தொகைப் பெருக்கமும் இல்லாமைக்கு ஒரு காரணமாவதை உணர்ந்து கருத்தடை பற்றி தைரியமாகப் பேசுகிறார். பெண் கல்வியை வலியுறுத்தும் பாவேந்தர்,

பெண்கட்குக் கல்வி வேண்டும்

குடித்தனம் பேணுதற்கே!
பெண்கட்குக் கல்வி வேண்டும்
மக்களைப் பேணுதற்கே!
பெண்கட்குக் கல்வி வேண்டும்
உலகினைப் பேணுதற்கே!
பெண்கட்குக் கல்வி வேண்டும்
கல்வியைப் பேணுதற்கே! (குடும்பவிளக்கு)

என்று பிள்ளைகளுக்குத் தானே வாத்திச்சியான தங்கம் கல்வியின் பயனை அனுபவிக்கும் தங்கத்தின் வாயிலாகவே பெண்கல்வியின் அவசியத்தை நமக்கு விளங்க வைக்கிறார். மேலும்,

"கல்வியில்லாப் பெண்கள் களர் நிலம்
இங்குப் புட்கள் விளைந்திடலாம்
நல்ல புதல்வர்கள் விளைவதில்லை."

கல்வி பயிலாப் பெண்களை களர் நிலமென்று கூறுவதோடு அவர்களின் வயிற்றில் வளரும் குழந்தைகள் நல்ல புதல்வராக வாழும் தகுதியில்லாதவர்களென்றும் சாடுகிறார்.

சாதாரணக்கல்வி மட்டுமின்றி வானூர்தி செய்தல் வரையிலான அறிவியல் கல்வி அனைத்தும் ஆணுக்கும் பெண்ணிற்கும் சமமாக வேண்டும் என்கிறார்.

'குடும்பவிளக்கு' நூலில் தங்கத்தின் பாத்திரத்தின் வழி சமைப்பது பெண்களின் தொழில் என்னும் நிலையை மாற்ற வேண்டும். ஆடவரும் சமையற்கலையை அறிய வேண்டும் என்ற கூற்று இன்று நூற்றுக்கு நூறு மெய்யாகியுள்ளது.

பெண்குலத்தின் உயர்வை நோக்கிய பாவேந்தர்,

"கலையிற் பெண்ணே இலகு, பல்
கலையிற் பெண்ணே இலகு" (குடும்பவிளக்கு)

என்று நகைமுத்தாள் பாத்திரத்தின் வழி நிறுவுகிறார்.

புரட்சிகரமான கருத்தை மாவரசர் வழியாகக் கூறும் பாவேந்தர்.

"பெண்ணுக்குச் சொத்துரிமை
இல்லை என்பார் நான் தருவேன்" (குடும்பவிளக்கு)

இன்றைக்குச் சட்டமாக்கப்பட்டுள்ள பெண்களின் சொத்துரிமையை அன்றே பேசிய பெருமையைத் தனதாக்கிக் கொள்கிறார்.

திருமணத்தில் பெண்களின் கருத்தறியவும் தம்நூலில் வித்திடுகிறார். நகைமுத்து,

வேடப்பினை நான் விரும்பியதுண்டு
வாழ்வின் துணையென்று சூழ்ந்தேன். (குடும்பவிளக்கு)

என்கிறாள்.

திருமணம் என்பது மணமக்களின் கருத்தறியாது ஏற்பாடு செய்வதாக இல்லாமல் இருவரின் உள்ளம் உள்ளம் ஒன்றிய திருமணமாக இருக்க வேண்டும் என்பதையும் விளக்கிக் கூறுகிறார்.

பெரியவர் ஒருவரிடத்தில் மலர்க்குழல் ஆர்வத்தின் காரணமாக என் பெண்ணிற்கு என்ன குழந்தை பிறக்கும்? என்று கேட்கிறாள். பெரியவர் உடனே சிரித்துக் கொண்டே 'பெண்ணே பிறந்தால் எங்கே போடுவீர்' என்கிறார் அதற்கு மலர்க்குழலாள்,

"மண்ணில் பட்டால் மாசுபடும் என்று என்
கண்ணில் வைத்தே காப்பேன் ஐயா" (குடும்பவிளக்கு)

என்கிறாள். ஆணையும் அப்படியே ஐயா என்கிறாள். ஆண் பிள்ளை உயர்வென்றும் பெண் பிள்ளை தாழ்வென்றும் எண்ணுகிற நிலையைக் களைய நினைத்தவர் பாவேந்தர் அவர்கள். அக்கருத்தையே தம் பாத்திரத்தின் வழி வலியுறுத்திக் கூறுகிறார்.

பெண் கல்வி சுற்று இல்லறம் நடத்தினால் மருத்துவமே தேவையில்லை என்றும் மூப்பும் நோயும் வராது என்றும் கூறுகிறார். பெண்கள் அரசியலில் ஈடுபட்டு அரசாண்டால் நாட்டில் போரும் குழப்பமும் விளையாது என்கிறார். அதற்கும் தம் பாத்திரப்படைப்பான மணிமொழியார் கூற்று வழி கூறவும் விளைகிறார்.

பகையில்லை, அங்கின்மையில்லை, பிணி இல்லை
பழியில்லை, என் துணைவி அரசாண்டதாலே (குடும்பவிளக்கு)

பெண்கள் அரசாளும் உலகும் செழிக்கும் என்று உறுதியளிக்கிறார்.

காதலியின் சிரிப்பும் காவலனும் காலில் விழும் நிலை ஏற்படும் என்பதை,

"பட்டாளச் சக்கரவர்த்தி பார்த்தாலும் உன்சிரிப்புக்
கட்டாணி முத்துக்குக் காலில்விழ மாட்டாரோ? (புரட்சிக்கவி)

பெண்ணின் சிரிப்புக்கு அரசனும் அடிபணியும் நிலையிமை எடுத்தியம்புகிறார்.

கைம்பெண்ணின் உள்ளக் கிடக்கையும் காதலன் அவள் மீது கொண்ட உடல் கவர்ச்சியற்ற உள்ளக் காதலை,

"கூடத்திலே மனப் பாடத்திலே - விழி
.....
உள்ளம் பறித்தது நாள் என்பதும் - என்றன்
உயிர் பறித்தது நீ என்பதும்"
(காதல் குற்றவாளிகள்)

பாடல் வழி விளக்குகிறார். இக்கருத்தை,

"இருநோக்கு இவள் உண்கண்ணுளது ஒருநோக்கு
நோய்நோக்கொன்று அந்நோய் மருந்து"
(திருக்குறள் 1091)

காதலியின் கடைவிழிப் பார்வை ஒன்று நோயை உண்டாக்கவும் மற்றொரு பார்வை அந்நோய்க்கு மருந்தாகும் வள்ளுவர் கருத்தோடு ஒத்த கருத்துடையவராக பாவேந்தர் மிளிர்கிறார்.

கைம்பெண் காதலை அங்கீகரிப்பதோடு அக்காதலும் உன்னதமுடைய தன்மையுடையது என்பதை,

"கோரிக்கை அற்றுக் கிடக்குதண்ணே இங்கு
வேரிற் பழுத்த பலா"
(கைம்மைப்பழி)

கோரிக்கையற்ற கைம்பெண் காதலை சமூகக் கண் கொண்டு சாடுகிறார். இவருடைய புதுமைக் கருத்தால் இன்று சமூகத்தில் கைம்பெண்மணம் வெகுவாக அங்கிகரிப்படுதல் பாவேந்தரின் பெண்ணியச் சிந்தனைக்குக் கிடைத்த வெற்றியாகும்.

நிறைவாக.....

பாவேந்தர் மொழிவரையறையால் தமிழ்க்கவிஞர். ஆனால் கருத்தளவையால், கவிதைச் சுவையளவையால், மொழி எல்லையையும் கடந்த உலகக் கவிஞர்களுள் ஒருவராகத் திகழ்கிறார். அவர் தம் பாடல்களில் பெண்ணியம் சார்ந்து பேசிய சொத்துரிமை, குடும்பக் கட்டுப்பாடு, கல்வி, வேலைவாய்ப்பு, காதல், மணமுறிவு போன்ற பல நிகழ்வுகள் பின்னாளில் சட்டமாக்கப்பட்டன. இவையனைத்தும் பாவேந்தரது பாடல்களின் வழி நம் பெண்ணியத்திற்குக் கிடைத்த பெரும் பேறாகும் என்றால் அது மிகையல்ல.

சிறுதெய்வ வழிபாடு – தோற்றமும், வளர்ச்சியும்

கோ.முனுசாமி,
முழுநேர முனைவர் பட்ட ஆய்வாளர்,
எம்.ஜி.ஆர்., கலை மற்றும்
அறிவியல் கல்லூரி, ஒசூர்.

முன்னுரை:

சிறுதெய்வ வழிபாடு நாட்டுப்புற பண்பாட்டியலின் ஒரு பெரும்பிரிவாகும். "சிறுதெய்வம" என்ற சொல்லின் தோற்றத்தைப் பற்றி முதன்முதலாக "சென்று நாம் சிறுதெய்வம் சேரோம் அல்லோம்" என்று அப்பர் தேவாரத்தில் அடிகள் பயின்று வருகிறது. அதுபோல சமூகத்தின் அடித்தளத்து மக்கள் வழிபடும் கடவுளரைச் சிறுதெய்வங்கள் எனவும், மேல்தளத்து மக்கள் வழிபடும் தெய்வங்களைப் பெருந்தெய்வம் எனவும் குறிப்பிடும் வழக்கம் அக்காலத்திலேயே இருந்திருப்பதாகத் தெரிகிறது.

சிறு தெய்வ வழிபாட்டில் பெண் தெய்வங்களே அதிக முக்கியத்துவம் பெறுகின்றன. பெண் தெய்வங்கள் காப்பதிலும், அழிப்பதிலும் மிகவும் சக்தி வாய்ந்தவனாகவும், சிறப்பாக பேசப்படுவதும் ஆகும். ஆகவே, சிறுதெய்வ வழிபாடு பற்றி இக்கட்டுரையில் காண்போம்.

தொடக்கநிலை வழிபாடு:

பழங்காலத்தில் இயற்கை மனிதனுக்கு ஒரு புதிராகத் தோற்றமளித்தது. இருள், சூரியன், இடி, மின்னல், மழை, ஆகிய இயற்கைப் பொருள்கள் மனிதனுக்கு புதிராகவும், அச்சத்தையும் ஊட்டின ஆயினும் மனிதன் இயற்கையே தனக்கு உணவை அளிக்கிறது என்று அறிந்து கொண்டான். அதனால் இயற்கையின் பேராற்றலை வணங்கத் தலைப்பட்டான். அதன் மூலம் தன்னைவிட உயர்ந்த சக்தியை வணங்கவும், அவற்றிடமிருந்து தங்களை காத்துக்கொள்ள பலியும் கொடுக்க முற்பட்டான்.

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தமிழ் விடுகதைகளின் இயற்கையும் உபிரினங்களும்

முனைவர் க. முருகேசன்
உதவிப்பேராசிரியர், தமிழாய்வுத்துறை, தேசியக் கல்லூரி (தன்னாட்சி),
திருச்சிராப்பள்ளி-620 001, தமிழ்நாடு, இந்தியா

விடுகதை என்பது விடுவிக்கப்பட வேண்டியது. மறைபொருளினின்றும் விடுவிக்கப்பட வேண்டிய கதையே விடுகதையாகும். விடுகதை என்னும் சொல்லுக்குப் புதிர்மைப் பண்புடையது என்றும் விடுவிக்கப்பட வேண்டிய பொருள் கதையாக அமைந்துள்ளது என்றும் தெளிவாகும். வினா எழுப்பும் வகையாகவும் விடையிறுக்கும் தன்மையாகவும் விடுகதைகள் உள்ளன. தமிழிலே புதிர்ப்பண்பை அடிப்படையாகக் கொண்டு எதிர்மறையிலேயே பெரும்பாலும் விடுகதைகள் தோன்றுகின்றன. அறிவூட்டுவதும் சிந்தனையைத் தூண்டுவதும் விடுகதையின் குறிக்கோளாகும். கதைக்கு ஆதாரமாகவும் செய்யுளுக்கு உயிராகவும் பொழுது போக்குச் சாதனமாகவும் உள்ளது. பெரியோர்களும் சிறியோர்களும் நல்ல உறவுநிலை வளர்க்க உதவுகிறது. விடுகதையின் அடிப்படைப் பண்பு உருவகமாகும். விடுகதைகளுக்கும் உருவகங்களுக்குமுள்ள தொடர்பினை முதல் முதலில் உணர்த்தியவர் இரேக்ப் பேறிஞர் அரிஸ்டாட்டில் ஆவார்.

"விடுகதையால் கூறுபவனின் உளப்பான்மை வளர்கிறது; ஆர்வத்தினின்றும் விடுதலை அடைக்கிறது. சிறியோர்க்கும் பெரியோர்க்கும் தொடர்பை ஏற்படுத்துகிறது என அறிஞர் ஜேம்ஸ் கூறுகிறார். 'கனவு மனிதனது அடிமன உணர்வுகளுக்கு வெளியீடுதருவது போல விடுகதைகளும் வெளியீட்டிற்கு உதவி வருகின்றன' என கார்லோக குறிப்பிடுகிறார். சில விடுகதைகள் கதையைப் போலவே விரிவாக இருக்கும். சின்னசின்ன விடுகதைகட்குப் புதிர் என்ற பெயரே மிகவும் பொருந்தும். கதைபோல் வருவனவற்றை விடுகதை என்று குறிப்பிடுவதுதான் பொருத்தமாக இருக்கும் என நாட்டுப்புறவியல் அறிஞர் இ.வா. ஜெகந்நாதன் குறிப்பிடுகிறார்.

விடுகதையின் வரலாறு தொல்காப்பியத்தில் தொடங்கி இன்று வரை தொடர்கிறது. இனிமேலும் தொடரும். விடுகதைக்கு உரையாசிரியர்கள் விளக்கம் தந்துள்ளனர். இடைக்காலப் புலவர்கள் விடுகதைகளைச் செய்யுள் வடிவில் பாடினர். இருபதாம் நூற்றாண்டில் விடுகதைகளைத் தொகுக்க ஆரம்பித்தனர். தற்பொழுது விடுகளைப் பற்றிய ஆய்வு பல நிலைகளில் மேம்பட்டு செம்மையாக நடைபெற்று வருகிறது.

விடுகதை மூலம் வட்டார் வழக்குகள் மக்களின் பழக்க வழக்கங்கள், நம்பிக்கைகள், கால மாற்றத்தின் சாயல்கள் முதலியவற்றை அறிய முடியும் மனித வாழ்வில் காணப்படும் கருப்பொருட்கள் அனைத்தையும் விளக்குகின்றன. மக்களிடையே காணும் ஒழுக்கம், அவர்கள் வழிபடும் தெய்வம், தொழில் முறைகள், சாதி வேறுபாடுகள் போன்ற பலவும் விடுகதையின் பின்னணியில் உணர்த்தப்படுகின்றன. மனித இனத்தின் சிந்தனைத் நிறனை அளவிட்டு அறிவிக்கும் கருவியாக நிற்பதோடு மட்டுமின்றி மக்களின் செயல்முறைகள், பழக்க வழக்கங்கள், நம்பிக்கைகள், சிந்தனைப்போக்கு கொள்கைகள், கோட்பாடு ஆகியவற்றை வெளிப்படுத்துவதன் மூலம் வரலாற்றுச் சான்றாகவும் விடுகதைகள் விளங்குகின்றன என டாக்டர் ச.வே. சுப்ரமணியம் கூறுவது குறிப்பிடத்தக்கதாகும். மனித சமுதாயத்திற்குத் தேவையான விழுமியக்குயிங்கள் பலவற்றை அறிய உதவும் வரலாற்றுப் பெட்டகமாகத் திகழும் மாண்பு விடுகதைக்கு உண்டு. அத்தகைய விடுதையின்

வழி அறியலாகும் மானுட விழுமியக் கருத்துகளை வெளிப்படுத்துவதே இவ்வாய்வின் கருதுகோளாகும்.

விடுகதையின் தொன்மை:

தொல்காப்பியர் யாப்பு முறையைக் குறிப்பிடும்போது விடுகதைப் பற்றியும் குறிப்பிடுகிறார்.

பாட்டு, உரை, நூலே வாய்மொழி, பிசியே,
அங்கதம், முதுசொல்லோடு அவ்வேழ் நிலத்தும்
வன்புகழ் மூவர் தண்பொழில் வரைப்பின்
நாற்பெயர் எல்லை அகத்தவர் வழங்கும்
யாப்பின் வழியது என்மனார் புலவர்
(தொல் - பொருளதிகாரம், செய்யுளியல் - 79)

மேலும், அடிவரையறையில்லாத ஆறுவகை யாப்பினையும் தொல்காப்பியர் உரைக்கிறார்.

நூலி லான உரையி னான
நெடியோடு புணர்ந்த பிசியி னான
ஏது நுதலிய முதுமொழி யான
மறைமொழி லெந்த மந்திரத் தான
கூற்றிடை வைத்த குறிப்பி னான
(தொல்-பொருளதிகாரம், செய்யுளியல் - 165)

இவற்றில் 'பிசி' என்பது விடுகதையைக் குறிப்பதாகும்.

ஒப்பொடு புணர்ந்த உவமத் தானும்
தோன்றுவது மிளர்ந்த துணிவி னானும்
என்றிரு வகைத்தே பிசிவகை நிலையே

என்று பிசிக்கு விளக்கமும் தருகிறார். ஊவமையாக அமைவதும் தெளிவுபட வருவதும் என விடுகதை இருவகையில் அமையும் என்கிறார் தொல்காப்பியர். விடுகதையை விளக்கியவர் தொல்காப்பியரே ஆவார்.

தொல்காப்பிய உரையாசிரியரான இளம்பூரணர் உவமை விடுகதைக்குச் சான்றைத் தருகிறார்.

அச்சப் போல பூப்பூக்கும்
அமலேயென்னக் காய்காய்க்கும்

பேராசிரியர் மூன்று விடுகதைகளும் தந்து அவற்றிற்கு விடையும் தருகிறார். விடுகதையைத் தொகுத்தவர்களில் பேராசிரியரே முதலாமவராவர்.

பிறை கல்வி மலை நடக்கும் (யானை)

முத்துப்போல் பூத்து
முதிரில் கனாவண்ண
நெஞ்சத்தோர் குருதி
நிறங்கொண்டு வித்துநிர்த்து (கடுகு)

நீராடான் பார்ப்பான்
நிறஞ் செய்யான் நீராடின்
ஊராடு நீரே காக்கை (நெருப்பு)

தமிழில் பிசி, நொடி, புதிர், விடுகதை என்றும் வழங்கப்படுகிறது. விடுகதை என்ற சொல்லாட்சி பண்டைத் தமிழ் இலக்கணங்களில் காணப்படவில்லை. இச்சொல்லாட்சி எக்காலத்துப் புகுந்தது என்பதற்குச் சான்றில்லை. 'பிசி' என்ற சொல்லே பின்னாளில் பிதிர் என்றாகிப் பின் 'புதிர்' என்றாகியிருக்க வேண்டும். கிராம மக்கள் அன்றாடப் பேச்சில் என்ன புதிர் போடுகிறாய் எனக் கூறுவதைக் கேட்கிறோம். மிகக் குறுகிய காலத்தில் கூறத்தக்கவாறு சுருங்கிய அமைப்புடையது என்ற கருத்தில் 'நொடி' என்ற சொல் கையாளப்பட்டிருக்க வேண்டும். திருச்சி, சேலம், தருமபுரி, திருஷ்ணகிரி மாவட்டங்களில் 'வெடி' என்ற சொல்லைப் பயன்படுத்துகின்றனர். திருநெல்வேலி மாவட்டத்தில் விடுகதையை அழிப்பாங்கதை என்கிறார்கள். ஒருவர் விடுகதைபோட, மற்றவர் அதனை விடுவித்து விட்டால் அவர் அதனை அழித்துவிட்டார் என்று பொருளாகும். எனவே 'அழிப்பாங்கதை' என்கிறார்கள். கதையில் ஏற்படும் சிக்கலை, புதிரை அவிழ்த்தல் என்ற பொருளில் அழிப்பாங்கதை என மாறிற்று எனக் கூறுவருமுளர். பேச வழக்கில் விடுகதை என்றும் இலக்கிய வழக்கில் 'புதிர்' என்றும் கொள்ளலாம்.

உலகில் பல்வேறு மொழிகளில் வழங்கும் சொல்லாட்சி பற்றி இங்குக் காண்போம். அவ்வம் மொழிகளில் வழங்கும் சொல்லாட்சி அதன் தன்மையை விளக்குவதுபோல் காணப்படுகின்றது.

தமிழ் : பிசி, நொடி, புதிர், விடுகதை, வெடிபோடுதல், அழிப்பாங்கதை

தெலுங்கு : விடிகத்தா, பொதபுக்கலு

கன்னடம் : ஒடகதா, விடிகதா

மலையாளம்: விடிகதா, கடன்கதா

வடமொழி : பிரம்மோத்யம், பிரஸ்னம், கூதம், பிரவக்லிகா, விவாத, சமஸ்யா, குடா

மராத்தி : உகானா

குஜராத்தி : வரத்

இராஜஸ்தான்: பஹேலி

அஸ்ஸாமி : சதுர்

English : Riddle

Germen : Ratsel

Greek : Enigma

African : Alo

பல்வேறு சொல்லாட்சிகள் பிறமொழிகளில் விடுகதைக்கு கையாளப்படுகிறது.

விடுகதையின் வகைகள்:

விடுகதைகளை ரோஜர் டி.. ஆப்ரஹாம் அவர்களும், ஆலன் டாண்டிஸ் அவர்களும் ஒன்பது வகையாகப் பகுக்கின்றனர். மரியா லீச் (Maria Leach) அவர்கள் இரண்டு வகையாகப் பகுக்கின்றார். பிரிட்டானியா கலைக்களஞ்சியம் இரண்டு வகையாகப் பகுக்கிறது. டாக்டர் ச.வே சுப்பிரமணியம் அவர்கள் பண்பு கருதி விடுகதைகளை இரண்டாகவும் பயன் அடிப்படையில் நான்காகவும் வகைப்படுத்துகிறார். ஆறு இராமநாதன் அவர்கள் விடுபுதிர், விடுகணக்கு முதலியவற்றை நாட்டுப்புற விடுகதையிலும் இருசொல் அலங்காரம், முச்சொல் அலங்காரம் முதலியவற்றை இலக்கிய விடுகதையிலும் அடக்குவார். விடுகதையைப் பாட்டு விடுகதை என்றும் உரைநடை விடுகதை என்றும் பிரிக்கிறார். விடுபுதிரை வினாவிடுபுதிர், உண்மைவிடு புதிர் என இரண்டாகப் பகுத்து வினாவிடுபுதிரின் கீழ் மெய்யறிவு வினாவையும், நகைப்பு வினாவையும் உண்மை விடுபுதிரை எதிர்மறை, எதிர்மறை அல்லாதது என இரண்டாகப் பகுக்கின்றார்.

விடுகதைச் சூழல்:

புதிரையும் நெடிவினாவையும் உலகிற்கு வழங்கிய பெருமை இலத்தின் மொழிக்கு உண்டு. ஜெர்மனியில் ஒரு காலத்தில் மணப்பெண்மை விடுகதை மூலம் தேர்ந்தெடுத்ததாக அறிகிறோம். தொடக்க காலத்தில் விநோதப் புதிர்களை அடிப்படையாகக் கொண்ட விடுகதைகள் காலப்போக்கில் சமயம் சார்ந்த விடுகதைகளாக மாறின. பைபிளிலும் குர்ரானிலும் விடுகதைகள் காணப்படுகின்றன. திருமணச் சடங்கு, இறப்பு, பலி, விழாக்காலங்களில் விடுகதைகள் போடப்பட்டன. ஆப்பிரிக்க விடுகதைகள் தான் சிறந்தது எனக் கூறுகின்றனர் ஆய்வாளர்கள். விடுகதைகள் இரவில் தான் போடப்படுகின்றன. இதற்குக் காரணம் புரியவில்லை. தமிழ்நாட்டில் சிறுவர்கள் ஒன்று சேர்ந்துவிட்டால் விடுகதை போடும் வழக்கத்தைச் சில கிராமங்களில் இன்றும் காணலாம்.

விடுகதையின் கருப்பொருட்கள்:

மக்கள் வாழ்க்கையின் பல்வேறு பகுதிகளையும் பிரதிபலிப்பனவான விடுகதைகள் வாழ்க்கையின் பயன்படுபொருள்களான கருப்பொருள்பாவற்றையும் விளக்கும் வகையினவாக அமைகின்றன.

இயற்கைப் பொருட்கள்:

இயற்கையின் எழில் கொஞ்சும், அழகில் மனிதன் மனமகிழ்வோடு வாழ்கின்ற நெறியினை வகுத்துக்கொண்டான். அந்நெறியில் பஞ்சபூதங்கள் என்றழைக்கப்படும் நிலம், நீர், காற்று, வானம், நெருப்பு ஆகிய இயற்கைக் கொடையின் போக்குக்கு ஏற்ப தம் வாழ்க்கை முறையினை அமைத்துக் கொண்டான். அதற்குச் சான்றாக

அவர்களுக்குப் பொழுதுபோக்கும் அம்சமாகவும், அறிவை விரிவு செய்யும் ஊடகமாகவும் விடுகதைகள் அமைந்தது எனலாம்.

மோதிய பின் மின்னும்
மின்னிய பின் வெடிக்கும்-(மின்னல் இடி.)

உலகுக் கெல்லாம் ஒரே துப்பட்டி
- (வானம்)

அள்ளலாம் இள்ள முடியாது - (தண்ணீர்)

ஏழை படுக்கும் பஞ்சணையை
எடுத்துச் சுருட்ட ஆளில்லை - (பூமி)

எஸ். எஸ். கன்றுக்குட்டி
இங்கிலீஷ் கன்றுக்குட்டி
தண்ணீர் பட்டால் செத்துப்போகும் -
(நெருப்பு)

இவ்விடுகதைகள் அனைத்தும் இயற்கையோடு மனிதனைப் பின்னிப் பிணைக்கும் நிகழ்வை செவ்வனே செய்கிறது.

விலங்குகள்:

மனிதன் தனக்கான வேலையைச் செய்யவதற்குச் சில விலங்குகளைப் பழக்கி அவற்றினால் நிறைந்த பயனையும் பொருளாதார உயர்வையும் அடைந்தான். அத்நிலையில் விடுகதைகளில் விலங்குகளைப் பாடுபொருளாக்க அவன் முயற்சித்ததோடு அவற்றில் வெற்றியும் பெற்றிருக்கின்றான். உதாரணத்திற்குத் தண்ணீர் இல்லாத நிலமான பாலைவனத்தில் வாழும் விலங்கான ஒட்டகத்தைக் குறிப்பிடும் போது 'தண்ணீர் இல்லாத தடாகத்தில் தாவிப்பாயுது ஒரு கப்பல்' என ஒட்டகத்தை கப்பலுக்கு உவமையாக்கு கின்றான். நன்றிமறவாமைக்கு நற்சான்றாய் விளங்கும் நாய்குறித்த விடுகதையில்,

உண்டதை நினைப்பான்
உதையை மறப்பான்
உயிரையும் கொடுப்பான் - (நாய்)

அறிவியல் யுகம் எவ்வளவோ வளர்ந்திருந்தாலும் இன்றைக்கும் சில குற்ற வழக்குகளில் காவல் துறைக்கு உற்ற நண்பனாக இருந்து துப்பறியவும் இயற்கைப் பேரிடர்களில் இடர்பட்டு கட்டட இடிபாடுகளில் சிக்கி உயிருக்குப் போராடும் மனிதர்களைத் தம் நுகர்தல் திறனால் காப்பாற்றும் பணியைத் திறம்பட செய்கிறது.

ஒற்றைக் காலி நாராயணன்
ஓடையிலே மீன் பிடிக்கிறான் - (கொக்கு)

இந்த விடுகதை தனக்கு இரையாக ஏற்ற மீன் வரும் வரை காத்திருக்கும் கொக்கின் முயற்சியும் அந்த முயற்சியை அடையும் வரை அயராது உழைக்கும் இயல்பும் மனிதர்களுக்கானப் பாடமாகவே கருதப்படுகிறது. இவ்விடுகதையோடு தொடர்புடைய கருத்தாக வரும்.

வினைவலியும் தன்வலியும் மாற்றான்
வலியும்
துணைவலியும் தூக்கிச் செயல்
(குறள்: 471)

ஒரு செயலைச் செய்கின்றவிடத்து அந்தச் செயலின் வலியும் செயலைச் செய்யும் தன்னுடைய வலியும் செயலுக்குத் துணையாகும் பிறவலிமையினையும் சீர்தூக்கி நமக்குச் சாதமாக நிலையிருந்தால் மட்டும் அச்செயலைச் செய்யச் சொல்லும் வள்ளுவரின் வரியும் அவ்விடுகதையோடு ஒத்தக் கருத்துடையதாகக் கருத இடமுண்டு சங்க இலக்கியத்திலோ,

யாரும் இல்லை தானே கள்வன்
தானது பொய்ப்பின் யானெவன் செய்கோ
நினைத்தா என்ன சிறுபகங் கால
ஒழுகுநீர் ஆரல் பார்க்கும்
குருகும் உண்டு தான் மனந்த ஞான்றே
(குறுந்தொகை)

இவ்விடுகதையோடு தொடர்புபடுத்த சான்றுகள் பல நம் இலக்கியத்தில் உண்டு. பண்டைய மறத்தமிழரின் வாழ்வியலோடு நெருங்கியத் தொடர்புடையது மாடாகும். இதனைத் தேவநேயப் பாவாணர் அம்மா என்ற சொல் முக்காரமிடும் 'ம்ம்மா' என்று சொல்லுக்கு இலக்கணம் பகர்கிறார். ஆயர்குலத் தோன்றலாகிய பெண்கள் தான் வளர்க்கும் காளையை அடக்காத வீரனை இம்மையில்

மட்டுமல்லாது மறுமையிலும் மணக்க நினைக்க மாட்டார்கள். அதனை,

'கொல்லேற்று கோடஞ்சுவானை மறுமையும்
புல்லாலே ஆய மகள்' (கலித்தொகை)

கடவுளாக வணங்கப்படும் மாட்டினங்களில் 'ஆ' என்பது பொதுப்பெயராகவும் பின் பசுவிற்குரிய சிறப்புப் பெயராகவும் வழங்கலாயிற்று.

பசுவினைக் குறித்த விடுகதையில்,

பந்தக்கால் நாலு, பவளப்பல் பத்து
வெள்ளிதடி இரண்டு, வெள்ளித்தடி இரண்டு
வெஞ்சாமரம் ஒன்று - (பசு)

இவ்விடுகதையில் மாட்டில் நான்கு கால்களும் பத்தக்காலாகவும், அதன் பற்கள் பத்தும் பவளிதிற்கு ஒப்பாகவும் அதனுடைய வால் வெஞ்சாமரமாகவும் உவமிக்கப்பட்டு விடுகதையாக்கப்பட்டுள்ளது.

பறவைகள்:

இந்தியப் பெருங்காடுகளை அழியாமல் பாதுகாக்கும் பணியினைத் திறம்படவே செய்திடும் உயிர்க்கூட்டம் பறவையினங்களாகும். அப்பறவையினத்தைக் குறித்த விடுகதையில்,

தங்க உடற்காரி தரமான ஆட்டக்காரி
மேகம் இருண்டு வந்தால் மோகம் கொண்டு
ஆடுவான் அங்கம் முழுவதும் தங்க நிறம் (மயில்)

இந்திய தேசியப் பறவையாகப் போற்றப்படும் மயிலினத்தின் இயல்பை அழகியலோடு பதிவு செய்யும் விடுகதையாகும். இவ்விடுகதையில் தங்க நிற உடம்பு, தரமான ஆட்டம், மேகம் இருண்டு வந்தால் மோகம் கொண்டு ஆடும் தங்க நிறத் தாரகையாகச் சுட்டப்படுகிறது மயில்.

கடையெழு வள்ளல்களில் ஒருவனான பேகன் மயிலுக்குப் போர்வை ஈந்த பெருமைக்குரியவன். ஆனால், இந்த விடுகதையில் மயிலின் இயல்பு சுட்டப்படுகிறது. மேகம் இருண்டால் மோகம் கொண்டு ஆடிடும் இயல்புடைய மயிலுக்குப் போர்வை ஈந்து கொடை மடம் பட்ட வையாவிக் கோப்பெரும் பேகனின் கொடைக்குச் சான்றாய் இவ்விடுகதை திகழ்கிறது.

பகலில் துயிலுவான்
இரவில் அலறுவான் (ஆந்தை)

பகலில் துயில் கொள்ளும் இயல்பும் இரவில் முழு வேகத்தோடு இயங்கிடும் ஆற்றலும் உடையது ஆந்தையாகும். இவ்விடுகதைக் கருத்தியலோடு தொடர்புடைய வள்ளுவரும்.

பகல்வெல்லும் கூகையைக் காக்கை
இகல்வெல்லும்
வேந்தர்க்கு வேண்டும் பொழுது (குறள்: 481)

பகலில் தன்னை விட வலிமையான கூகையை வெல்லும் ஆற்றலைப் பெற்றிடும் இயல்பு காகத்திற்கு உண்டு. இக்குறளில் கூகை மாற்றரசர்களாகவும் காகம் காலமறிந்து செயல்படும் வேந்தனுக்கு ஒப்பாகவும் பகைமையை வெல்ல காலமறிதல் வேந்தனுக்கு முக்கியமான அரணாகவும் குறிக்கப்படுகிறது.

தாவரங்கள்:

தமிழர்களின் இல்ல நிகழ்வுகளில் (மங்கல நிகழ்வு) முக்கிய இடம் தாவரங்களுக்கு உண்டு. அதிலும் குறிப்பாக வாழைக்கு முக்கியத்துவம் மிகுதி. அத்தகைய வாழையைக் குறிக்கும் விடுகதையில்.

மரமுண்டு அடுப்பெரிக்க விறகுமாகாது
சீப்புண்டு தலைகோதி வார முடியாது
பூவுண்டு கொண்டையிலே முடிக்க முடியாது (வாழை)

மரத்தின் அனைத்து பாகங்களும் பயன்படும் இயல்புடையது வாழையாகும். இவ்விடுகதையில் வாழைமரம் அடுப்பெரிக்க விறகாக பயன்படாமையும், வாழைச்சீப்புண்டு அதை வைத்து தலைவார முடியாமையும், அவ்வாழைப்பூ

கொண்டையிலே சூட முடியாத நிலையில் அமைத்துள்ளதையும் எதிர்மறைப்பொருளாக இவ்விடுகதை பேசினாலும் காளமேகப் புலவருக்கோ அழகியலோடு பெண்ணை வாழையோடு ஒப்பிடுவதற்கு ஊக்கியாக இவ்விடுகதை அமைந்ததெனலாம்.

தலைவிரிக்கும் பூச் சூடும் தண்டை அணியும்
இலைவிரிந்து நல்லுணவை ஈயும்-
விலைமதிக்க
ஒன்னா பரம்பரையை உற்பத்தி செய்திடும்
நற்பெண்ணாகும் வாழை மரம்
(காளமேகப் புலவரின் தனிப்பாடல்)

பெண்ணுக்குரிய எல்லா இயல்புகளையும் பெற்றிடும் சிறப்பு வாழைக்கு உண்டு என்பதை இப்பாடல் நமக்குப் புலப்படுத்துகிறது. மேலும், வாழைமரம் குறித்த விடுகதைகள் பலவாகும்.

அம்மிக் குழவிபோல் பூ இருக்கும்
அரிவாள் பிடிபோல் காய் காய்க்கும் (வாழை)

எனவும்,

அடி மலர்ந்து நுனி மலராத பூப்பூக்கும் (வாழை)

வாழைப்பூவில் அடியில் பூக்கும் பூக்கள் வாழைக் காய்களாகவும் மாறும் இயல்புடையது. மலர்கள் எல்லாம் நுனியில் பூக்கும் இயல்புடையது ஆனால் வாழை நுனியில் மலராத இயல்பில் அமைக்கப்பட்டுள்ளதை இயற்கையின் படைப்பதிசயமாகவே கருதமுடிகிறது. சுற்பகத் தருவாய் தன் அனைத்து பாகங்களையும் மக்களுக்குப் பயன்படும் விதத்தில் கொண்டுள்ள தென்னை ஒரு புல் வகையைச் சார்ந்ததென்கிறார் தொல்காப்பியர்.

புறக்காழெனவே புல்லென மொழிப
புல்லும் மரனும் ஒரறி வினவே
பிறவும் உளவே அக்கிளைப் பிறப்பே
(தொல்காப்பியர்)

புல், மரம் என்ற இருவகையும் ஒரறிவுயிராகும். புல் என்பது புறத்தில் வயிரமுடையன - பனை, தெங்கு, கமுகு, மூங்கில் போல்வன மரம் என்பது அகத்தில் வயிரமுடையன - புளி, மா, பலா, வேம்பு முதலியனவாகும்.

அடி பெருந்தேன் குந்தாணியானேன்
தலைவிரித்தேன் சடைச்சியானேன்
(தென்னை)

எனவும்,

ஓகோ ராசா உயர்ந்த ராசா
தோள்மேல் என்ன தொண்ணூறு முடிச்சு
(தென்னை)

என்று தென்னையில் இயல்பினை இவ்விடுகதை எடுத்தியம்புகிறது. அதோடு பிள்ளையைப் பெற்றால் கண்ணீர் தென்னை வச்ச இளநீர் என்ற பழமொழியில் மனித உறவு நிலைச் சிக்கலைத் தென்னை வழி அறியமுடிகிறது.

பழந்தமிழரின் நீர் மேலாண்மைக்கும் அந்நீர் ஆவியாதலை தடுத்து நீர்மட்டம் கீழே செல்லாமல் தம் வேரினால் நீர் மட்டத்தை மேலே விடாமல் பார்த்துக் கொள்ள இயற்கையின் கொடையாக விளக்குகின்ற மரம் தான் பனையாகும். அவற்றை விளக்கும் விடுகதையிலோ,

ஆழக்குழி வெட்டி
அதிலே ஒரு முட்டையிட்டு
அண்ணாந்து பார்த்தால்
தொண்ணூறு முட்டை (பனை)

என நுங்கின் குழையழகைப் பதிவு செய்கிறது. மேலும்,

அவிழ்ந்த தலை முடியாத சிறுக்கி
அவள் பெற்ற பிள்ளைகளுக்கு
வகைவகையாய் பெயராம் (பனை)

பனையின் உருவ அமைப்பும் அதற்கு ஒவ்வொரு நிலையிலும் வழங்கப்படும் பெயரினையும் அறிய முடிகிறது.

நிறைவாக:

விடுகதை அறிவுக்கு உரைகல்லாகவும் சிந்தனையைத் தெளிவாக்கும் ஊக்கியாகவும் இரண்டுபொருள் பட மொழியும் நிலைடைச் செய்யுளுக்கு உயிராக விளங்கும் பாங்குடையது. பொழுதுபோக்கிற்குத் துணையாக விளங்கிடும் காரணியாகவும், திகழ்வது விடுகதையாகும். நாகரிக முன்னேற்றம். அறிவியல் வளர்ச்சி உரைநடையின் வளர்ச்சிப் போக்கு விடுகதையின் வளர்ச்சிக்கு முட்டிக் கட்டையாய்த் திகழ்ந்தாலும் என்றென்னும் மக்களுடைய பண்பாட்டில் பழக்க வழக்கத்தில் நம்பிக்கை மற்றும் சடங்குகளில் நாம் கடைபிடித்த வாழ்வியலை நமக்குப் படம் பிடித்துக் காட்டும் காலக் கண்ணாடியாய்த் திகழ்வது விடுகதையாகும். அவற்றையெல்லாம் சேகரித்து வகைப்படுத்தும் போது விடுகதை என்றென்னும் அழியா வரம் பெறுவதோடு வாழ்வியல் விழுமியங்களைத் தாங்கிப் பிடிக்கும் அறிவுக் கருவூலமாகத் திகழும் என்ற கருத்தைத் துணியலாம்.

பார்வை நூல்கள்:

1. அகத்தியலிங்கம், ச. நாட்டுப்புறவியல்.
2. இராமநாதன், ஆறு, காதலர் விடுகதைகள்.
3. சக்திவேல், சு நாட்டுப்புறவியல் ஆய்வு.
4. சக்திவேல், சு சண்முகம்பிள்ளை, ஆ. விடுகதைத்தொகுப்பு
5. வரதராசன், மு. திருக்குறள் தெளிவுரை.

திருவாசகத்தில் மெய்பாட்டுக் கூறுகள்

சி.க. ரேணுகா
முனைவர் பட்ட ஆய்வாளர், ஜமால் முகம்மது கல்லூரி (தன்னாட்சி),
திருச்சிராப்பள்ளி-620 020, தமிழ்நாடு, இந்தியா

மெய்ப்பாடு என்பதற்கு பொருட்பாடு, வெளிப்பாடு, புலப்பாடு என்று பொருள். உண்மை அல்லது உயிர் தங்கியிருக்கும் கூடு என்;பது மெய்யாகும். பஞ்சபூதங்களால் ஆக்கப்பட்டது. அதாவது மெய் என்பது உடல். பாடு என்பது மெய்ப்பாடு. மெய்ப்பாடு என்பதற்கு பாடுதல், பாடப்படும் பொருள் விளக்கம், உடலிலிருந்து வெளிப்படும் வெளிப்பாடுகள் என்று பல பொருள் உண்டு. மெய்யில் படுவது மெய்ப்பாடு. உள்ளத்து உணர்ச்சிகள் உடலில் தோன்றுவது மெய்ப்பாடு. தொல்காப்பியர் பொருளதிகாரத்தில் மெய்ப்பாட்டியல் என்பதை வகுத்து, உடலில் தோன்றும் மெய்ப்பாடுகளை 8 வகையாகக் கூறி, அது தோன்றும் நிலைக்களன்களை நான்கு நான்காகப் பிரித்துக் காட்டியுள்ளார். அது மட்டுமின்றி பிற மெய்பாடுகளாக 32 மெய்ப்பாடுகளை இவற்றிலிருந்து வேறுபடுத்தி காட்டியுள்ளார். உரையாசிரியர்கள் மெய்ப்பாடுகளை கூறி மெய்களவைகள் என்கின்றனர்.

பசி, தாகம், பாலுணர்வு, உறங்குதல், விழித்தல் முதலானவை மனித உயிர்களுக்கு உண்டான பொதுவான அகத்தெழுச்சி உணர்வுகளாகும். சுவை, ஒளி, ஊறு, ஓசை, நாற்றம் ஆகிய ஐந்தும் புறத்தெழுச்சி உணர்ச்சிகளாகும். தொல்காப்பியம் காட்டும் மெய்ப்பாட்டு உணர்ச்சிகள் மனம் உந்திய உடல் வெளிப்பாடாகும்.

திருவள்ளுவர் மெய்பாடுகளை விளக்கும் வகையில் மெய்யுணர்தல் என்ற ஒரு அதிகாரத்தைப் படைத்திருக்கிறார். ஒரு பொருள் எந்தத் தன்மையாகத் தோன்றினாலும் அத்தோற்றத்தை மட்டும் கண்டு மயங்காமல், அப்பொருளின் உண்மையான இயல்பை அறிவதே மெய்யுணர்வாகும்.

எப்பொருள் எத்தன்மைத் தாயினும்
அப்பொருள்
மெய்ப்பொருள் காண்பது அறிவு
(குறள் 355)

பிறப்பென்னும் பேதமை நீங்கிச்
சிறப்பென்னும்
செம்பொருள் காண்பது அறிவு
(குறள் 358)

பிறவாமை என்னும் செவ்வியப் பொருளைக் காண்பதே மெய்யுணர்தல் என்கிறார் திருவள்ளுவர்.

பண்ணைத் தோன்றிய என்நான்கு பொருளும்
கண்ணிய புறனே நானான்கு என்ப
(மெய்ப். 1)

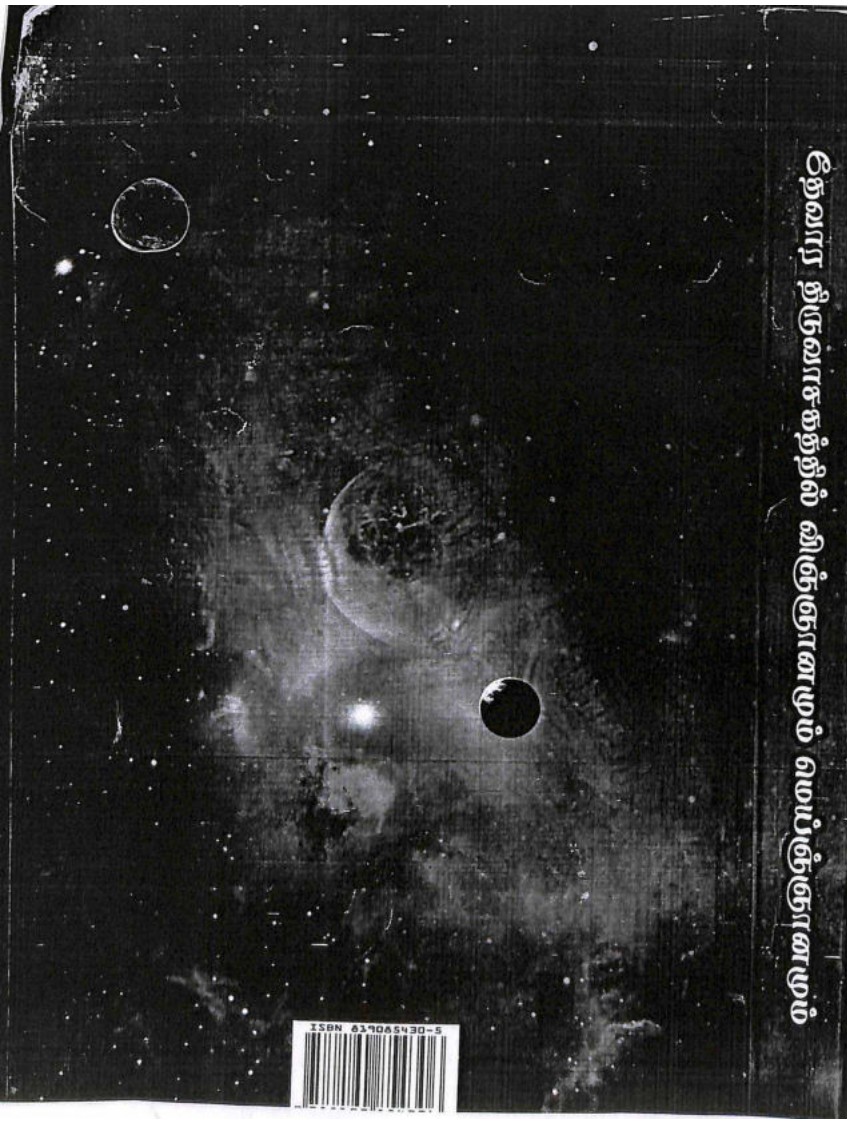
இச்சூத்திரம் மெய்பாடுகளின் வகைகளைக் குறிப்பிடுகிறது. 32 மெய்பாடுகளைச் சுருக்கி,

நாலிரண்டாகும் பாலு மாருண்டே
(மெய்ப். 2)

என கூறுகிறார்.

மெய்ப்பாடுகளின் வைப்பு முறை

இன்ப விளையாட்டின் நிகழ்ச்சிகளோடு தொடர்புடைய விளையாட்டுப் பொருளாவது நகை என்பதால் அதனை முதற்கண் வைத்தார். நகைக்கு மறுதலையாவது அழுகை ஆதலின் அதனை அதன்பின் வைத்தார். அழுகையும், இளிவரலோடு ஒக்கும் ஆதலால் அழுகையின் பின் இளிவரலை வைத்தார். தாம் இளிவந்த



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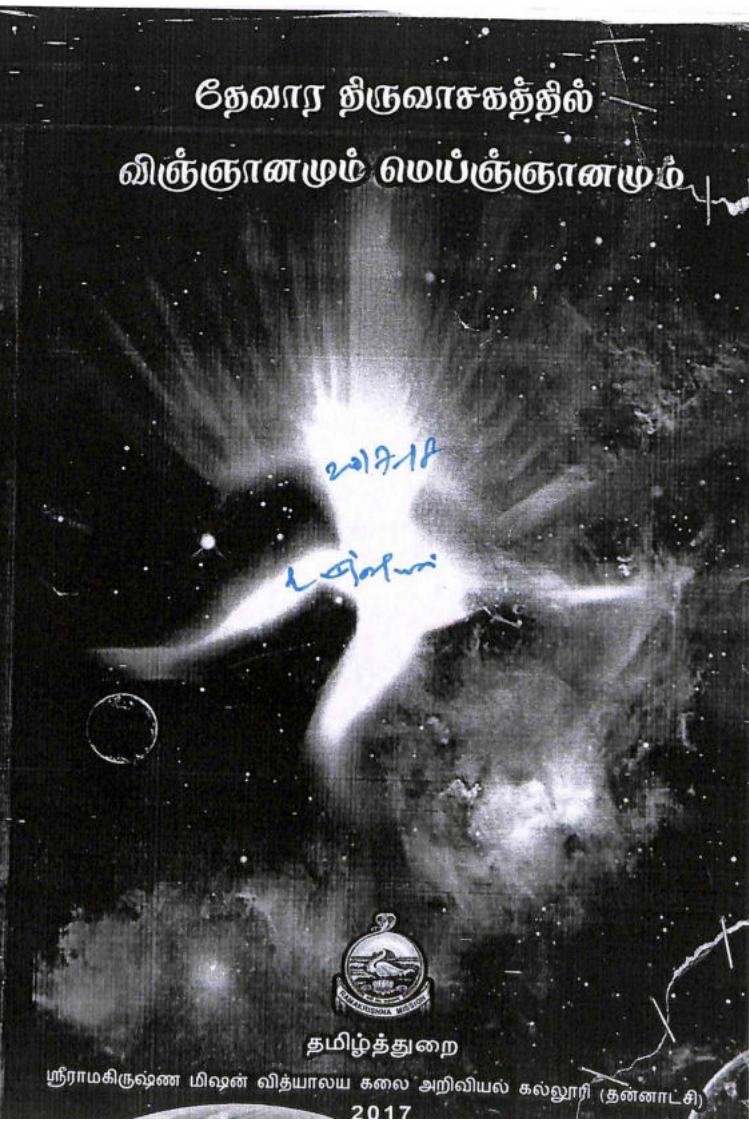
தேவார திருவாசகத்தில் விஞ்ஞானமும் மெய்ஞ்ஞானமும்



தேவார திருவாசகத்தில் விஞ்ஞானமும் மெய்ஞ்ஞானமும்

தமிழ்த்துறை
ஸ்ரீராமகிருஷ்ண மிஷன் வித்யாலய கலை அறிவியல் கல்லூரி (தன்னாட்சி)
2017

திருவாசகத்தில் ஒருமைப்பாடு

பத்தி ஒருமை நிலையை அடைய வேண்டும் என்றால் முழுமுதற் பொருளாகிய சிவபெருமானையே வணங்குதல் வேண்டும். சிவபெருமான் ஒருவனே இறைவன் என்பதை மாணிக்கவாசகர்

"தென்னாடுடைய சிவனே போற்றி
எந்நாட்டவர்க்கும் இறைவா போற்றி"

என்னும் அடிகளில் தெளிவுபடுத்துகிறார். எந்நாட்டவர்க்கும் இறைவன் ஒருவனேதான். அவனைத் தென்னாடு சிவனே எனப் போற்றுகிறார். சைவப் பெருமக்கள் சிவபெருமானைத் தவிர வேறு எந்தத் தெய்வங்களையும் வணங்கக்கூடாதென்பது மாணிக்கவாசகர் கொள்கையாகும் என்பதை,

"கொள்ளேன் புரந்தான் மாலயன் வாழ்வு குடிகெடினும்...
உள்ளேன் பிறதெய்வம் உன்னையல்லா தெங்கள்
உத்தமனே"

பாடல் வழி உணர்த்துகிறார். பிறதெய்வங்களை நினைக்கமாட்டேன் என்று சொன்னதோடு, ஏனைத் தெய்வங்கள் வீடுபேற்றைத் தரமுடியாதவை ஆகையால் அவை பொய்த் தெய்வங்கள்

"அத்தேவர் தேவரவர் தேவரென் றிங்ஙன்
பொய்த்தேவு பேசிப் புலம்புகின்ற பூதலத்தே"

என்று கூறுகிறார்.

முடிவுரை:

மனித வாழ்வினை நெறிப்படுத்த தோன்றிய சமயங்கள் மனதை ஒருமைப்படுத்தி நிலைமையை விடுத்து பரம்பொருளை அடைவதில் மாணிக்கவாசகரின் திருவாசகம் முதன்மையாக வெளிப்படுத்துகிறது. மெய்ஞ்ஞானங்களை உணர்ந்து மனிதன் ஒழுக்கமுடன் வாழ திருமுறைகள் முக்கிய அங்கம் வகிக்கிறது.

ॐ ॐ ॐ

திருநாவுக்கரசர் தேவாரத்தில் விஞ்ஞானமும் மெய்ஞ்ஞானமும்

முனைவர் கூ. முத்தையன்*

முன்னுரை

விஞ்ஞானம் மெய்ஞ்ஞானம் ஆகிய இரண்டும் இரண்டுகண்கள். மீக்களுடைய புறவாழ்விற்கு விஞ்ஞானம் இன்றியமையாத ஒன்று. அக வாழ்விற்கும் மன அமைதிக்கும் மெய்ஞ்ஞானம் அவசியமாகிறது.

விஞ்ஞானத்தை ஒதுக்கிவிட்டு மெய்ஞ்ஞானம் பெறவிரும்பும் ஞானிகள் இருந்ததாகத் தெரியவில்லை.

மிகப்பெரிய மெய்ஞ்ஞானிகள் கூட விஞ்ஞானக் கருத்துக்களை அவ்வப்போது கூறிக்கொண்டுதான் இருந்தனர். அதேபோல் மெய்ஞ்ஞானம் இல்லாத விஞ்ஞானமும் முழுநிறைவைத் தருவதில்லை. ஆகவே மனிதகுல மேம்பாட்டிற்கு இந்த இரண்டுமே உறுதுணையாக இருக்கின்றன. சைவசமய குரவராக விளங்கும் திருநாவுக்கரசு நாயனார் அனுபவம் மிக்க ஞானத்தமிழ்ப் பாடியவர். அவருடைய பாடல்களில் விஞ்ஞான, மெய்ஞ்ஞானச் செய்திகளும் இடம் பெற்றுள்ளன. அவற்றில் ஒரு சிலவற்றை இவண் காண்போம்.

விஞ்ஞானம்

'விஞ்ஞானம்' என்ற சொல்லுக்கு மேலான ஞானம் என்று பொருள். மனிதனுக்கு உள்ள ஆறாவது அறிவைக் கொண்டு வாழ்வாதாரங்களைப் பூர்த்திச் செய்கின்ற அறிவிற்கு விஞ்ஞானம் என்று பெயர்.

பல்லாயிரக்கணக்கான ஆண்டுகட்கு முன்பே நமது இந்தியாவில் விஞ்ஞானரீதியான கருத்துக்கள் இடம்பெற்றிருந்தன. உதாரணமாக இருக்கு வேதத்தில் அண்டங்களின் அமைப்பு பஞ்ச பூதங்களைப்பற்றிய செய்திகள்' முதலான கருத்துக்கள் இடம் பெற்றுள்ளமை யாவரும் அறிந்ததே. கந்தபுராணத்தில் அண்டகோசப்படலம் என்று ஒரு பகுதி

*உதவிப் பேராசிரியர், தமிழாய்வுத்துறை
. தேசியக்கல்லூரி (தன்னாட்சி), திருச்சிராப்பள்ளி.

அமைந்துள்ளது. அதில் ஏராளமான அண்டங்கள் பற்றி எடுத்துரைக்கப்படுகின்றது. சோதிட நூல்களில் கிரகங்கள் நவக்கிரங்கள் பற்றிய புள்ளிவிபரங்கள் நம்மை மெய்சிலிர்க்க வைக்கிறது. ஓராண்டிற்குப் பிறகு நிகழும் அமாவாசை, கிரகணம் பற்றிய வானிலை மாறுதல்களைத் துல்லியமாகக் கணக்கிட்டு உரைக்கும் சோதிட நூல்கள் நமது பாரத நாட்டிற்கே உரிய சொத்தாகும்.

தேவாரத்தில் விஞ்ஞானம்

'தேவாரம்' என்றாலே அது திருநாவுக்கரசர் தேவாரத்தையே குறிக்கும். திருநாவுக்கரசர் கி.பி. ஏழாம் நூற்றாண்டில் வாழ்ந்தவர்.

தமிழ்மொழியில் ஓசை ஒலி என்னும் சொற்கள் வழக்கத்தில் இருந்து வருகின்றன. இரண்டு சொற்களும் பெரும்பான்மை சப்தத்தை உணர்த்துகின்றன. தமிழ் இலக்கியங்களிலும் பெரும்பான்மை ஒரேபொருளில் தான் கையாளப்படுகின்றன. ஆனால் இவ்விரண்டுக்கும் நுட்பமான வேறுபாடு இருப்பதை நாவுக்கரசர் விஞ்ஞானரீதியில் எடுத்துரைக்கின்றார். இன்றைய விஞ்ஞானம் ஒலியலை பற்றியும் அதிர்வெண் பற்றியும் எதிரொலி பற்றியும் ஆய்வு செய்கிறது. ஒலியலை மூலம் கடலின் ஆழம் கணக்கிடப்படுகிறது.

வேற்றுக்கிரகங்களில் இருந்து பேசுகிற வார்த்தைகளைக் கேட்கும் அறிவியலும் வளர்ந்து வருகிறது. வேற்று நாட்டிலிருந்து பேசுகிற வார்த்தையைக் கேட்க ஒரு கருவி (செல்.போன்) கண்டறியப்பட்டது போல வேற்றுக் கிரகங்களில் பேசும் வார்த்தைகளைக் கேட்பதற்கு ஒரு கருவி கண்டுபிடிக்க வாய்ப்பு இருக்கின்றது. இப்படி ஒலியின் ஆராய்ச்சி மிக நீண்டு போகக்கூடிய ஒன்று. இங்கே ஓசை என்பது ஒரு வரையறை செய்யப்பட்ட, இயற்கையிலிருந்து சற்று ஒழுங்கு செய்யப்பட்ட சப்தத்தைக் குறிக்கும். மனிதன் பேசுகின்ற பேச்சுக்களை ஒலி என்று கூறுகின்றோம். ஒலி எழுப்புதல் என்று கூறுவதிலிருந்து இது சற்றுச் செயற்கையானது என்பதைப் புரிந்து கொள்ளலாம். அருவி கடல் முதலான இயற்கையில் எழுகின்ற நாதங்கள் கட்டுப்பாடற்றவை. முறையாக இருந்தாலும் கேட்பதற்கு இனிமையாக இருப்பினும் அவை ஓசை ஆகும். பாத்திரங்கள் விழுவது, பொருள் உடைவது போன்றவையும் ஓசையில் அடங்கும். அவற்றுக்குப் பொருள் கிடையாது. ஆனால் மனிதன் எழுப்பும் சப்தத்திற்கும் பறவைகள் மிருகங்களின் சப்தத்திற்கும் பொருள் இருக்கின்றன. எனவே பொருள் உள்ள

சப்தத்திற்கு ஒலி என்று பெயர். இந்த நுட்பமான வேறுபாட்டைப் புலப்படுவதற்காக நாவுக்கரசர் பெருமான்

"ஓசை ஒலி எலாம் ஆனாய் நீயே"

என்றுபாடுகின்றார்.

நீராவி

'கிரீன்நாக்' என்னும் ஊரில் பிறந்த 'ஜேம்ஸ்வாட்' என்பவர் முதன் முதலில 1736 நீராவி எந்திரத்தைக் கண்டுப்பிடித்தார். ஜேம்ஸ்வாட் கண்டு பிடித்த நீராவி எந்திரம் ரெயில் போக்குவரத்தின் வரலாற்றையே மாற்றியது. பல தொழில்களுக்கு உகந்தவாறு நீராவி எந்திரங்கள் உருவாக்கப்பட்டன. மனிதன் மற்றும் விலங்குகளின் வலிமையையே நம்பியிருந்த தொழில் உலகம் ஜேம்ஸ் வாட்டின் நீராவி எந்திரம் வந்த பிறகு நெசவாலை முதல் உற்பத்தி ஆலைகள் வரை இயந்திரமயமாயின. இந்த நீராவியின் ஆற்றல் மிகவும் மனித குலத்திற்குத் தேவையானது என்பதை உணர்ந்த திருநாவுக்கரசர் 1300 ஆண்டுகளுக்கு முன்பே 'நீராவி' என்ற சொல்லைப் பயன்படுத்தி இருக்கின்றார்.

"நீராவி யான நிழலே போற்றி"

என்பது அவர்தம் கூற்று.

மின்விளக்கு

மேலும் திருநாவுக்கரசர் திருவாட்போக்கி என்னும் தலத்தில் **"ஏற்றுமின்விளக்கை இருள்நீக்கவே"** என்று பாடுகின்றார். இதில் விஞ்ஞானம் மெய்ஞ்ஞானம் இரண்டும் விரவி இருக்கிறது. ஏற்றுமின் விளக்கை என்பதற்கு விளக்கினை ஏற்றுங்கள் என்று பொருளாகும். இதேவாக்கியம் இன்றைய உலகிற்குப் பொருத்தமாக 'ஏற்றும்மின்விளக்கை' என்று சிலேடையாகப் பொருள் தருகின்ற தமிழ்வளத்தை ஆழ்ந்து சிந்திக்க வேண்டும். இப்போது 'மின்விளக்கு' என்ற சொல்லே பயன்பாட்டில் உள்ளமை காண்க.

மேற்கண்டவாறு பலப்பல இடங்களில் விஞ்ஞானக் கருத்துக்களை அப்பர்பெருமான் வெளியிட்டு மகிழ்கின்றார்.

மெய்ஞ்ஞானம்

"மெய்ஞ்ஞானமாகி மிளிர்கின்ற மெய்ச்சுடரே"

என்பது திருவாசகம்.

மெய்ஞ்ஞானம் என்பது உண்மை ஞானம் என்ற பொருளைத் தருகிறது. மெய் என்ற சொல் வருகின்ற இடமெல்லாம் ஆன்மா சம்பந்தமாகவே அமைந்திருக்கின்றது. ஆன்மா உறுதியான இன்பத்தை அடைதற்கு வேண்டிய இறையியல் சார்ந்த ஞானமே மெய்ஞ்ஞானம் ஆகும். இதனைச் சேக்கிழார்பெருமான் 'உணர்வறிய மெய்ஞ்ஞானம்' என்று அடைமொழி கொடுத்துப் பாடுகின்றார்.

"உவமையிலாக் கலை ஞானம்
உணர் வறிய மெய்ஞ்ஞானம்"

ஆகவே மெய்ஞ்ஞானம் எளிதில் உணரத்தக்கதன்று.

ஆண்டவன் பால் ஆறாத அன்பு மிக்க ஞானிகளுக்கே மெய்ஞ்ஞானம் சிறிது புலனாகும். இறைவனைப் பற்றிய அறிவுபதிஞானம் என்றும் உயிர்களைப் பற்றிய அறிவு பசுஞானம் என்றும் உலகத்தைப்பற்றிய அறிவுபாசஞானம் என்றும் கூறப்படும். விஞ்ஞானம் என்றே உலக அறிவு மெய்ஞ்ஞானத்தின் ஒரு பகுதியாகிய பாசஞானமே ஆகும். எனவே மெய்ஞ்ஞானத்திற்குள் எல்லாம் அடக்கமாகும்.

இறைவனைக் காண்பதும், அறிவதும், அடைவதும் பதிஞானத்தின் கூறுகளாகும். இறை இயல்புகளைப்பற்றி திருக்குறுந்தொகையில் நயம்பட எடுத்துரைக்கின்றார்.

"விறகில் தீயினன் பாலில்படு நெய்போல்
மறைய நின்றுளன் மாமணி சோதியான்
உறவுகோல்நட்டு உணர்வுக் கயிற்றினால்
முறுக வாங்கிக் கடைய முன்னிற்குமே"

இறைவன் பாலில் நெய் போல எங்கும் இருக்கின்றான். மறைந்திருக்கின்றான் என்பன போன்ற உண்மைகள் இப்பாடலில் இடம் பெறுகின்றன.

மேற்கண்டவாறு மனிதவாழ்வுக்குத் தேவையான விஞ்ஞான, மெய்ஞ்ஞானக் கருத்துக்களும் நாவுக்கரசர் தேவாரத்தில் இடம்பெற்றுள்ளன.

ॐ ॐ ॐ

தேவாரத்தில் சிவபெருமானின் வேக வடிவங்கள்

முனைவர் சு. சதீஷ்குமார்*

முன்னுரை

தனது சிறப்பியல்பாகிய சொரூப நிலையில் தனக்கென ஓர் உருவும் பெயரும் தொழிலும் இல்லாத இறைவன் உலகை நோக்கித் தடத்த நிலையில் உயிர்களின் பொருட்டுப் பற்பல உருவும் பெயரும் தொழிலும் உடையவனாகிறான். உயிர்கள் படிமுறையால் தன்னை உணர்ந்து ஓதல் வேண்டும் எனும் பெருங்கருணையினால் தூலம், சூக்குமம், அதிசூக்குமம் ஆகிய மூவகைத் திருமேனிகளைக் கொள்வான். அவை முறையே உருவம், அருவுருவம், அருவம் என்று அழைக்கப்பெறும். உருவத் திருமேனி சகளம் என்றும், அருவத் திருமேனி நிட்களம் என்றும், அருவுருவத் திருமேனி சகளநிட்களம் என்றும் கூறப்படும். இம்மூன்றனுள் உருவத் திருமேனி என்பது கண்ணுக்குப் புலப்படக்கூடியது. கை, கால், முகம் முதலிய உறுப்புகளுடன் விளங்குவது. உருவத் திருமேனியைப் போக வடிவம், யோக வடிவம், வேக வடிவம் என மூன்றாகப் பிரித்து சைவ நூல்கள் உரைக்கின்றன. தேனினும் இனிய பாக்களாக அமைந்த தேவாரத்தில் இடம்பெற்றுள்ள இறைவனின் வேக வடிவங்களை எடுத்துரைக்கும் வகையில் இக்கட்டுரை அமைகின்றது.

வேக வடிவம்

உயிர்களுக்கு உண்டாகும் துன்பத்தைப் போக்க இறைவன் கொள்ளும் வடிவம் வேக வடிவமாகும். காமதகனர், காலாந்தகர், சலந்தரவதர், திரிபுராந்தகர், கஜாரி, வீரபத்திரர், ஆகியன சிவபெருமானின் வேக வடிவங்களாகும்.

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கொங்குநாடு கலை அறிவியல் கல்லூரி, கோயம்புத்தூர்.

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செம்மொழித் தமிழ்

(பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்)

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15 பகுதி-1 Part -1

தமிழ் இலக்கியங்களில் நீதி

முனைவர் ப.சுமதி
உதவிப்பேராசிரியர், தமிழ்த்துறை, தேசியக் கல்லூரி (தன்னாட்சி),
திருச்சிராப்பள்ளி - 620 001, தமிழ்நாடு, இந்தியா

முன்னுரை

அறம், நீதி என்ற சொற்கள் ஒருபொருள் பயப்பனபோல் தோன்றுகின்றன, நுணுகி ஆராய்ந்தால் அறம் என்பது தரும சாத்திரங்களில் கூறப்பெறும் உண்மை என்பதும், நீதி என்பது நீதி சாத்திரங்களில் நுவலப்பெறும் உண்மை என்பதும் தெளிவாகும். நீதி சாத்திரங்களில் நுவலப்பெறும் உண்மைகள் காலத்திற்குக் காலம் மாறக் கூடியவை. நீதி சாத்திரங்களை அவ்வப்போது தேவைக்கும் நடைமுறைக்கும் ஏற்ப, சட்ட மன்றங்களில் இயற்றப்பெறும் சட்டங்களுக்கும் ஒப்புமை காட்டலாம். மக்களின் நலன்கருதி சட்டங்களும் இயற்றப்படுகின்றன. பண்டையத் தமிழ்நாட்டில் அருந்தமிழ் மக்கள் ஐந்தினை மருவி வாழ்ந்து வந்தனர். பெரும் பான்மையோர்க்குப் பயிர்த் தொழிலே வாழ்க்கையை நடத்துவதற்கேற்ற வழித்தொழிலாக அமைந்திருந்தது. இவ்வாறு அமைதியாக வாழ்ந்து வந்தாலும் அவர்கள் பல்வேறு இடையூறுகளைச் சந்திக்க நேர்ந்தது. அத்தகைய இடையூறுகளை நீக்கத் தலைவனை தேர்ந்தெடுத்தனர். இலக்கியங்களின் வழி தலைவனின் 'நீதி' நெறியானது பொதுமக்களின் வாழ்க்கை நிலையினை மேம்படுத்தியுள்ளதை எடுத்துக் கூறுவதாக இக்கட்டுரை அமைகிறது.

அரசனின் செங்கோன்மை

மக்கள் தங்கள் வாழ்க்கையில் ஏற்படும் இடையூற்றினைக் காக்க உடலாற்றல், அறிவாற்றல், காத்தற்பண்பு முதலியவற்றால் மேம்பட்டு நிற்கும் வீர தலைவனை வேண்டினர். இத்தகுதிகள் அமைந்தவன் தான் தமக்குத் தக்க 'காவலன்' ஆவான் என்று துணிந்தனர். தலைவனை 'காவலன்' என்ற சொல் ஒன்றே அவர்தம் கருத்தினை அறிவுறுத்தி நிற்கும் இங்ஙனம் அரசனின் இன்றியமை-யாமையை உணர்ந்த நம் பண்டைய மூதாதையர் மோசிக்கீரனார்.

நெல்லும் உயிரன்றே நீரும் உயிரன்றே
மன்னன் உயிர்த்தே மலர்தலை உலகம்
அதனால், யான் உயிர் என்பது அறிகை
வேன்மிகு தானை வேந்தர்க்குக் கடனே

என்ற புறநானூறு (186) பாடலில் கூறுகிறார். நெற்பயிருக்கு நீர் எப்படி இன்றியமையாததோ அதுபோல உலகில் எல்லாப் பகுதிகளிலும் அரச பரம்பரை தோன்றியிருக்க வேண்டும். உயிரும் உடம்பும் கூடி நின்ற வழி உயிருக்குயிராய் நின்றியக்கும் திருவருள் போல அரசு முறை இன்றியமையாதது ஆகும்.

செங்கோலாட்சி செய்யும் மன்னனை வள்ளுவர் இறைவனோடு வைத்துப் பேசுகின்றார். இதனை

முறைசெய்து காப்பாற்றும் மன்னவன் மக்கட்கு
இறையென்று வைக்கப்படும் (கு.எண்.388)

என்று திருக்குறளில் கூறுகின்றார். அதனைச் செலுத்தும் தானே உலகிற்கு உயிராதலை அறிகின்றான். அரசன் உயிர்தான் நிற்னும் உடம்புக்கு உலிதாகும். அதுபோலவே அரசனும் உலகு புரத்தற்கண் உள்ள துன்பம் அனைத்தையும் தான் ஏற்று அதனைக் காக்கின்றான். இதனை அரசன் தன் கடமையாகவே கொள்கின்றான்.

இழத்தொறூஉம் காதலிக்கும்
சூழிதுபோல் துன்பம்
உழத்தொறூஉம் காதற்று உயிர் (942).

என்று வள்ளுவர் கடறுதலால் உயிரது செயல் நலம் தெளியப்படும். துன்பம் படப்பட உடலோடு வாழும் வாழ்க்கையில் உயிருக்கு ஆசை வளர்க்கின்றது. என்ற உண்மையை இக்குறளின் உவமைத் தெளிவாக்குகின்றது.

மாநிலம் காக்கும் மன்னன் உண்மையான காவலராக இருப்பின் அவன் அறம் காக்கும் அரசனாகின்றான் அதனோடு நீதியும் காக்கப்படுகிறது. என்பது சேக்கிழாரின் கருத்து

மாநிலம் காவலாவான்
மன்னுயிர் காக்கும் கானலத்
தானத னுக்கிடையூறு
தன்னால்தன் பரிசனத்தால்
ஊனமிகு பகைதிறத்தால்
ஆனபயம் கள்வரால் உயிர்த்தம்மால் தீர்த்(து)
அறங்காப்பான் அல்லனோ?

என்று பெரியபுராணத்தில் (திருநகரச் சிறப்பு - 36) கூறப்படுகிறார்.

மனுநீதிச் சோழனைச் சிலப்பதிகாரம்

வாயிற்கடைமாணி நடுநா நடுங்க
ஆவின் கடைமாணி புகுநீர் நெஞ்சுடத்
தான்தன்
அரும்பெறற் புதல்வனை ஆழியில்
மடித்தோன்

என்று அறிமுகப்படுத்துகிறது. இளவரசன் தேரின் மீது உலாப் போக்குங்கால் இளைய ஆன்கன்று ஒன்று தேர்க்கால் இடைப்புகுந்து இறந்து படுகின்றது. அதற்கு அரசன் தன் மகனுக்கு விதித்த தண்டனை இது என்பதை

ஒரு மைந்தன் தன்குலத்துக்(கு)
உள்ளான் என் பதும் உணரான்
தருமன்தன் வழிசெல்கை
கடனென்று கடன் மைந்தன்
மருமம் தன் தேராழி
உற உளர்த்தான் மனுவேந்தன்

என்று சேக்கிழார் காட்டுவர். இதனைப் பழமொழி ஆசிரியர் முன்றுரையினார்

சால மறைந்தோம்பிச்
சான்றவர் கைகரப்பக்
காலை கழிந்த தன்
பின்றையும் - மேலைக்
கறவைக்கன்(று) உளர்ந்தானைத்
தந்தையும் ஊர்ந்தான்
முறைமைக்கு மூப்பு இளமை
இல்

என்று கூறுவர். சில சமயம் அமைச்சர்கள் பழைய நிகழ்ச்சிகளை எடுத்துக்கூறி அடிப்பட்டு வந்தமையால் இது பெருங்குற்றமல்ல என்று கூறுவர். அந்தணர்கள் அல்லது அரச புரோகிதர்கள் பொன்னால் ஆன்கன்று செய்து அவர்களுக்கு அளித்தல் கறவைக் கன்று ஊர்ததால் ஏற்பட்ட பாவம் தொலையும் என்று கூறி அத்தீமையினின்றும் அவரைப் பாதுகாக்க முயல்வர். இவற்றையெல்லாம் கருதாது முறை செய்ய வேண்டும் என்பது கருத்து.

பராங்குச நாயகி (நம்மாழ்வார்) செல்வம் அரசர்களைக் கண்டால் திருமாலைக் கண்டதாகவே சொல்லுவாராம். 'திருவுடை மன்னரைக் கண்டால் திருமாலைக் கண்டேனே என்றும் (திருவாய் 4:4:8) (என்ற பாசுர அடிநோக்குக) விஷ்ணுவின் அம்சமில்லாமல் அரசனாக முடியாது என்பது வைணவ சாத்திர சம்பிரதாயம்.

கோ ஆகி மாநிலம்காத்து நங்கன் முகப்பே
மாஏகிச் செல்கின்ற மன்னவரும்- பூமேவும்
செங்கமல நாபியான் சேவடிக்கே
ஏழ்பிறப்பும்
தண்கமலம் ஏய்ந்தார் தமர்

என்ற பூதத்தாழ்வாரின் பாசுரம் இக்கருத்தினை அரண் செய்கின்றது.

புறநானூற்றுக் காலத்தில் மன்னனை உயிராகவும் மக்களை உடம்பாகவும்

காட்டப்பெற்றது. காரணம் இக்கருத்து அக்காலத்தில் நிலவி வந்ததால், கம்பன் காலத்தில் இக்கருத்து மெல்ல மெல்ல மாறி வந்து மக்கள் உயிராகவும் மன்னன் உடம்பாகவும் மாற்றப்பெற்றிருப்பதால் மக்களாட்சிக்கு வித்திட்டது போன்ற ஒரு புதுக்கருத்தைக்காண முடிகின்றது. தசரத சக்கரவர்த்தி நாட்டைப் பாதுகாத்தல் சிறப்பைப் பற்றிக் கூறி வந்த கம்பர் இராமாயணத்தில் (பாலகாண்டம், அரசியல் - 10).

வயிரவான் பூண்அணி மடங்கல்
மொய்ம்பினான்
உயிரெல்லாம் தன்உயிர் ஒம்ப ஒப்பலால்
செயிர்இலா உலகினில் சென்று நின்று
வாழ்
உயிரெலாம் உறைவதோர் உடம்பும்
ஆயினான்

என்ற பாடல் வரிகளின் மூலம் அரசனின் நீதிப்பண்பினை உணர்த்துகிறார். வேறோரு இடத்தில் வசிட்டன் இராமனுக்கு உறுதிப் பொருளைக் கூறும்போது

வையம் மன்னுயி ராகவும் மன்னுயிர்
உய்யத் தாங்கும் உடலன்ன மன்னன்

என்று அயோத்தியா காண்டம் (மந்தரை சூழ்ச்சி -11) பகுதியில் கூறுவார். இந்த இரண்டு இடங்களிலும் கவிஞன் மாநிலத்தில் வாழும் மக்களை உயிராக்கி விட்டான். மன்னனை அவ்வுயிரைத் தாங்கும் உடலாக்கி விட்டான். மக்களுக்காக மக்களால் 'மக்களாட்சி' என்று அமெரிக்க நாட்டு ஆப்ரஹாம் லிங்கன் உரிமைக்குரல் எழுப்புவதற்கு முன்னரே கம்பநாடன் மக்களே நாட்டின் உயிர்நாடி என்ற குரலை எழுப்பி விட்டான். அம்மக்களாட்சி நாட்டில் அரசாட்சிமுடி, செங்கோல், முரசு, குடை இவை அரசர்க்குச் சிறந்த அடையாளங்களாகும். ஒருபாற் கோடாது செவ்விய கோல் போலிருத்தலின் அரசனால் செய்யப்படும் தன்மை 'செங்கோன்மை' எனப்பட்டது. இன்று உயர்நீதி மன்றங்களில் நீதிபதிகள் தம் அறையிலிருந்து நீதி வழங்கும் இடத்திற்குச் செல்லும் போதும், அறைக்குத் திரும்பும் போதும் வெள்ளியாலான தடித்த கோலொன்றைத் தாங்கிய வண்ணம் ஓர் ஆள் அவர் முன்னே செல்வதைக் காணலாம். இது நீதி வழங்குவதற்கு அடையாளம் இன்று நீதிபதிகள்முன் தாங்கிச் செல்வதுபோல் ஒரு கோல் பண்டையக் காலத்தில் அரசர்கள்முன் தாங்கிச் செல்லும் வழக்கம் இருந்திருத்தல் வேண்டும். இவற்றினை இலக்கியப் பாடல்கள்

அறம் துஞ்சும் செங்கோல் (புறம் -30)

அறமபுரிந் தன்ன செங்கோல் நாட்டம்
(புறம் - 35)

மெலிவில் செங்கோல் நீ புறங்காப்ப
(புறம் - 42)

கோதில் செம்மையில் சான்றோர் பல்கி
(புறம் - 117)

அறவோர் புகழ்ந்த ஆகோலன்
(புறம்- 221)

என்று கோல்பற்றி குறிப்புகளைப் பண்டைய இலக்கியங்களில் காணலாம். 'செங்கோல்' அரசனின் செந்நெறியினை விளக்கிக் கொண்டிருக்கும் சிறந்த அடையாளம் என்பதை அறிய முடிகிறது. செங்கோல் அரசனின் தலைமையால் அறக்கட்டளை மேவி குடிமக்களைக் காக்கிறது என்றும் கூறப்படுகின்றது.

செம்மை சான்ற செங்கோல் உள்ள இடத்து வேந்தன் அல்லலை செய்து காப்பான் என்றும் கருத்தினால் சான்றோர் பல்குவர் என்று சாற்றப்படுகின்றது. அறநெறிய மக்கள் அறத்தின் திண்மை கண்டு புகழ்ந்துரைப்பர் என்று போற்றப்படுகின்றது. அரசின் செல்வ நெறியைக் குலைக்கும் கொடிய பகையைக் கடிவதும் குடிமக்கள் கலகத்தினைத் தவிர்ப்பதும் ஆகிய பிற செங்கோலின்

நீர்வார் கண்ணை எம்முன் வந்தோய்
யாரை யோநீ மடக்கொடி யோய்

என்று வினவுகின்றான். ஊனும் உயிரும் துடிக்கத்தான் வந்த காரணத்தை இன்னும் உய்த்துணராமல் வேந்தன் விளம்பிய வெற்றுபசார மொழிகளைச் செவிமடுத்த வீரகண்ணகி

தேரா மன்னா - செப்புவ துடையேன்

என்று பளிச்சென்று மறுமொழி தந்து பேசுகின்றாள். இந்தப் பேச்சில் சோழநாட்டு அறத்தின் வழி நின்ற நீதி ஆட்சி முறையினைக் கூறுகின்றன.

பாண்டிய மன்னன் ஆராயாது செய்த குற்றத்திற்காக வருந்தி உயிர்துறக்கின்றான். உத்தம நங்கையாகிய பாண்டிமா தேவியும் 'கணவனை இழந்தோர்க்குக் காட்டுவதில்' என்று கூறி மன்னன் இணையடி தொழுது வீழ்கின்றாள். அவள் உயிரும் போய் விடுகிறது. இதனை சிலப்பதிகாரத்தில்

மன்னவன் செல்வழிச் செல்க யான்எனத்
தன்உயிர் கொண்டு அவன் உயிர்தே
டினள்போல்

என்று இளங்கோ அடிகள் பாடிய பாடல் வரிகள் நீதியினை வழி தொடர்ந்து வாழ்ந்த பெண்ணினத்தைப் போற்றுகிறார். சேரன் செங்குட்டுவனின் நீதி உணர்வு பற்றியும் சிலப்பதிகாரத்தில் அறிய முடிகின்றது.

மழைவளங் கரப்பின் வான்பே ரச்சம்
குடிபுர உண்டும் கொடுங் கோல் அஞ்சி
மன்பதை காக்கும் நன்குடிப் பிறத்தல்
துன்பம் அல்லது தொழுதக இல்

என்ற வரிகள் சேர மன்னனின் ஆட்சியில் குடிமக்கள்பால் அவன் கொண்டிருந்த அற உணர்வு நீதி உணர்வு வெறிப்படுகின்றதைக் காண்கின்றோம்.

நீதி வழங்கல்

திருவள்ளுவர் காலத்திலும் அவர் காலத்திற்கு முன்பும் பின்பும் முடியாட்சியே நடைமுறையிலிருந்தது. இந்தக் காலங்களில் நீதி வழங்குவதைச் சில சமயம் அரசனே மேற்கொண்டிருந்தான். இலக்கியப்பாடலான பழமொழியில் கரிகாற் பெருவலித்தான் என்ற சோழ வேந்தன் முதியோர் வேடம் பூண்டும் நரைமுடியுடன் அவைக்கு எழுந்தருளி நீதி வழங்கினான் இதனை

உரைமுடிவு காணான் இளமையோன் என்ற
நரைமூது மக்கள் உவப்ப - நரை முடித்துச்
சொல்லால் முறைசெய்தான் சோழன்
குலவிச்சை
கல்லாமல் பாகம் படும்

என்ற பழமொழிப்பாடலில் கரிகல் பெருவளத்தான் ஆராய்ந்து நீதி கூறிய முறையைத் உணர்த்துகிறது.

புழுப் போன்ற சாதாரண பிராணிகட்கும் முறை உண்டு. சாதாரணமாக ஒரு மனித மூளையின் எடை மூன்று இராத்தல்கள். மனிதனுடைய மூளை எண்ணச் செல்வம் உடையது. நல்லவற்றையும் தீயவற்றையும் சிந்திக்கும் செழிப்புடையது. படித்தவனாக இருந்தால் தன் செயலை நியாயப்படுத்திக் காட்டும் பாங்கு அவனுடையதாக இருப்பதைக் காணலாம். வள்ளுவர் திருக்குறளில்

நுண்ணிய நூற்பல கற்பினும் மற்றுந்தன்
உண்மை அறிவே மிகும் (373)

என்று அறவழியில் நிற்கும் அறிவுத் திறனும் நீதி வழங்கும் முறைப்பற்றிய தெளிவான கருத்து கூறுவதைக் திருக்குறளில் காணமுடிகிறது.

குடிபுறம் காத்தோம்பிக் குற்றம் கடிதல்
வடுஅன்று வேந்தன் தொழில் (549)

என்னும் குறளில் நாட்டின் தலைவனது தலையாயக் கடமை பயிறைக் காப்பாற்றக்

களையைப் பிடுங்கி எறியும் உழவனுடைய தொழில் போன்றது நீதி வழங்கும் முறை என்று கூறுகிறார்.

இறைபெறும் நெறி

செய்யும் திறம் அறிந்து தீமை இல்லாத வழியில் சேர்ந்தப் பொருளை இறையாகப் பெறுதல் அரசனின் நீதி சார்ந்த ஆட்சியாகும். மக்களின் நலன் கருதி அரசன் தன் கடமையினை செவ்வனே செய்ய வேண்டும். அரசன் குடிமக்களிடம் இறை வாங்குதல் குறித்து 'பழமொழி' பாடல்

பொருத்தம் அழியாத பூந்தண்டார் மன்னர்
அருத்தம் அடிநிழ லாரை - வருத்தாது
கொண்டாரும் போ போ தே கோடல்
அதுவன்றோ
வண்டேதா (து) உண்டு விடல்

என்ற பாடலில் வண்டுகள் பூமொட்டுகளை அவற்றில் தேன் இல்லாதது கண்டு ஊதிச் சிதையாது. அவை தேன் நிறைந்து மலர்ந்த காலத்தில்தான் தேனை எளிதாக உண்ணும் அதுபோல அரசர்கள் குடிகளிடத்திலிருந்து வாங்கும் இறைப்பொருள்களைக் காலமறிந்து வருந்தாது வாங்க வேண்டும் என்று கூறும்போது அரசாட்சி நீதியினை உணர்த்துகிறது.

நாடாளும் அரசனுக்கு உரியபொருள் இன்னது என்பதையும் அறுதியிடுகின்றார் வள்ளுவர் இக்கருத்தினை

உறுபொருளும் உல்கு பொருளுந்தன் ஒன்னார்த்
தெறுபொருளும் வேந்தன் பொருள்
(கு.எண். 756)

என்று திருக்குறளில் அரசாட்சி செய்யும் அரசனின் இறைபெறும் நெறியினை அறியமுடிகிறது.

சாதியொழிப்புமுறை

சாதிக்கொருநீதி வழங்கும் முறை மனுதர்ம சாத்திரமும் வடமொழியில் திகழ்கின்றது. சாதிக்கொரு நீதி ஏட்டளவில் தான் உள்ளது. நடைமுறைப்படுத்தப் பெறவில்லை.

பிறப்பொக்கும் எல்லா உயிர்க்கும்
சிறப்பொவ்வா
செய்தொழில் வேற்றுமை யான்
(கு.எண். 972)

என்ற வள்ளுவர் மொழி, சாதி வேற்றுமையை ஒழிக்க வல்லதாக அமைந்திருந்தும் அது சரியாகப் பயன்படுத்தப் பெறவில்லை. வள்ளுவரின் அறவுணர்வு நீதியினை நன்குணர்ந்த பேராசிரியர் சுந்தரம் பிள்ளை அவர்கள்

உள்ளுவரோ மறுவாதி
ஒருகுலத்துக் கொரு நீதி

என்று தமது மனோண் மணீயத்தில் சாதி ஒழிப்பு நீங்கி சீர்திருத்தம் பெறும் முறையினைக் கூறுகிறார். சமூக நீதி சரியான முறையில் வழங்கப்பெற வேண்டும். நாட்டுக்கும் சமூகத்திற்கும் அநீதி நீங்கி நீதியினை நிலை நாட்ட வேண்டும்

எல்லாரும் ஓர்குலம் எல்லாரும் ஓரினம்
எல்லாரும் ஓர்நிறை எல்லாரும் ஓர் விலை
எல்லாரும் இந்நாட்டு மன்னர் - ஆம்
எல்லாரும் இந்நாட்டு மன்னர்

என்ற பாரதியாரின் கனவு நனவாகும்... சாதி ஒழிப்புத் திட்டத்தில் விடுதலை பெற்றுச் சமூக நீதி பெற்றவர்களாக மக்களை உருவாக்க வேண்டும் என்பதை இலக்கியங்கள் நீதியினை நிலைத் நிறுத்திக் கூறுகிறது.

முடிவுரை

நீதி சமூக விரோதிகளைத் தண்டித்து சமூகத்திற்கு மேலும் தீங்குகள் ஏற்படாது. நன்மை ஏற்படுத்தும் வகையில் காணப்படுகிறது. அரசனின் செங்கோல் கடமை நீதி வழங்கும்

ஒளி விளக்காகத் திகழ்கின்றனர். இவர்கள் பொதுமக்களின் வாழ்க்கை கெடாமல் சீர்பட வேண்டும் என்ற இறைநெறியில் அரசன் தலையாயக் கடமையில் அரசாட்சி நடத்தினர் என்பதை இலக்கியங்களின் வாயிலாக அறிப்பட்டன. எல்லாரும் ஓர்குலம் எல்லாரும் ஓரினம் என்ற பாரதியாரின் கனவு நனவாகும் வகையில் சாதிப்பாகுபாடு என்ற அநீதியினை நீக்கி அனைவரும் சமூக நீதி உணர்வோடு செயல்பட வேண்டும் என்பதை இலக்கியங்களின் வழி உணர்த்தப்பட்டதை இக்கட்டுரையில் காண முடிகின்றது.

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6. பாரதியார் - பாரதியார் கவிதைகள் (எஸ். ஆர்.கப்பிரமணிய பிள்ளை வெளியீடு)
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குறிஞ்சி நில மக்களின் வாழ்க்கைமுறை

முனைவர் ஜெ.புவனேஸ்வரி
உதவிப்பேராசிரியர், தமிழ்த்துறை
தேசியக்கல்லூரி (தன்னாட்சி)
திருச்சி.

முகவுரை

குறிஞ்சி மலையும் மலை சார்ந்த நிலமுமாகும், இங்கு வாழும் மக்களைக் குறவர், கானவர் என அழைப்பர். மலையின் பக்கத்தே உள்ள சிறிய ஊர்களில் இவர்கள் வாழ்வர். இவை பாக்கம், சிறுகுடி எனப்பெறும்.

குறவர் குடிசை

குறவர் காட்டிலிருந்து வெட்டிக் கொணர்ந்த கால்களை நட்டுக் கட்டிய குச்சி வீடுகளில் வாழ்வர். இக்குடிசை 'நடுநாற் குரம்பை' (நற். 285 : 7) எனப்படும்.

வரகினது வைக்கோலை மேலே வேய்ந்து குடிசை அமைத்து, அதன் மேல் காட்டு மல்லிகையை வளர்ப்பர். அம்மல்லிகை மலர்ந்து மணம் பரப்புவது,

'கான்மிகு குளவிய வன்புசே ரிருக்கை' (பதிற். 30 : 23)

எனச் சிறப்பிக்கப்பட்டுள்ளது.

குறிய இறப்பையுடைய சிறிய வீட்டில் வாழ்வர். இம்மனை, 'குறியிறைக் குரம்பை' எனப்பெறும். காட்டுப் புல்லால் வேயப்பட்ட குடிசை 'புல்வேய் குரம்பை' என அழைக்கப்பெறும்.

பகல் வாழ்க்கை

குறவர்களின் நடைமுறை வாழ்க்கை ஆறு சிறுபொழுதுகளின் அடிப்படையில் பகுத்துக் காணக்கூடியதாக இல்லை. பகல், இரவு என்ற இரு நிலைகளில் மட்டும் காணத்தக்கதாக உள்ளது. பகற்பொழுதில் மலை உச்சியின்கண் இருக்கும் தேனை எடுப்பதை நடைமுறையாகக் கொள்வர். மலைப்பகுதியில் இயற்கையாக விளைந்து இருக்கும் கிழங்குகளைச் சேகரிப்பர். தினை விதைத்தல், தினை காத்தல், தினை அறுத்தல், தினை குற்றுதல் போன்ற செயல்பாடுகளில் இருபாலரும் பங்காற்றுவர். தினைகாத்தலில் மகளிர் ஈடுபடுவது குறிப்பிடத்தக்கதாகும். கானவர் பகற்பொழுதில் வேட்டையாடுவர்.

குறிஞ்சிநில மக்கள் தம் தேவைகளைப் பண்டமாற்று மூலம் நிறைவேற்றிக் கொள்வர். தம் நிலத்துப் பொருட்களை வேற்று நிலங்களுக்குக் கொண்டு சென்று தமக்குத் தேவையானவற்றையும் பெறுவர்.

குறவர் பகற்பொழுது வாழ்க்கையில் உணவுசார்ந்த நிகழ்வுகளும் பொழுதுபோக்கு சார்ந்த நிகழ்வுகளும் குறிப்பிடத்தக்கனவாக அமைகின்றன.

குறவர் முசுக்கலை ஏற முடியாத மலை உச்சியின் கண்ணும் கண்ணேணியை வைத்து அதன் வழியே ஏறுவர். தேனீக்கள் ஈட்டி வைத்த தேனை எடுப்பர். கண்ணேணி என்பது கணுக்களில் அடி வைத்து ஏறியிறங்கும்படி அமைந்துள்ள மூங்கிலாகும். இதனை 'மால்பு' எனவும் கூறுவர். குறவர் உச்சிப் பாறையில் உள்ள தேனை அறுத்தெடுக்க முயல்வதை,

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புனக் காவல் போதும் என்று கூறித் தினை கொய்யத் தொடங்குவர். இதனை,

'குளிர்படு கையள் கொடிச்சி செல்கென
நல்ல வினிய கூறி மெல்லக்
கொய்தொடங் கினரே கானவர் கொடுங்குரல்'
(நற். 306 : 3 - 5)

எனும் பாடல் வரிகள் வெளிப்படுத்தும். குறவர் பலரும் கூடிப் பகற்பொழுதில் தினை கொய்வர்.

குறவர் தினைக் கதிரைப் பாறையின் மேல் போட்டுக் களிற்றியானையைக் கொண்டு காலில் மிதிக்கச் செய்வர். இதனை,

'..... அகன்கட் பாறை
மென்றினை நெடும்போர் புரிமார்
உறங்குகளி றெடுப்பும்' (நற். 125 : 10 -12)

என்பார் கச்சிப் பேட்டுக் கதக்கண்ணனார்.

குறமகளிர் சிவந்த தினையைப் பாறையை மேல் பரப்பி உலர வைப்பர். அச்சமயம் யானையின் பிளிறல் கேட்கக் குறமகளிர் அதனை இடியோசை என எண்ணி உலர வைத்த தினையை ஒன்று திரட்டும் நிகழ்ச்சியை நற்றிணை பாடல்,

'..... உயர்வரைப்
பெருங்கல் விடரகம் சிலம்ப, இரும்புலி
களிறு தொலைத் தூரறுங் கடியிடி மழைசெத்துச்
செந்தினை உணகல் தொகுக்கும்' (நற். 344 : 8 - 11)

என்றவாறு உணர்த்தும்.

குறமகளிர் நன்கு காய்ந்த ஐவனம் என்னும் வெண்ணெல்லைத் தந்தையின் மலைவளத்தைப் பாடிக் கொண்டே குற்றுவர்.

வெண்ணெல்லைப் பாறையாகிய உரலில் இட்டு யானைக் கோட்டாலும் சந்தன மர உலக்கையாலும் குற்றுவர். முங்கிலின் வெண்ணெல்லைப் பாறையாகிய உரலில் யானைக் கோட்டினை உலக்கையாகக் கொண்டு குற்றுவர். சேம்பின் இலையைச் சுளகாகக் கொண்டு புடைப்பர். தினைப்புனத்தில் முற்றித் தாழ்ந்த கதிரை உருவிச் சந்தன மரத்தால் செய்த உரலில் பெய்து யானைக் கோட்டால் வகுத்த உலக்கையை உயர்த்திக் குற்றும் நிகழ்ச்சியை,

'.....வயக்களிற்றுக்
கோடு உலக்கையாக, நற்சேம்பின் இலை சுளகா
ஆடுகழை நெல்லை அறை உரலுள் பெய்து, இருவாம்
பாடுக, வா - வாழி, தோழி!' (கலி. 40 : 3 - 5)

எனும் பாடலடிகள் தெளிவாய் விளக்கும்.

இவற்றால் குறமகளிர் பகற்பொழுதில் வெண்ணெய், முங்கில், நெல், தினை போன்றவற்றைக் குற்றிப் புடைத்துத் தூய்மைப்படுத்துவதை நடைமுறையாகக் கொண்டிருந்ததை அறியலாம்.

கானவர் பகற்பொழுதின் பெரும்பகுதியை வேட்டையாடுவதில் கழிப்பர். 'வேட்டையாடி உணவு சேகரிக்கும் பழங்குடிகள் பெரும்பாலும் தனித்தனியான சிறு குழுக்களாகப் (ஐளழடயவநன டீயனெள) பிரிந்து செல்வர்' (சீ. பக்தவத்சல பாரதி, பண்பாட்டு மானிடவியல், ப. 470) என்பார் சீ. பக்தவத்சல பாரதி.

கானவர் அகன்ற நிலப் பிளவின் வாயிலில் வார்களால் பின்னப்பட்ட கண்ணியும் வலையும் அமைப்பர். பன்றியை வேட்டை நாய்களைப் கொண்டு ஏவித் துரத்தி அப்பிளவில் விழச் செய்வர். வலையில் பட்டுச் சிக்குறும். அதனைத் தம் சிறுகுடிக்குக் கானவர் கொண்டு வருவர்.

வேட்டை நாய்களுடன் பசிய தூறுகளை அடித்து வேலியில் தொடர் வலைகளைக் கட்டிக் குறுமுயல்களை அவ்வலையகத்தே விழுமாறு வளைத்துப் பிடிப்பர்.

பாறைகள் செறிந்த குன்றுகளில் முழைகள் கண்டு அவற்றின் வாயிலில் கற்பலகையால் கதவமைப்பர். அதனுள்ளே ஆடுகளைக் கட்டிப் புலிகளை அதனுள் புகுவிப்பர். அவை ஆடுகளைத் தாக்கும் போது வாயிற்கதவாகிய கற்பலகை விரைய மூடிக் கொள்ளுமாறு பொறியமைப்பர். இதற்குக் 'கல்லடார்' என்று என்று பெயர். இவ்வேட்டை முறையை,

'இரும்புலி வேட்டுவன் பொறியறிந்து மாட்டிய
பெருங்கல் லடார்' (புறம். 19 : 5 - 6)

என்பார் குடபுலவியனார்.

குறவர் வேட்டைக்குச் செல்லும் போது பலாப்பழத்தின் சுளையினின்று விளைந்த கள்ளை நிறையக் குடிப்பர். தோளில் முங்கிலால் ஆன வலிய வில்லை வைத்திருப்பர். அவர்களுடன் விலங்குகளைத் துரத்திப் பற்றும் இயல்புடைய நாய்கள் உடன் செல்லும். ஏவல் இளையரும் பின்னே செல்வர். இவ்வாறு சென்ற குறவர் காட்டிலுள்ள மல்லிகைப் புதர் உதிரத்தோடு அசைந்திட முள்ளம் பன்றியைக் கொன்று வீழ்த்துவர். (அகம். 182 : 2 - 8)

களிற்றியானைமேல் அம்பு செலுத்திக் கொன்று அதன் கோடுகளைக் கொண்டு வந்து தனது ஊகம் புல்லால் வேய்ந்த குடிசையில் புலால் நாற்றம்

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வீச ஊன்றுவர். யானையை வேட்டையாட அதன் கோடுகளைப் பிய்த்தெடுத்து அவற்றை அகன்ற பாறையில் உலர வைப்பர். யானையின் பசிய ஊனை அறுத்தெடுத்துத் தசையையும் பாறையில் உலர்த்துவர். கானவர் கோட்டுக்காகவும் தசைக்காகவும் யானைகளை வேட்டையாடியதனைக் கபிலரின்,

'..... யானை
நற்கோடு நயந்த அன்பில் கானவர்' (நற். 65 : 5 - 6)

என்ற பாடலடிகள் உணர்த்தும். கானவர் காட்டில் வேட்டையாடிக் கொன்ற யானையின் கோடுகளைக் காவு மரமாகக் கொண்டு, பன்றி முதலியவற்றின் தசை நிறைந்த வட்டிகளைச் சுமந்து வருவர்.

கானவர் வேட்டையாடி வந்த இறைச்சியைத் தம்முள் பகுத்துக் கொள்வது நடைமுறையாகும். இதனை, □வேட்டையாடி உணவு சேகரிக்கும் சமுதாயங்களில் பொதுப்படியான பரிமாற்றம் பெரும்பாலும் உணவுப் பொருள்களைப் பரிமாறிக் கொள்வதாக அமைகிறது. வேட்டைக்குச் செல்லும் குழுவினர் வேட்டையாடிப் பெற்ற இறைச்சியை அவர்களின் உறவினர்களுடன் சமமாகப் பகிர்ந்து கொள்வர். அல்லது உறவு நெருக்கத்தின் அடிப்படையில் பகிர்ந்து கொள்வர்□ (சீ. பக்தவத்சல பாரதி, பண்பாட்டு மானிடவியல், ப. 476) என்பார் சீ.பக்தவத்சல பாரதி.

கானவர் வில்லாற் கொன்று கொணர்ந்த ஆண் பன்றியை மனைமகளிர் துண்டித்து ஊரிடத்து வாழ்வோரது குடிமுறைக் கேற்பப் பகுத்தளிப்பர். இந்நிகழ்வு,

'..... கானவன்
வில்லின் தந்த வெண்கோட் டேற்றைப்
புனையிருங் கதுப்பின் மனையோள் கெண்டிக்
குடிமுறைப் பகுக்கும்' (நற். 336 : 3 - 6)

எனக் கபிலரால் குறிப்பிடப்பட்டுள்ளது. குடிமுறை என்பது கானவருள் உயர்வுதாழ்வு இருந்தமையை நன்குணர்த்தும். இவர்கள் ஒரு குழுவாக வேட்டையாடுவதும் இறைச்சியை அனைவரும் தகுதிக்கேற்ப பிரித்துக் கொள்வதும் நடைமுறை வழக்கமாக இருந்துள்ளது. .

கானவர் வீழ்த்திக் கொணர்ந்த முள்ளம் பன்றியின் ஊனைக் குறமகளிர் சிறுகுடியில் வாழும் ஏனைய குறவர்க்கும் பகுத்துக் கொடுப்பர். கானவர் தம் முன்றிலில் உடும்பினைச் சுட்டு அறுத்துத் தம்மவரினையே பங்கிட்டுக் கொள்வர். இதனை உடும்பினைப் பற்றிக் கொணர்ந்த கானவர் அதனைப் பகுத்தளித்தற் பொருட்டு நெருப்பில் வேக வைப்பர். அப்பொழுது எழும் மணம் தெருவெல்லாம் மணக்கும் என்பதைப் புறப்பாடல் (புறம். 325 : 7 - 8) நன்கு உணர்த்துகிறது

குறவர் தம் நிலத்தில் கிடைக்கும் பொருட்களைப் பண்டமாற்றாகப் பயன்படுத்துவர். ஆமாவின் இறைச்சியுடன் களிற்றி யானையின் கோட்டையும் கொண்டு வந்து கொடுத்து விட்டு, அவற்றின் விலைக்கு ஈடாகப் பொன்னையும் கள்ளையும் பெறுவர். இதனை,

'செங்கோட் டாமா னூனொடு காட்ட
மதனுடை வேழத்து வெண்கோடு கொண்டு
பொன்னுடைய நியமத்துப் பிழிநொடை கொடுக்கும்' (பதிற். 30 : 10 - 12)

என்ற பாடலடிகள் விளக்கி நிற்கின்றன.

சிறுகுடியிலுள்ள குறவர் உணவின்றிப் பசித்தாராயின் யானைக் கோட்டை விற்று அவ்விலையில் உணவைக் கொள்வர். தேனையும் கிழங்கையும் நெய்தல் நிலத்துக்குக் கொண்டு வந்து கொடுத்துவிட்டு அதற்கு விலையாக மீன் நெய்யையும் நறவையும் பெறுவர். குற மகளிர் மான் தசையைக் கொண்டு வந்து கொடுத்துவிட்டு உழவர் மகளிடமிருந்து கடகம் நிறைய வெண்ணெல் பெறுவர்.

குறவர் தினைச்சோறு, இறைச்சி, பலாப்பழம் ஆகியவற்றைப் பகற்பொழுதில் உணவாகக் கொள்வர்.

குறமகளிர் மோரை உலையாக வார்த்துப் புளியம்பழத்தின் இனிய புளிப்பையும் கலந்து மூங்கிலரிசிச் சோறு ஆக்குவர். இவ்வுணவை, 'மனை தோறும் பெறுகுவீர்' என்று புலவர் குறிப்பிடுவதால் இவ்வாழ்க்கை முறை குறவர் அனைவருக்கும் பொதுவானதாக இருந்துள்ளமை புலனாகும்.

குறவர் நெய்யில் பொறித்த தசையினையும், தினைச் சோற்றையும் உணவாகக் கொள்வர். இதனை,

'பருஉக்குறை பொரிந்த நெய்க்கண் வேவையொடு
குரூஉக்கண் இறடிப் பொம்மல் பெறுகுவீர்' (மலை.168 - 169)

எனும் பாடலடிகள் மூலம் அறியலாம்.

பலாப்பழத்தின் விதையோடு மானின் தசையினையும், பன்றியின் தசையினையும் உடும்பின் தசையோடு கலந்து கறி செய்து உண்பர். பலாப்பழத்தினைச் சில நாளைக்கு வைத்து உண்ணும் உணவாகக் கொள்வர்.

இதனை,

'குறவர்க்கு அல்குமிசை வாகும்' (புறம். 236 : 2)

என்னும் வரி நன்குணர்த்தும். பலாப்பழமும் அதன் விதைகளும் குறவர்க்கு எளிதாக இயற்கையாகக் கிடைக்கும் உணவுகள் ஆகும்.

கானவர் பகற்பொழுதில் 'கையாடு வட்டில்' கொண்டு விளையாடிப் பொழுது போக்குவர். இதனை,

'கைஆடு வட்டின் தோன்றும்' (அகம். 108 : 17)

என்று புலவர் கூறுகிறார். இது கையின்கண் வட்டினை வைத்து ஆடும் ஒருவகை விளையாட்டாகும்.

குறவர் வேலையில்லாத பொழுது கள்ளுண்டு மகிழ்ந்து பொழுது போக்குவர். மனமகிழ்ச்சியின் பொருட்டு விடியற்காலத்தே கள்ளுண்டு களிப்பர். நறவை நாட்காலத்தே குடித்த குறவர் தம் மகளிரோடு சிறுபறை ஒலிக்கக் குரவையாடுவர்.

வைகறைப்பொழுதில் மூங்கிற் குழாய்கள் பெய்த முற்றிய தேனாற் செய்த கள்ளின் தெளிவை நிரம்ப உண்பர். நெல்லாற் சமைத்த கள்ளை உண்டு மகிழ்வர். குழலின் கண் மனைவி தேனாற் செய்த கள்ளை வார்த்துக் கொடுக்கக் குறவர் உண்டு மகிழ்ச்சி மிக்கு இருப்பர்(குறிஞ்சி. 153 - 155). பகற்பொழுதில் வேங்கைப் பூக்களைச் சூடித் தொண்டகப் பறையின் தாளத்திற்கேற்ப ஆடவர் பெண்டிரோடு தெருக்களில் ஆடி மகிழ்வர்.

இரவு வாழ்க்கை

குறவர் இரவில் பஞ்சாலாகிய வெள்ளிய திரியையுடைய விளக்கினைத் தம் வீடுகளில் ஏற்றுவர்(குறுந். 353:4-5). தம் ஊருக்குள் கொடிய விலங்கினங்கள் புகாவண்ணம் ஊர்க்காவலர் பாதுகாப்பர். மூங்கிலரிசிச் சோற்றையும், புலால் உணவையும் இரவு உணவாகக் கொள்வர். ஊர் அம்பலத்தில் பொழுது போக்குவர். புலித்தோல் படுக்கையில் தூங்குவர். குறவர்களுக்கு இரவில் தினைப்புனங்காத்தலும், வேட்டையாடுதலும் குறிப்பிடத்தக்க வாழ்க்கை முறைகளாக இருந்துள்ளன.

கானவர் இரவில் மூங்கிலரிசிச் சோற்றில் நெல்லரிசி விரவி அவரை விதையாற் சமைத்த புளிங்கூழை உணவாகக் கொள்வதை,

'வேய்கொள் அரிசி மிதவை சொரிந்த
சுவல் விளை நெல்லின் அவரையும் பைங்கூழ்
அற்கிடை உழந்தநும் வருத்தம் வீட' (மலை. 435 - 437)

எனும் பாடல் உரைக்கும்.

வெள்ளாட்டை அரிந்து அதன் தசையோடு சேர்த்துச் சமைத்த அரிசிச் சோற்றுத்தடியைத் தினை மாவுடன் கலந்த உணவை இம்மக்கள் நாள்தோறும் செய்வர். இதனை 'அல்கலும்' எனப் புலவர் குறிப்பிடுவதால் இது நடைமுறை வாழ்க்கையில் தினந்தோறும் இடம்பெற்ற உணவுமுறை என்பது தெளிவுறும்.

குறவர் இரவில் ஊர் அம்பலத்தில் கூடிப் பேசிப் பொழுது போக்குவர். இதனைக் கபிலர்,

'மன்றுபா டவிந்து மனைமடிந் தன்றே' (அகம். 128 : 1)

என்பார். இங்கு மன்று என்பது ஊர்ப்பொழுது இடமாகிய அம்பலத்தைக் குறிக்கும்.

கானவர் இரவில் புலித்தோலால் செய்யப்பெற்ற படுக்கையில் துயில்வர். இதனை,

'வரியதள் படுத்த சேக்கை' (அகம். 58 : 4)

என மதுரைப் பண்டவாணிகன் இளந்தேவனார் குறிப்பிடுவார்.

குறவர் இரவில் கொடிய விலங்குகளிடமிருந்து தங்களைப் பாதுகாத்துக் கொள்ளக் காவல் காப்பர். அதற்குத் தொண்டகமாகிய சிறு பறையைப் பாதி இரவிலும் விடாது ஒலிப்பதை,

'இரவுஅரி வாரின், தொண்டகச் சிறுபறை
பானாள் யாமத்தும் கறங்கும்
யாமம் காவலர் அவியா மாறே' (குறுந். 375 : 4 - 6)

எனப் புலவர் குறிப்பிடுவார்.

சில சமயங்களில் ஊருக்குள் வர முயலும் விலங்குகளை அனைவரும் சேர்ந்து வெருட்டுவர். தம் குடிக்குள் வர முயலும் யானையைத் தடுக்க அம்பு செலுத்துவர். கிணைப்பறையைக் கொட்டுவர். கையிலுள்ள கவணால் கல் எறிவர். விளிக்குரல் எழுப்புவர். ஊருக்குப் புறத்தே நின்று ஆரவாரம் செய்வர்.

இரவில் குறவர் தினைப்புனம் காத்தமை குறிப்பிடத்தக்கதாகும். இரவில் தினையை மேய்ந்த யானையின் கூட்டம் நிலை கெட்டு ஓட, உயர்ந்த பரணிலிருந்து கவணகல் எறிவர். யானைகள் அஞ்சி ஓடும் பொருட்டுக் கொள்ளிக் கட்டையை இரவு முழுவதும் எரிய விடுவர். ஒளி விளங்குகின்ற குறைக் கொள்ளியை உடையராய் வில்லினை உடையராய்க் களிறு வந்ததென்று தினைப்புனம் காக்க கானவர் ஆரவாரம் செய்வர் .

நடு இரவில் யானை நடக்கும் ஓசையைக் கேட்ட

கானவர் உயர்ந்த மலையில் ஆசினிப் பலாவின் மேல்இட்ட பரணில் ஏறிக் கவண் மூலம் கல் எறிந்து ஓட்டுவர். நள்ளிரவில் மலையிடத்தே பரண் மீதுள்ள கானவன் இரவில் மேய்தலைப் பொருந்தி வரும் யானையின் நடையைக் கூர்ந்து அறிந்து கவணால் கல் எறிந்து துரத்துவதை,

'..... யானைக்
கால்வல் இயக்கம் ஒற்றி நடுநாள்
வரையிடக் கழுதின் வன்கைக் கானவன்
கடுவிசைக் கவணின் எறிந்த சிறுகல்' (அகம். 292 : 8 - 11)

எனக் கபிலர் விளக்குவார்.

இரவில் காட்டுப் பன்றிகளின் தொல்லை அதிகமாக இருக்கும். இவை கூட்டமாக வந்து தினைப்பயிரை அழித்துவிடும். எனவே இக்காட்டுப் பன்றிகளைத் தினைப்புனத்திலிருந்து கானவர் ஓட்டுவர்.

சிறிய கண்ணினையுடைய பன்றியின் பெருங் கூட்டத்தை ஓட்டுவதற்கு முற்றிய தினைப்புனத்தைக் காத்திருப்போர் அனைவரும் காலத்தை நினைந்து காத்திருப்பர். ஊது கொம்பினை ஓசையோடு ஊதுவர். பரண் மீது அமர்ந்து பன்றிவரும் திறம் நோக்கி நீண்ட சுடரின் ஒளியினைக் கொளுத்தி வைத்திருப்பர்.

இதனை,

'புருவைப் பன்றி வருதிறம் நோக்கிக்
கடுங்கைக் கானவன் கழுதுமிசைக் கொளீஇய
நெடுஞ்சுடர் விளக்கம்' (அகம். 88 : 4 - 6)

என ஈழத்துப் பூதன்தேவனார் குறிப்பிடுவார்.

விலங்குகளை விரட்டக் கொள்ளிக் கோலினைக் கையில் வைத்திருத்தல் இயல்பு. இதனை,

'ஏனலஞ் சிறுதினைச் சேணோன் கையதைப்
பிடிக்கை அமைந்த கனல்வாய்க் கொள்ளி'
(அகம். 73 : 14 - 15)

என எருமை வெளியனார் குறிப்பிடுகிறார்.

குறவர் கூதிர் கால நடு இரவில் காட்டில் விலங்குகளை வேட்டையாடுவர். இந்நிகழ்வு,

'..... பாணாட் கங்குல்
காடுதேர் வேட்டம்' (அகம். 58 : 2 - 3)

எனக் கூறப்பட்டுள்ளது. இவர்களது நடுயாம வேட்டை 'அரைநாள் வேட்டம்' எனவும் சிறப்பிக்கப்பெறும்.

குறவர் நடுயாமத்தில் பன்றி நீருண்ண வரும் வருகையை எதிர்பார்த்து மூடு குழிகளின் அகத்தே மறைந்திருந்து வேட்டையாடுவர்.

இவ்வாறு குறிஞ்சி நிலக் குறவர்கள் பகற்பொழுதில் தேன் எடுத்தல், கிழங்கெடுத்தல், கொல்லையில் தினை பயிரிடுதல், வேட்டையாடுதல் ஆகியவற்றை மேற்கொள்வர். குறமகளிர் பகற்பொழுதில் தினையைக் காப்பர். குறவர்கள் இறைச்சியை பிற நிலத்திலுள்ள மக்களிடம் கொடுத்து அதற்குப் பதிலாக மீன் நெய், நறவு, நெல் ஆகியவற்றைப் பெறுவர். இரவில் வீட்டில் விளக்கேற்றி மூங்கிலரிசிச் சோற்றை உணவாகக் கொள்வர். புலித்தோலிற் துயில்வர்.

06.12.17

இருபதாம் நூற்றாண்டுத் தமிழ் இலக்கியங்களும் தமிழறிஞர்களும்

(பன்னாட்டு ஆய்வுக் கருத்தரங்கம்)

தொகுதி - I

பதிப்பாசிரியர்கள்

முனைவர் க. முருகேசன்

முனைவர் சு. குமரன்

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தமிழ்த்துறை

கொங்குநாடு கலை அறிவியல் கல்லூரி

(தன்னாட்சி)

நேசிய மதிப்பீடு, மீள் தர நிர்ணயக் குழுவின் 'A' தகுதி பெற்றது

தனிச்சிறப்புத் திறன் கல்லூரித் தகுதி பெற்றது

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தே. எ. ஸ்வரன்

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(பன்னாட்டு ஆய்வுக் கருத்தரங்கம்)

பதிப்பாசிரியர்கள் : **முனைவர் க. முருகேசன்**
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முனைவர் சு. இராமலிங்கம்

பதிப்புரிமை : பதிப்பாசிரியர்கள்

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கொங்குநாடு கலை அறிவியல் கல்லூரி
கோயம்புத்தூர் - 641029.

கணினி : பிரடாக் பிரிண்ட், கோயம்புத்தூர் - 29.

அச்சாக்கம் : பிரடாக் பிரிண்ட்,
476, பூமாதேவி கோவில் அருகில்
கவுண்டர் மில்ஸ் (அஞ்சல்)
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பொருளடக்கம்

6

இரசிகமணி டி.கே. சிதம்பரநாத முதலியாரின் தமிழ்ப்பணி

முனைவர் ச. ஈஸ்வரன்
இணைப்பேராசிரியர் & தலைவர், தமிழாய்வுத்துறை
தேசியக் கல்லூரி (தன்னாட்சி)
திருச்சிராப்பள்ளி - 620 001.

முன்னுரை

டி.கே.சி. என்ற மூன்று எழுத்துக்களால் தமிழுலகில் நன்கு அறிமுகமானவர் டி.கே. சிதம்பரநாத முதலியார். டி.கே.சி.யில் உள்ள டி - தகப்பனார் பெயர் தீத்தாரப்ப முதலியாரைக் குறிக்கும். கே - கிளாங்காடு (ஊரின் பெயரைக் குறிக்கும்). 1927 முதல் 1930 வரை சட்டமன்ற மேலவை உறுப்பினராகப் பணியாற்றியுள்ளார். அப்போதைய வெள்ளை அரசு பாரதியின் பாடல்களைத் தடைசெய்து இயற்றிய சட்டத்தை எதிர்த்துப் பேசியுள்ளார். 1930 முதல் 35 வரை இந்துமத அறநிலையத்துறை ஆணையராக இருந்த போது 'மகேஸ்வர பூஜை' என்னும் பெயரால் சமபந்தி விருந்து நடத்தியுள்ளார். திருநெல்வேலி வண்ணாரப்பேட்டையில் தமது இல்லத்தில் 1935இல் 'வட்டத்தொட்டி' என்ற இலக்கிய வட்டத்தை ஏற்படுத்தியுள்ளார். அந்த இல்லத்தின் வட்டமான முற்றத்தில் இலக்கிய நண்பர்கள் சுற்றி அமர்ந்து இலக்கியம், கலை தொடர்பான பேச்சுக்களில் ஈடுபட்டு வந்தனர்.

இந்த அமைப்புதான் டி.கே.சியை இலக்கியத் திறனாய்வுத் துறையில் ஈடுபடுத்தக் காரணமாக இருந்தது. 'பண்பாடு' என்ற சொல்லை உருவாக்கினார் டி.கே.சி. இவரை 'ரசிகமணி' என்று பாராட்டி மகிழ்ந்தார் கல்கி. ரா.கிருஷ்ணமூர்த்தி. டி.கே.சி. 1941இல் 'இதய ஒலி' எனும் கட்டுரைத் தொகுப்பு நூலை வெளியிட்டுள்ளார். 'கம்பர் யார்?', 'அற்புதரஸம்' போன்ற நூல்களையும் எழுதியுள்ளார். பத்தாயிரத்திற்கும் மேற்பட்ட கம்பன் பாடல்களில் 1,515 பாடல்கள் மட்டுமே கம்பன் பாடியவை எனக் கொண்டு 'கம்பர் தரும் ராமாயணம்' எனும் நூலை 1952-55 ஆம் ஆண்டுகளில் டி.கே.சி மூன்று பாகங்களாகப் பதிப்பித்தார். இதனால் பலரின் எதிர்ப்புக்கு உள்ளானார்.

1943இல் 'முத்தொள்ளாயிரத்தை'த் திறனாய்வுக் குறிப்புகளுடன் டி.கே.சி. வெளியிட்டார். முத்தொள்ளாயிரப் பதிப்பில் பாடல்களை டி.கே.சி. திருத்தவில்லை. தமிழிசை இயக்கம் மற்றும் மறையும் நிலையிலும் ஒரு சாராருக்கே உரிய நிலையிலும் இருந்த 'பரதநாட்டியக் கலைக்குப்' புத்துயிர் தந்து சிறப்புற வாழும்படிச் செய்த தொண்டு டி.கே.சி.யைச் சாரும். ரசிகமணியின் குரலாக இப்போது கிடைத்திருப்பதெல்லாம் அவருடைய கடிதங்களே. கடித இலக்கியச் செழுமைக்கு டி.கே.சி.யும் ஒரு காரணம். பாஸ்கரத் தொண்டைமான், மகாராஜன், பட்டாபிராம், இராஜேஸ்வரி போன்றோர்க்கு டி.கே.சி. எழுதிய இலக்கியக் கடிதங்கள் தனித்தனி நூல்களாக வெளிவந்துள்ளன. டி.கே.சியின் பெருமையினை உணர்ந்த தமிழக அரசு

அவர்தம் நூற்றாண்டு விழாவை 23.08.1981 குற்றாலத்தில் கொண்டாடியது. ஆங்கிலத் தேதியை விடுத்து ஸ்ரீஜெயந்தி நாளிலேயே அரசு, விழாவினை நடத்தியது. இக்கட்டுரையில் டி.கே.சி. யின் தமிழ்ப் பணிகள் குறித்து ஆராயலாம்.

கம்பராமாயணப் பாடல்களைத் திருத்தம் செய்தல்

டி.கே.சி. கம்பராமாயணப் பாடல்களைத் திருத்தம் செய்தார். பின்வரும் பாடல், முதல் அடியில் 'மாதர்கள் வயதின் மிக்கார்' என்பதை, 'மாதர்கள் ஆண்டின் மிக்கார்' எனத் திருத்திப் பதிப்பித்தார் டி.கே.சி. கம்பன் கழகப் பதிப்பில் **(ப. 264)** 'மாதர்கள் கற்பின் மிக்கார்' என்றுள்ளது.

கவிஞர்

ரசிகமணி ஒரு கவிஞரும் கூட. அவருடைய கவிதை இதோ.

"விண்ணிடை நின்று
விரைவொடு வந்து
வெண்நகை யொடுங்விளையாடித்
தின்எனக் குதிக்கும்
அருவியின் ஒலிதான்
திருச்செவி அடைத்தது
கொல் லோ!"

கவிதைகளை ரசிக்க வேண்டும். பிறருக்கு உணர்த்த வேண்டும் என்ற ரசிகமணி டி.கே.சி.யின சிந்தனைகளைப் பின்பற்றி வாழ்ந்தால் ஏற்றம் பெறலாம்.

டி.கே.சி.யின் திறனாய்வுப் பார்வை

தமிழில் அழகியல் வாதத் திறனாய்வு

தமிழில் முதன்முதலில் அழகியல் வாதத் திறனாய்வுப் பார்வையில் இலக்கியத்தை அணுகியவர் வ.வே.சு. ஐயர். இவரைத் தொடர்ந்து டி.கே.சி., க.நா.சு., சி.சு.செல்லப்பா, வெங்கட் சாமிநாதன், தருமுசிவராம், பிரேமிள் ஆகியோர் இலக்கியத்தின் அழகியல் கூறுகளை வலியுறுத்திக் காட்டுவதில் தீவிரம் காட்டினார்.

டி.கே.சி.யும் அழகியல் வாதமும்

டி.கே.சி.யின் அழகியல்வாதத் திறனாய்வுப் பார்வை, க.நா.சு., சிசு. செல்லப்பா ஆகியோர்தம் அழகியல் வாதங்களுக்கு முற்பட்டது. இவர், தம் வாழ்நாள் முழுவதும் இரசனை மயமாகவே திகழ்ந்து அவ்வுணர்விலேயே காலம் கழித்து 'ரசிகமணி' என்ற பட்டம் பெற்றார். இரசனை என்பதற்கே தனி இலக்கணம் வகுத்தார். வாழ்க்கையின் சிறு சிறு நிகழ்ச்சிகளிலும் இரசனைத் தன்மை கண்டு அனுபவித்தார். தம் உயிரோடு ஒன்றிவிட்ட இவ்ரசனை உணர்வினால் இலக்கியம் முதலான கலைகளையும் இரசனை அடிப்படையில் ஆராய்ந்து சில முடிவுகளைக் கூறினார். க.கைலாசபதி திறனாய்வு வகைகளை எடுத்துக்காட்டும்போது, 'நவீனத் திறனாய்வு பற்றிய கண்ணோட்டத்தில் ஆங்கிலம் கற்ற தமிழ்க்காதல் உடைய டி.கே.சி. முதலானவரின் இரசனை முறைத் திறனாய்வு' **(கணேசன், பு.சி., க.நா.சு.வும் கைலாசபதியும், பக். 87,88 (மேற்)** எனக் குறிப்பிடுவார்.

பதிப்புக் கலையில் டி.கே.சி.யின் பங்கு

பதிப்புக்கலை எளிய மக்களையும் சென்றடையுமாறு முதன்முதல் அதனை எளிமைப்படுத்தித் தந்த பெருமை டி.கே.சி.யைச் சாரும். இவர் தாம் பதிப்பிக்க எடுத்த நூல்களை மிக எளிய மக்களைக் கருத்தில் கொண்டு எளிய முறையில் பதிப்பித்தலில் ஆர்வம் காட்டினார். 'கம்பராமாயணமும் முத் தொள்ளாயிரமும் தமிழர்கள் படித்து அனுபவிப்பதற்காகப் பிரசுரிக்கப்பட்டவை. ஆராய்ச்சி செய்யவாவது அல்லது விமரிசனம் செய்யவாவது பிரசுரிக்கப்படவில்லை' **(பாஸ்கரத் தொண்டைமான், தொ.மு., ரசிகமணி டி.கே.சி., ப.123)** எனப் பாஸ்கரத் தொண்டைமான் கூறுவதன் மூலம் அறிய முடிகிறது. இந்நோக்கத்திற்காக இவர், தம்முடைய பதிப்புப் பணியில் இரசனை முறைத் திறனாய்வையும், ஏடுகளை ஒப்புநோக்கித் தெரிதலுக்கு இடந்தராத மூலபாடத் திறனாய்வையும் ஒருசேரக் கலந்தார். இவரது பதிப்பில் உள்ள எளிமைத் தன்மையைப் பின்னுள்ளோரும் பின்பற்றினர்.

பாவம்

டி.கே.சி. தம் பதிப்பில் 'பாவம்' (உள்ளக் குறிப்பு) என்ற சொல்லில் உள்ள 'பா' வைத்தடித்த எழுத்தில் பதிப்பித்திட்டார். ஆனால் வ.சுப.மாணிக்கம் இவ்வாறு பதிப்பித்தலை ஓர் ஒலிக்கு ஓர் எழுத்து என்பது மொழியறம். ஒலிவேறு பொருள்வேறு கொண்டால் எழுத்தும் வேறு கொள்ளல் வேண்டும்.

டி.கே.சி.யின் கம்பராமாய்ணப் பதிப்பு

செருக்குகவிகளைக் களைந்தும், திருத்தங்கள் பல செய்தும் டி.கே.சி. உருவாக்கிய கம்பரது காவியம், 'கம்பர் தரும் ராமாயணம்' என்ற தலைப்பில் பல பகுதிகளாகப் பதிப்பிக்கப்பட்டது. டி.கே.சி.யின் இலக்கிய இயக்கம், பதிப்புக்கலை வரை வளரலாயிற்று. 1953இல், 'கம்பர் தரும் ராமாயணத்தின்' முதல் பகுதியை வெளியிட்டார். மொத்தம் மூன்று பாகங்களாகக் 'கம்பர் தரும் ராமாயணம்' பதிப்பிக்கப்பட்டது. கம்பர் பாடியவை அல்ல என்று நீக்கம் செய்யப்பட்டவைகளுள், 1,515 பாடல்களையும் டி.கே.சி. யாவரும் எளிதில் படித்து அனுபவிக்கக் கூடிய முறையில் சரிபார்த்துப் பதிப்பித்தார்.

டி.கே.சி.யின் கடித இலக்கியப் பணி

தமிழ்க் கடித இலக்கியச் செழுமைக்குக் காரணமாக விளங்கியவர்களுள், டி.கே.சி.யும் ஒருவர். வாழ்க்கையின் பலதரப்பட்ட துறைகளைப் பொருளாகக் கொண்டனவாய் இவர் எழுதிய கடிதங்கள் திகழ்கின்றன. இவர்தம் கடிதங்கள் நேருக்கு நேர் பேசுவது போன்ற அமைப்பினைப் பெற்றுள்ளன. பேச்சுமொழியையே கடித இலக்கிய மொழியாகவும் இவர் கையாண்டுள்ளார்.

வெளியான கடித நூல்களின் பெயர்கள்

'ரசனையின் ஒலி', 'பேசும் கடிதங்கள்', 'ரசிகமணி கடிதங்கள்', 'ரசிகமணி டி.கே.சி.யின் கடிதங்கள்' (பொதிகைமலைப் பதிப்பு, தென்காசி)

டி.கே.சி.யின் கலைப்பணி

டி.கே.சி.யும் தமிழிசையும்

உண்மையில் தமிழிசை இயக்கத்தைத் தொடங்கி, அதற்கு வலுவான அடிப்படை அமைத்து அது வளர்ந்த நிலையில் திறப்பு விழாவும் நடத்தியவர் டி.கே.சி. தமிழ் நாட்டில் பதினைந்து ஆண்டுகளாகத் தமிழ்ப்பற்று வளர்ந்து பெருகுவதற்கும், தமிழகத்தின் பழம்பெரும் செல்வமான ஆடற்கலை புத்துயிர் பெறுவதற்கும், தமிழிசை இயக்கத்திற்கும் இவரே பொறுப்பாளி.

சங்கீதத்தைப் பயிலும் முறை

சங்கீதத்தைப் பயிலும் முறை குறித்து டி.கே.சி. பின்வருமாறு எழுதுகிறார். 'நேரில் கேட்டு பாவங்களை அனுபவிப்பதே முக்கியம். அனுபவிக்க பாவம் இதயத்தில் ஏறி நிற்கும், உணர்ச்சியொன்றை மாத்திரம் கைவிடாது. பற்றிக் கொள்வோமானால் பாவ சங்கீதமாகவே பாடவரும். பதங்களில்தான் ராகங்களின் மூர்ச்சைகளைத் தெளிவாய்த் தெரியக் காணலாம். இந்த முறையில் உபயோகிப்பதற்காகவே புஸ்தகம் ஏற்பட்டது. அப்படியே சங்கீதத்தை நம்மவர்கள் பயிலுவார்களானால் உலகத்தில் எங்குமில்லாத பாவமயமான சங்கீதத்தை தமிழ்நாடெங்கும் ஒலிக்கக் கேட்கலாம்' **(சிதம்பரநாத முதலியார், டி.கே. தமிழ் இசைப்பாட்டுகள், முகவுரை ப.7 (நடராஜன், அ.லெ.) (ப.ஆ.)** என்கிறார் டி.கே.சி. இதன் மூலம் பாடல்களை நன்கு அனுபவித்தல், வாய்விட்டுப் பாடுதல் ஆகியன சங்கீதத்தைப் பயிலும் முறைகளாக டி.கே.சி. எண்ணினார் என்பதனை உணரமுடிகிறது.

தமிழிசையின் பெருமை

தமிழிசையின் பெருமைகளை 'பரத நாட்டியத்தைவிட நூட்பமான கலை சங்கீதம், அற்புத உணர்ச்சி என்றால் அது; சங்கீதத்தில் வெளிப்பட வேண்டும். சங்கீதத்துக்குப் பாவந்தான் பிரதானமானது. இதய பாவம் இல்லாது போனால் மட்டமான சங்கீதம்தான். நம்முடைய முன்னோர்கள் பாவத்தையே முக்கிய அம்சமாக எண்ணினார்கள். மேலை நாட்டார் கூட எண்ணுகிறார்கள் என்று டி.கே.சி. விளக்குகிறார்.

வில்லிசைக் கலையும், டி.கே.சி.யும்

டி.கே.சி. தாம் பழகிய மேல்மட்ட உயர் குடும்பத்தினருக்கும், வில்லுப்பாட்டை அறிமுகம் செய்து, அதுவும் ரசிக்கப்பட வேண்டிய ஒரு கலை தான் என உணர்த்தினார். சாத்தூர் பிச்சைக் குட்டியின் வில்லுப்பாட்டைப் பாராட்டிப் பிரபலப்படுத்தினார். அதன் மூலம் வில்லுப்பாட்டுக்கும் தக்கதோர் உயர்நிலை கிடைத்தது.

டி.கே.சி.யின் சிற்பக்கலை வளர்ச்சிப் பணி

மனித உள்ளத்தில் பதிந்து கிடக்கும் உண்மைத் தத்துவங்கள் செம்பிலும், வடிக்கப்பெற்று உயிர்த் துடிப்புடைய வடிவங்கள் எய்திப் பன்னெடுங்காலமாக வாழ்ந்து வரும் வரலாற்றைக் கோயில்களும் அவற்றில் காணும் சிற்பங்களும் நன்கு எடுத்துரைக்கின்றன. தென்காசிக் கோவில் மகாமண்டபத்தில் பத்துத் தூண்களில் வடித்துள்ள சிற்பங்களை டி.கே.சி. உலகறியச் செய்தார். இப்பொழுது வடநாட்டினரும், அயல்நாட்டினரும் அச்சிற்பங்களைக் கண்டு வியந்துசெல்கிறார்கள்.

டி.கே.சி. 1930 முதல் 1935 வரை சென்னை மாகாண அறநிலையத்துறை ஆணையாளராக இருந்தார். அப்போது பல கோயில்களுக்கும் சென்று சிற்பக் கலைகளைக் கண்டு ரசித்து இன்புற்று, அவற்றைப் பாதுகாக்க வேண்டியதன் அவசியத்தை உண்டாக்கினார். தென்காசிக் கோயில் கோபுரம், சிற்பம் எல்லாம் மிக்க உணர்ச்சிக்கு உரிய பொருள்கள். உணர்ச்சி இல்லாமல் பார்த்தால் பாண்டியன், பக்தி, பாடல் எல்லாம் தென்காசியில் இருக்கின்றன. **(மகாராஜன். எஸ்., (தொ.ஆ) ரசிகமணி கடிதங்கள், ப.21)**

செங்கல்லையும், கண்ணாம்பையும் வைத்துக்கொண்டு குவித்து விளையாடினால் சிற்பம் ஆகுமோ? ஆகாது. ஏதோ குட்டிச் சுவருக்குத் தம்பி என்றுதானே சொல்ல வேண்டும் **(மகாராஜன். எஸ்., (தொ.ஆ) ரசிகமணி கடிதங்கள், ப.296)** எனக் குறிப்பிடுவதிலிருந்து இதயத்தை அக்கலையில் செலுத்தி, அதற்கேற்றாற் போல் அனுபவித்து மகிழ்ந்தால் இன்பம் பிறக்கும் என்று டி.கே.சி. வலியுறுத்தி இருப்பதைத் தெளிவாக அறியமுடிகிறது.

தொகுப்புரை

1. டி.கே.சி. ஒரு இரசனை முறைத் திறனாய்வாளர்.
2. பதிப்பாளர்.
3. கடித இலக்கியச் செழுமைக்குக் காரணமானவர்.
4. கவிஞர்.
5. கலைத்தொண்டு புரிந்தவர்.

முடிவுரை

இவ்வாறாக இரசிகமணி டி.கே.சி. தமிழுக்குப் பெரும் தொண்டாற்றியுள்ளார். இவரின் பூத உடல் மறைந்தாலும் அழகியல் திறனாய்வு, கடித இலக்கியம் ஆகியவை என்றென்றும் புகழ்பெற்று வாழும் எனலாம்.

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நவீனத் தமிழாய்வு

(பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்)

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15 பகுதி-1 Part -1

வெளிப்படையானதாகும். நவகாளிப் பகுதியில் நடைபெற்ற இந்து-இசுலாமியக் கலவரம் சமய சார்பற்ற இந்திய நாட்டமைப்புக்காக ஏற்பட்ட அறைகூவல் என்பதுடன், வரலாற்றில் நீக்க இயலாத கறையாகிவிட்ட நிகழ்ச்சியாகும். இந்த நவகாளிக் கலவரம் பற்றி அறிந்த நாமக்கல் கவிஞர், 'வடநாட்டில் கொடுமை' என்ற தலைப்பில் பாடிய பத்துப் பாடல்களும் படிப்பவர் மனதை நெகிழச் செய்வதுடன் நிந்திக்கவும் தூண்டுகின்ற வகையில் அமைந்துள்ளன.

"அன்விய மதமென அடிக்கடி பழிய
அயலுள மக்களைக் சொல்லுவதை
என்னென் றுரைப்பது ஏதென வெறுப்பது
எண்ணவுங் கூடத் தகுமோதான்"

(நாமக்கல் கவிஞர் பாடல்கள், ப.205)

என்ற பாடலில் வடநாட்டில் நடந்த கொடூர நிகழ்ச்சியைப் பற்றிய வெறுப்பினை வெளிப்படுத்திய கவிஞர், அக்கொடுமை மேலும் பரவாது தடுத்து நிறுத்தவும் முற்படுகின்றார்.

உலக அமைதிக்கு அகிம்சை:

போர் ஒன்றுதான் இம்சையிலேயே பெரிதெனக் கருதப்படும், அதனால்தான் மீண்டும் போர் வருவதை ஒருவரும் விரும்பமாட்டார்கள். இத்தகையப் போர்களை வெறுத்தவர் காந்தியடிகள். உலகத்தின் சிக்கல்கள் அனைத்தையும் அமைதி வழியிலும், அகிம்சை வழியிலும் தீர்க்க வேண்டும் என்பதே காந்தியின் அவா. அவர்தம் எண்ணத்தைப் புரிந்து கொண்ட நாமக்கல் கவிஞர்,

"யுத்தக் கொடுமைகள் உலகிலில் ஒழிய
உத்தமம் காந்தியின் உயர்ந்தநல் வழியை
இத்தரை யெங்கணும் பரப்பிடும் கடமை
இந்திய மக்களின் பரம்பரை உடைமை"

(நாமக்கல் கவிஞர் பாடல்கள், ப.147)

எனும் பாடல் மூலம் மக்களின் கடமையினை உணர்த்துகின்றார். போரில் ஈடுபட்ட ஒவ்வொரு நாடும் அமைதி காண முன்வரவேண்டும் என்று விரும்புகின்றார்; எதிர்பார்க்கின்றார். ஆகவே காந்தியின் அகிம்சை வழியினை நன்கு புரிந்துகொண்ட கவிஞர்,

"ஒய்ந்திடும் சண்டையின் ஒவ்வொரு நாடும்
ஒப்பரும் காந்தியின் உரைகளைத் தேடும்"

(நாமக்கல் கவிஞர் பாடல்கள், ப. 53)

என்று பாடுகின்றார். உலக அமைதிக்கு வழிக்காட்டுவது காந்தியின் உயிர்க் கொள்கைகளில் ஒன்றான அகிம்சையே என்பதனை நாமக்கல் கவிஞர் புலப்படுத்துகிறார்.

முடிவுரை:

காந்தியின் உயிர்க்கொள்கையாகிய அகிம்சை எத்தகைய சக்தி வாய்ந்தது என்பதையும், அத்தகைய அகிம்சையினைப் பின்பற்றினால் பல நன்மைகள் உண்டாகும் என்றும், பின்பற்றாமல் விட்டால் பல்வேறு இன்னல்கள் ஏற்படும் என்றும் தம் பாடல்கள் வழியாக நாமக்கல் கவிஞர் பெரிதும் விளக்கிக் காட்டுகின்றார்.

பாவேந்தரின் காதல் புனைவுகள்

முனைவர் க. முருகேசன்
உதவிப்பேராசிரியர், தமிழாய்வுத்துறை, தேசியக் கல்லூரி (தன்னாட்சி),
திருச்சிராப்பள்ளி-620 001, தமிழ்நாடு, இந்தியா

இருபதாம் நூற்றாண்டுத் தமிழ்க் கவிதை இலக்கிய வரலாற்றில் அழுத்தமான பதிவுகளை ஏற்படுத்தித் தனக்குப் பின்னே பாட்டுக் குயிலின் பட்டாளத்தை உருவாக்கிய பெருமைக்குரியவர். கவித்தேரின் சாரதியாய் தம் கவிதை வரிகளால் தமிழ், பெண்ணியம், இளைஞர் இலக்கியம், சமூக முரண்பாடு, பெண்கல்வி, புதிய சொல்லாட்சிகளைக் கையாளும் திறன், வழியோர்க்குக் கல்வியின் இன்றியமையாமையை உணர்த்திய விதம், தொழிலாளர் நிலை, குடும்பக் கட்டுப்பாடு முதலிய பல பொருண்மைகளின் யாப்புனைந்து தம் கண்டனக் கணைகளைப் பாய்ச்சி புத்துலக படைப்பிற்கு வித்திட்டவர் பாவேந்தர் பாரதிதாசனென்றால் அது சாலப் பொருந்தும்.

உலகக் கவிஞர்களோடு பாரதிதாசன்:

பாவேந்தரை உலகக் கவிஞர்கள் பலரோடு ஒப்பிட்டுப் பாராட்டும் போக்கினை 1940களில் இருந்து அறிய முடிகிறது. குறிப்பாகக் கவிஞர்க்குச் சென்னையில் நடந்த நிதியளிப்பு விழாவினையொட்டி வெளியிடப்பட்ட கவிஞர் மலர் (28.07.1946) இத்தகு மதிப்பீடுகள் பலவற்றைத் தாங்கியுள்ளது.

"மேடு பள்ளங்களைக் கண்டே - தலம்
விளைக்க எழுத்துழுவோன் எழுத்தாளி"
(பாவேந்தர் கவிதைகள் இரண்டாம் தொகுதி)

எழுத்தும் எழுத்தாளனும் எவ்வாறிருக்க வேண்டும் என்ற பாவேந்தரின் எண்ணம் நமக்கு நன்கு புலனாகும்.

பன்மொழிப் புலவர் கா. அப்பாத்துரையாரின் மதிப்பீடு (புரட்சிக்கவிஞர் பக்-37) "பாரதிதாசன் மொழிவரையறையால் தமிழ்க் கவிஞர். ஆனால் கருத்தளவையால், கவிதைச் சுவையளவையால், மொழி எல்லையையும் கடந்த உலகக் கவிஞர்களுள் ஒருவர்" என்ற கூற்று உண்மை; வெறும் புகழ்ச்சியில்லை என்ற அவருடைய பாடலையே சான்றாக்கலாம்.

தமிழ்நாட்டு 'வால்ட்விட்மன்' என்ற தலைப்பில் கவிமணி தேசிய விநாயகம் பிள்ளை பாவேந்தர் குறித்த கருத்தில், (கவிஞர் மலர் பக்.12)

"மதங்களிலும் பழைய ஆசாரங்களிலும் ஊறிக் கிடந்த மக்களிடையே இவருடைய பாடல்கள் ஒரு பெரிய மாற்றத்தை உண்டு பண்ணியிருக்கின்றன. ஆதலால் இவர் ஒரு புரட்சிக்கவி. அமெரிக்கப் புரட்சிக்கவி வால்ட்விட்மன்"தமிழ்நாட்டுப் புரட்சிக்கவி பாரதிதாசன் இக்கவிஞரைப் பலதுறையிலும் பாராட்ட வேண்டியது தமிழ் மக்களின் கடமையாகும்" என்கிறார். பாவேந்தரோ இக்கருத்தை மெய்ப்பிக்கும் விதத்தில்

"உலகம் உண்ண உண்! உடுத்த
உடுப்பாய்!
புகல்வேன்; உடைமை மக்களுக்குப்
பொது,
புவியை நடத்துப் பொதுவில் நடத்து!"

என்று மானுட விடுதலைக்குக் குரல் கொடுக்கிறார்.

கட்டுகளற்ற உலகைக் கனவு காணும் பாரதிதாசன் விழித் தெழுந்த மனிதனை நோக்கி வீடுகளிடையில் கவரை இடித்து, விதிகளிடையில் திரையை விலக்கி, நாட்டொடு நாட்டை இணைத்து, வானை இடிக்கும் மலைமேல் ஏறிப்

பாரடா எங்கும் பரவிய மக்களை, என அறிவுறுத்துகிறார். 'இத்தகைய கருத்துடைய பாவேந்தரை

'புரட்சியில் பூக்கும் புது உலகு' என்னும் கட்டுரையில் (பக்.37) இரா. நெடுஞ்செழியன்,

பாரதிதாசனைப் புரட்சிக் கவிஞராக்கியது அவரது சூழ்நிலையேயாகும். ரஷ்யா ஒரு புஷ்கினையும், ஆங்கில நாடு ஒரு ஷெல்லியையும், பிரான்சு ஒரு ஹீகோவையும், அமெரிக்கா ஒரு வால்ட் விட்மனையும் கண்டவாறு திராவிடமும் ஒரு பாரதிதாசனைக் கண்டதென்கிறார்.

ஒப்பாய்வுக் களத்தில் உரைத்துக் காட்டுவது ஒளிமிக்கது. "மனிதர்களைப் பாகுபடுத்தும் ஊர், நாடு, குலம், இனம், சாதி, சமயம் முதலிய எல்லைகளையெல்லாம் கடந்து, பரந்து விரிந்து செல்லும் உலக வானில் பாரதிதாசக்குயில் பாடி மகிழ்கிறது. இதனை,

தன்னுணர்வுப் பாடல்களில் மிகுந்து இருக்கும் 'நான்' பாரதிதாசனிலே ஒரு எல்லையற்ற 'நானாக' மாறுகிறது. 'நான்' பரந்து பட்டவன்: நான் பல்லாயிரக் கணக்கானவன்" என்ற வால்ட் விட்மனைப் போல "காக்கை குருவி எங்கள் ஜாதி, நீள் கடலும் மலையும் எங்கள் கூட்டம், நோக்க நோக்கக் களியாட்டம் நோக்கும் திசையெல்லாம் நாமன்றி வேறில்லை"என்ற பாரதியைப் போல் பாரதிதாசனும் தன்னை மானுட மகா சமுத்திரமாக உருவகித்து" மாவிட சமுத்திரம் நான் என்று கூவ என்று கூவும் எக்காளக் கூற்றிலே மானுடத்தின் முழு வெற்றியையும் காணமுடிகிறது."பேராசிரியர் கா. செல்லப்பன் கருத்துரை (ஒப்பியல் தமிழ் பக்-48-49) இயல்பு நவிற்சியாகவே அமைகிறது.

'மாறுவது இயற்கை' என்பது பாரதிதாசன் ஆத்திருடி. இருக்கும் நிலையை மாற்றிப் புரட்சி மனப்பான்மையை ஏற்படுத்துதல் பிறர்க்கு உரைக்கும் எழுத்தாளர்களின் கடமை என்பது பாரதிதாசன் கருத்து. "தம் எழுத்தால் புதிய சொல்லாட்சியில் ஆட்சி செய்கிறார். "உலகத்தாய், உலகப்பன், உலகப் பொன்விலக்கியம், வையநூல் ஆகிய புதிய சொல்லாக்கங்களை வழங்குகிறார். "பாவேந்தர் தம் பாவிலக்கியத்தில் 'காதல்' என்ற ஒற்றைச் சொல்லை மிக வலிமையான ஆயுதமாக்கித் தம் படைப்புகளில் பாத்திரங்களில் வழி சமூக மாற்றத்திற்கு வித்திடுகிறார்."அவருடைய கவிதையில் 'காதல்' எவ்வாறெல்லாம் புனையப் பட்டுள்ளதென்பதை விளக்குவதே இவ்வாய்வுக் கட்டுரையின் நோக்கமாகும்.

பாவேந்தரின் படைப்புகளில் காதல்:

பாவேந்தர்,

பிறமாந்தரினும் கூரிய தொலை நோக்குடையவன் கவிஞன் (தேவல் பெருமகனார்) என்ற சான்றுக்கு இலக்கணமாகத் திகழ்ந்தவர். 'காதல்' இன்பத்தரும் இனிய உறவாக மட்டும் கொள்ளாமல், பலவிடங்களில் அக்காதலால் சமூக ஏற்றத்தாழ்வுக்குச் சமாதிகட்டவும் செய்கிறார். காதலி தாய் வீடு செல்லினும் அத்தீங்கு எத்தகையதாயிருக்கும் என்பதை,

"எனக்கும் உனக்கும் இடையில் சிறிதே
இடுக்கிருந் தாலும் துன்பம் பொறிதே
அனுப்பு இன்றனை முல்லைச் சிரிப்பை
அதனால் என்மேல் சொரிந்தாய்
நெருப்பை" (வந்தாள்)

என காதலுக்கு இடைவெளி கூடாதென்பதை எடுத்தியம்புகிறார்.

'காதல்' என்ற ஒற்றைச் சொல் இவ்வையத் தலைமை கொள்ளும் தன்மையுடையது.

'அத்தகைய காதலை,

"செம்புலப் பெயல்நீர் போல
அன்புடை நெஞ்சத் தாங் கலந்தனவே"
(குறுந்தொகை)

சங்க இலக்கிய பாடலின் சாரத்தினை பல விடங்களில் பதிவு செய்கிறார்."அதனை,

"உண்டாலே தேன் மலரின் தேன் - இவன்
கண்டாலே தித்திக்கும் தேன்."
(இவன்? தேன்!)

காதலியின் பார்வைக்குத் தேனை உருவகிக்கிற பாங்கு நோக்கத்தக்கது.

சொல்லிலும் செயலிலும் புதுமைக்கு வித்திட்ட புரட்சிக் கவிஞர் 'காதல்' என்னும் சொல்லாட்சியில் பல புதுமைகளையும் சமூக ஏற்றத் தாழ்வுகளையும் எள்ளி நகையாடுகிறார். 'காதல்' என்ற உணர்வு ஏற்பட்டுவிட்டால் சமூகம் எந்த எந்த மாற்றங்களுக்கு தன்னை மாற்றிக் கொள்கிறது என்பதை தம் கவிதைகளில் நயமுற எடுத்தியம்புகிறார்.

வாழ்க்கையின் தொடக்கமும் இடையும்
இறுதியும் எல்லாம்
காதலின் செயல்களே" (லாஃவந்தேன்)

என்பாருடைய கூற்றின் வழி காதலுற்ற காளை ஒருவனின் செயல்களை"சஞ்சீவி பர்வதத்தின்சாரல்" என்ற தலைப்பிலான கவிதையில் மேற்கண்ட சான்றுக்கு வலுசேர்க்கும் கவிதைக் குவியலை காதலி அவமதித்துக் கோவை உதடு நிறந்தாள். காதலன் பறந்து வேலையில் ஈடுபடுகிறான் இக்காட்சியைக் கூற வந்த பாவேந்தர்,

கிட்டரிய காதற் கிழத்தி இடும்வேலை
விட்டெறிந்த கல்லைப்போல் மேலேறிப்
பாயாதோ!
கண்ணின் கடைப்பார்வை காதலியர்
காட்டிவிட்டால்
மண்ணில் குமரருக்கு மாமலையும்
ஓர்கடுகாம்'''' (சஞ்சீவிபர்வதத்தின் சாரல்)

என்று கடைக்கண்பார்வையின் மகிமையினை எடுத்துரைக்கிறார்.

சஞ்சீவ பர்வதத்தின் சாரலில் இராமனுக்காக சஞ்சீவி பர்வதத்தை தூக்கி விளையும் அனுமனின் செயலால் இடுக்கிட்ட குப்பனும் வஞ்சியும் செய்வதறியாது நிகைத்த போது, பாவேந்தர் தம் பைந்தமிழ் பாவால் வஞ்சியின் உள்ளக் கிடக்கையையும் குப்பனாவது தப்பிச் செல்ல மாட்டானா? என்ற காதல் மனநிலையையும் மிக அழகாக எடுத்துரைக்கிறார்.

வம்பு புரிந்தாய்! மலையும் அதிர்ந்திடுதே
முத்தம் கொடுத்து முழுநேர
மும்தொலைத்தாய்
செத்துமடி யும்போது முத்தம் ஒரு கேடா?
என்றனுயி ருக்கே எமனாக வாய்த்தாயே!
உற்றன் உயிரைத்தான்; காப்பாற்றிக்
கொண்டாயா?"
(சஞ்சீவிபர்வதத்தின் சாரல்)

என வஞ்சி கூறுமிடத்தில் உண்மைக் காதலன்பை உருகவிடுகிறார்.

'பில்கணீயம்' என்ற வடநூலைத் தழுவிப் பாவேந்தர் எழுதிய 'புரட்சிக்கவி'யில் காதலியின் கண்ணாடிக் கன்னத்தைக் காட்டி உள்ளத்தைப் புண்ணாக்கிப் போகாதே என்ற கருத்தை வலியுறுத்தும் பாடலில்,

கண்ணாடிக் கன்னத்தைக் காட்டிஎன்
உள்ளத்தைப்
புண்ணாக்கிப் போடாதே போபோ
மறைந்து விடு!
காதல் நெருப்பால் கடலுன்மேல்
தாவிடுவேன்
சாதி எனும் சங்கிலியின் தாளைப்
பிணித்ததடி! (புரட்சிக்கவி)

கடல்போன்ற உன்மேல் தாவத்துடிக்கும் தலைவனின் நெஞ்சம் 'சாதி' என்ற ஒற்றைச் சங்கிலியால் தம் கால்கள் பிணைக்கப் பட்டிருக்கும் நிலையில் இப்பாடல் நமக்கு வருணாசிரம நிலையை எடுத்துக் காட்டுகிறது.

"கருத்தெலாம், உணர்வெலாம்,
களிப்பெலாம் மெய்யில்
உருத்தெழும் ஆற்ற லவையெலாம் காதல்
குருத்தெழும் உணர்வில் அடங்கி அதன்
அழல்
திருத்துவ தன்றித்தம் செயலெதும்
இலவே" (காலரிட்ஜ்)

கருத்துகளிலும் உணர்விலும் மகிழ்விலும்

மெய்யில் உருத்தெழும் ஆற்றல் அவையெல்லாம் காதலேயாகும் என்ற காலரிட்ஜ் அவர்களின் கருத்தோடு ஒன்றிய தன்மையுடையனவாக பாவேந்தரின் வரிகளும் அமைந்துள்ளதை அறியலாம்.

"ஆரத்தழுவி அடுத்தவினா டிக்குள் உயிர்
தீரவரும் எனினும் தேன்போல்
வரவேற்பேன்!·
நெஞ்சார உன்மேல் நேரிழையாள்
கொண்டுள்ள
மிஞ்சுகின்ற காதலின்மேல் ஆணையிட்டு
விள்ளுகின்றேன்!
இன்னும் என்ன? என்றாள். உதாரன்
விரைந்தோடி.
அன்னத்தைத் தூக்கியே ஆரத்
தழுவினான்" (புரட்சிக்கவி)

உள்ளம் ஒன்று கலந்தால் உயர்வும் தாழ்வும் காதலுக்கில்லை என்பதனை இக்கவி நமக்கு அறிவுறுத்துகிறது. உதாரன், அன்னம் இருவின் காதலும் உள்ளார்ந்தவையாக பாவேந்தர் படைத்துள்ளார். மேலும்,

பட்டாளச் சக்கரவர்த்தி பார்த்தாலும்
உன்சிரிப்புக்
கட்டாணி முத்துக்குக் காலில்விழ
மாட்டாரோ? (புரட்சிக்கவி)

காதலியின் சிரிப்புக்குக் காவலனும் (அரசனும்) காலில் விழும்நிலை ஏற்பட்டு விடும் என்பதையும் நயமுற நவில்கிறார்.

'காதல்' என்ற தலைப்பில் மாந்தோப்பில் மணம் என்ற பகுதியில்,

கன்னியனுப்பும் புதுப்பார்வை - அவன்
கட்டுடல் மீதிலும் தோளிலும் - சென்று
மின்னலின் மீண்டது! கட்டழகன் - தந்த
விண்ணப்பம் ஒப்பினன் - புன்னகையால்!
(காதல்)

என்ற கவிதை,

குறிப்பறிதல் (இன்பம்) அதிகாரத்தில் வள்ளுவக் கருத்தை ஒத்ததாக அமைந்துள்ளது. வள்ளுவர் கண்ணால் பார்த்து, பார்த்தவனைக் கவர்ந்து கொள்கிற அந்தச் சிறுபார்வை ஒரு நிமிடப் பார்வைதான். ஆனால் அந்தப் பார்வை இருக்கிறதே அது இன்ப விளையாட்டில் பாதி அல்ல பெரும் பகுதியாகும் என்பதை,

கண்களவு கொள்ளும் சிறுநோக்கம்
காமத்தில்
செம்பாகம் அன்று பெரிது (குறள் 1092)

குறளில் விளக்கியுள்ளார். இக்கருத்தோடு பாவேந்தரும் ஒத்தக் கருத்துடையராகவே விளங்குகிறார்.

நாடிப் பெறுங்காதல் நன்று; அதலிலும்
நவிதன்று
நாடாது பெற்றிடும் காதல்
(ஷேக்ஸ்பியர்)

ஷேக்ஸ்பியரின் கருத்தோடு ஒன்றிருந்திய எண்ணம் உடைய பாவேந்தர் கைம்பெண்ணிற்கு காதல் வந்தால் சற்றமும் மற்றவரும் தம்மை நகையாடுவார் என்பதை தம் காதலனுக்குத் தெரிவிக்கிறாள். இதனை,

நிற்றிடை வாய்த்நிறந்தாள் அதுதான் -
இன்பத்
தேவின் பெருக்கன்று; செந்தமிழே!
கற்றத்தார் மற்றவர் பார்த்திடுவார் - என்
தோழிகள் இப்பக்கம் வந்திடுவார்"
(காதல்)

இக்கவி வரிவாயிலாக அறியமுடிகிறது.

உண்டார்கண் அல்லது அடுநறாக்
காமம்போல்
கண்டார் மகிழ்செய்தல் இன்று
(திருக்குறள். 1090)

கள் உண்டால் தான் போதை ஆனால் இந்தக் காமம் கண்டாலே வெறிகொள்ளச் செய்யும் இயல்புடையது. "இத்தகைய குறளின் கருத்தைப் பாவேந்தர் அழகுற செப்புகிறார்.

காதல் அடைதல் உயிரியற்கை! அது
கட்டில் அகப்படும் தன்மையதோ?- அடி
சாதல் அடைவதும் காதலிலே"- ஒரு
தடங்கல் அடைவதும் ஒன்றுகண்டாய்!-இவி

நீதரு மாற்றம் அகற்றிவிடு! - கை
நீட்டடி! சத்தியம்! நான் மணப்பேன்- அடி
கோதை தொடங்கடி! என்று சொன்னான்
- இன்பம்
கொள்ளை! கொள்ளை!! கொள்ளை!!!
மாந்தோப்பில்!" (காதல்)

காதலின் வலிமையை அழகாக எடுத்துரைக்கிறார்.

காதலும் காதன்மை கூறும்
அமுக(ண்)னீர்
கோதாட்டிக் கொள்ளப் பெறின்
(ஸ்காட் - ஏரிக்கரைச் சிமாட்டி)

காதலும் காதலின்பமும் கண்ணீரை வரவழைப்பதாக இருப்பினும் அது நன்றே எனல் கவிஞர்களின் வரையறை. இதனை,

கூடத்திலே மனப் பாடத்திலே - விழி
கூடிக் கிடந்திடும் ஆணழகை,
ஓடைக் குளிர்மலர்ப் பார்வையினால்-
அவள்
உண்ணத் தலைப்படு நேரத்திலே,
பாடம் படித்து நிமிர்ந்த விழி - தவிற்
பட்டுத் தெறித்தது மாளின் விழி!
ஆடைதிருத்தி நின்றாள் அவள்தான்-
இவன்
ஆயிரம் ஏடு திருப்புகின்றான்!
உள்ளம் பறித்தது நான் என்பதும்-
என்றன்
உயிர் பறித்தது நீ என்பதும்.
(காதல் குற்றவாளிகள்)

கைம்பெண்ணின் உள்ளக் கிடக்கையும் காதலன் அவள் மீது கொண்ட உடல் கவர்ச்சியற்ற உள்ளக் காதலையும் இக்கவிதை நமக்கு எடுத்துக் காட்டுகிறது. இக்கருத்தை வள்ளுவரும்,

இருநோக்கு இவள் உண்கண்உனது
ஒருநோக்கு
நோய்நோக்கொன்று அந்நோய் மருந்து"
(திருக்குறள் 1091)

காதலியின் கண்பார்வைக்கான சக்தியினை இருவிதமாகக் கூறி ஒன்று நோயை உண்டாக்கவும் மற்றொரு பார்வை அந்நோய்க்கு மருந்தாகவும் அமைகிறதென்கிறார்.

என் நெஞ்சிற்கினிய அமுதே, உன்னுடன் நான் கழித்த காலக் கூறுகளையெல்லாம் ஒரு முத்தாரமாகக் கோத்து, அம்முத்துக்களையே கையில் வைத்துக் கருத்திலும் உருட்டி வருகிறேன்; அதுவே என் வழிபாட்டு மனி மாலையாயிருக்கிறது" (ராபர்ட் காமிரான் ரோஜரிஸ்)

இக்கருத்தையே சற்று வித்தியாசமாக பாவேந்தர் கையாள்கிறார்.

கொழிக்கும் ஆணழகன்! - அவன்
கொஞ்சி வந்தே எனது
விழிக்குள் போய்ப் புகுந்தான் - நெஞ்ச
வீட்டில் உலாவு கின்றான்
(காதற்பெருமை)

நெஞ்சாங்கூட்டில் உலாவும் தலைவனாக பாவேந்தர் காதலனை உருவகிக்கிறார்.

"இக்கருத்தோடு பொருந்துமாறு
வள்ளுவனும்,
உடம்பொடு உயிரிடை என்னமற் றன்ன
மடந்தையொடு எம்மிடை நட்பு
(நிருக்குறள் 1122)

உடம்புக்கும் உயிருக்கும் உள்ள தொடர்பு அவருக்கும் எனக்கும் உள்ள உறவு. உயிரை உடல் பிரிய முடியாதது போலவே நானும் அவளும் என்ற கருத்து பாவேந்தரின் கருத்தோடு ஒத்தக் கருத்துடையதாக அமைகிறது.

காதலனும் காதலியும் ஒரு சோலையை அடைகிறார்கள் குறிரையை ஒரு மரத்தில் கட்டிவிட்டு உலாவுகின்றனர். "இதனை,

வந்து சேர்ந்தோம் மலர்ச்சோ லைக்கண்!
என்விரு தோளும் உன் உடல் தாங்கவும்
உன்விரு மலர்க்கைகள் என்மெய்
தழுவவும்
ஆனது! நகரினை அகன்றோம் எனில்!

இன்பக் காதலின் வாயிலை அடைந்த காதலர்களின் மனநிலையை பாவேந்தர் படம்பிடித்துக் காட்டுகிறார்.

காதல் என்னும் பெருந்தலைப்பில் தொழுதெழுவான் என்ற பகுதியில் காதலின் பெரும் விருப்பத்தினை மிக அழகாகப் பேசுகிறார்.

"அறைவாயி லூட்பு குந்தேன்
அத்தான்: தன்கையால் அள்ளி
றிறைவாயின் அமுது கேட்டுக்
கவிவிதழ் நெடிது நிஞ்சி
மறைவாக்கிக் கதவை, என்னை
மணிவினைக் கொளியிற் கண்டு
நதுமவர்ப் பஞ்ச ணைமேல்
நவியாதுட் கார வைத்தான்" (காதல் - தொழுதெழுவான்)

காதல் செக்கச் சிவந்த செவ்வல்லி இது சித்திரையில் பூத்திடும் இயல்புடையது என்கிறார் கவிஞர் பார்ன்ஸ். அதனை,

ஆ என்காதல் ஓர் செக்கச் சிவந்த
செவ்வல்லி
ஆர்வமுறச் சித்திரையிற் பூத்திடும் அதன்
பொலிவு
ஆ என்காதல் ஒரு செவிக்கினிய யாழின்
பண்
ஆரிய புதிய செல்வழிகள் ஆக்கிய
பொழிவும் ஆங்கதுவே"(கவிஞர் பார்ன்ஸ்)

தொழுதெழுவான் குறுந்தலைப்பிலான கவிதையில்,

இமையாது நோக்கி நோக்கி
எழில்நுதல் வியர்வை போக்கி
தென்றலும் போதா தென்று
சிறிறி கைக் கொண்டு வீசி
அன்றிராப் பொழுதை இன்பம்
அறாப்பொழு தாக்கி என்னை
நன்றுறத் துயிலிற் சேர்த்தான்
நவிலுவேன் கேட்பாய் தோழி" (காதல் - தொழுதெழுவான்)

இரவுப் பொழுதை இன்பம் இனிக்கும் பொழுதாக்கும் தலைவனின் காதலை தலைவியின் உள்ளக் கிடக்கை வழி அறிய முடிகிறது.

ஆடவன் முதலில் காதலையே காதலித்து நாளடைவில் பெண்ணைக் காதலிக்கின்றான். ஆனால் பெண்டிரோ முதலில் ஆடவனைக் காதலித்துபி இறுதியில் காதலே காதலிக்கிறாள் (நெமி-டி-கூர்மாண்ட்)

'சொல்லும் செயலும்' கவிதையில் காதலைக் காதலிக்கும் காதலியின் மனநிலையைப் படம் பிடித்துக் காட்டுகிறார் பாவேந்தர்.

முல்லைவிலை என்ன என்றான்
இல்லைஎன்று நான் சிரித்தேன்
பல்லைஇதோ என்று காட்டிப்
பத்துமுத்தம் வைத்து நின்றான்

காதலுடன் தலைவிக்கு கிடைக்கும் முத்தமே இக் காதல் காட்சிக்கு சான்றாகும்.

மனிதன் அவாக்களின்' முடிந்த முடிவு இல்வாழ்வில் இன்பம் பெறுதலே.

திருமணம் என்பது ஓர் உணர்ச்சிக்
காப்புறுதி, மனமொப்பு
அதன் தனர்ச்சிப்பாடு"- (ரஸ்லல் பிரீன்)

மனிதனின் அவாக்களின் முடிவே திருமணமாகும் அத்திருமணமும் எப்படி காதல் வழி அமைய வேண்டுமென்பதை பாவேந்தர் பாடல் நமக்குப் புலனாக்குகிறது.

திருமணம் எனது விருப்ப மாகும்
ஒருத்தியும் ஒருவனும் உள்ளம் கலத்தல்
திருமணம் என்க. (நல்லமுத்துக்கதை)

உள்ளக் கலப்பே திருமணமாகும். "அத்தகைய திருமணம் மணக்கொடை (வரதட்சனையை) யினை சாடுமாறு அமைந்திருப்பது பாவேந்தரின் சமூகம் பற்றிய தனது பெருவிருப்பத்தின் வெளிப்பாடாகக் கருதலாம்.

நானும்என் துணைவியும் நானும்
முயல்வதில்
சிறைப்படல் காதல் தேனருந் துவதாம்!
இறப்புறல் எங்கள் இன்பத்தி
னெல்லையாம்! (நல்லமுத்துக்கதை)

என்று எல்லை வரையறுக்கிறார்.

மணவினையுட் புகாதவர் புக விரும்புகின்றனர்; புகுந்தவர் வெளியேற விரும்புகின்றனர். அப்படியானால், திருமணம் கேள்வி எழுப்பி ஆராய்வதற்குரிய செய்தி அல்லவா?" (எமர்சன்)

இக்கருத்தை,

'பொன் அத்தான்' என்ற தலைப்பிலான கவிதையில்

என்,
சீரைத்தான் கோரித்தான்
தேரிற்றான் ஏறித்தான்
திரும்புகின்றான் தோழிப் பெண்ணே
என் அத்தான் - அவன்
விரும்புவதும்
உலகத்தில் என்னைத்தான்

(காதல் கவிதைகள் - பொன்அத்தான்)

பாவேந்தர் எடுத்தியம்புகிறார்.

முடிவுரை:

தன் இனத்தையும் மொழியையும் பாடாத கவிதை, வேரில்லாமரம் கூடில்லாத பறவை என்று பாடிய உருசியக் கவிஞர் இரசூல் கம்சதோவின் கவி வரிக்கு தமிழ் அடையாளம் பாவேந்தர் ஆவார்.

'காதல்' இரு உள்ளக் கலப்பாக மட்டும் தம் பாடல்களில் பதிவு செய்யாமல் சமூக மாற்றத்திற்கான நல்ல கூராயுதமாகக் காதலைப் பதிவு செய்துள்ளார்.

காதல் குறித்த உலகப் பெருங்கவிஞர்களோடு நிகரின்றி தனித்தியங்கும் தனிப்பெரும் படைப்பாளியாய் காதலிலும் தம் மொழியடையாளத்தை இழக்காத மொழியுணர்வு காதலையே வலியுறுத்துகிறார்.

காதலன் ஒரு சராசரி மானுடனாகவும் காதலி அரசுக்குரியவளாகவும் படைத்து இல்விருவரின் காதல் வெற்றி சமூகத்திற்கு கிடைத்த வெற்றியாக களிப்படைகிறார்.

கைம்பெண் காதலை அங்கிகரித்து அக்காதலும் உன்னதமுடைய தன்மையது என்பதை,

கோரிக்கை அற்றுக் கிடக்குதண்ணே இங்கு
வேரித் பழுத்த பலா (கைம்மைப்பழி)

கோரிக்கையற்ற கைம்பெண் காதலை சமூக கண் கொண்டு சாடுகிறார். இவரின் புதுமைக் கருத்தால் இன்று கைம்பெண் மணம் வெகுவாக அங்கிகரிக்கப்படுதல் பாவேந்தருக்குக் கிடைத்த வெற்றியாகும். ஆதலால் காதல் செய்வீர் - பாரதியின் வழி காதலைக் காதலுக்காகவே செய்யும் மகத்துவத்தைச் செய்வோம்.

நவீனத் தமிழாய்வு (பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்) தொகுதி 6, எண்.1, ஜனவரி-மார்ச் 2018 ISSN:2321-984X
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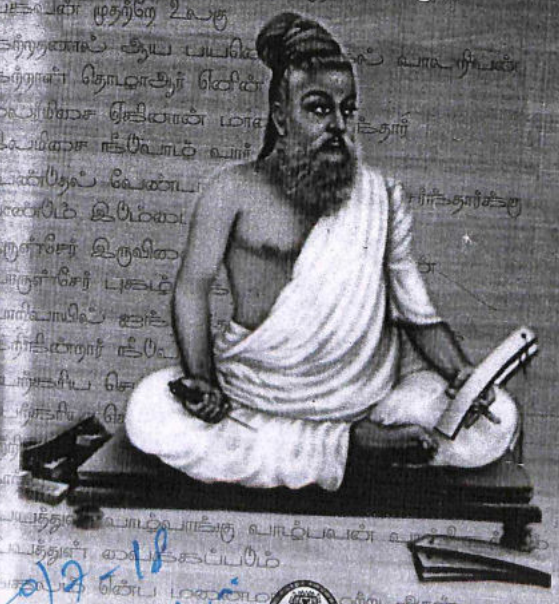
திருக்குறள் விழுமியங்கள்

முனைவர் கோ. தேவிபூமா

திருக்குறள் விழுமியங்கள்

தொகுப்பாசிரியர்
முனைவர் கோ. தேவிபூமா



மன்னர் திருமலை நாயக்கர் கல்லூரி (தன்னாட்சி)

67. திருக்குறள் சுட்டும் நீர் வளம்

முனைவர் கூ.முத்தையன்

உதவிப்பேராசிரியர், தமிழாய்வுத்துறை, தேசியக்கல்லூரி (தன்னாட்சி), திருச்சிராப்பள்ளி

நீர் மக்களின் பசிப்பிணியைப் போக்கி,
வாழ்வியல் சூழலினை மேம்பாடு அடையச் செய்கிறது.
இயற்கைச் சமநிலையைக் காக்கிறது.

இத்தகைய நீரின் தன்மை இன்று நம்மிடையே இன்மையால் வறட்சியும், வறுமையும் நம்மைச் சூழ்கின்றன. இதை உணர்ந்த வள்ளுவப் பெருந்தகையர் பல ஆண்டுகளுக்கு முன்பே நீரின் முக்கியத் தன்மையைச் சுட்டிக்காட்டி, நீர்தான் ஒரு நாட்டின் வளத்தை மேம்படுத்த முடியும் என்ற ஆழ்ந்த கருத்தை தன் வாக்குத் திறத்தால் சுட்டிக்காட்டியதை இக்கட்டுரை வாயிலாகக் காண்போம்.

மக்களின் அறவாழ்க்கைக்கு அடிப்படையாக அமைவது, அவர்கள் வாழும் நாட்டின் வளம். இயற்கை வளம் நிறைந்த நாட்டில் வாழும் மக்கள்தான், நூல்களில் கூறியுள்ள அறத்தை நெறிபிறழாமல் கடைப்பிடிக்க முடியும். அதனால் அறவாழ்க்கைக்கு வழிக்காட்ட வந்த வள்ளுவப் பெருந்தகையார்,

நீரின்றி அமையாது உலகெனின் யார்யார்க்கும்
வான்இன்று அமையாது ஒழுக்கு. கு-20

எவ்வகையால் உயர்ந்தவரும் நீர் இல்லாமல் இவ்வுலகில் வாழ முடியாது. என்பதை நீரின் இன்றியமையாமையை பல ஆண்டுகளுக்கு முன்பே நீரின் சிறப்பை வான் சிறப்பு என்ற அதிகாரத்தில் சுட்டியுள்ளார்.

மேலும்,

வானோக்கி வாழும் உலகெல்லாம் மன்னவன்
கோல்நோக்கி வாழும் குடி. கு-542

மன்னவன் தன் முறைசெய்யும் செங்கோலை நோக்கி மக்கள் வாழ்வது போல் உலகத்து உயிர்களெல்லாம் மழையை நோக்கி வாழ்கின்றன. மழை பெய்யவில்லை என்றால் இப்பெரிய உலகத்திலே தானமும் தவமும் நடைபெறா என்பதை

தானம் தவமிரண்டும் தங்காவியன் உலகம்
வானம் வழங்கா தெனின். கு-19

இக்குறள் மூலம் நாட்டின் கண் வாழும் மக்களின் வாழ்வு நிலை எவ்வாறு மாறும் என்பதை நன்கு உணர்த்தியுள்ளார்.

பண்டைய மக்கள் மழைநீரினை வீணாக்காமல் மட்பாண்டங்களில் சேமித்தனர். மழைபொழியும் போது சுட்ட மட்கலனோடு சுடாத மட்கலனும் கலந்திருந்து அச்சுடாத மட்கலம் மழையில் கரைந்து அழிந்தது என்பதை

ஈர்மண் செய்கை நீர்ப்படுபசுங்கலம்
பெரு மழை பெயற்கு ஏற்றாங்கு. நற்றிணை - 308.

என்ற பாடல் நற்றிணையில் நீர் சேமித்தலின் முக்கியத்தை உணர்த்துகிறது.

ஏனைய எல்லாத் தொழிலைக் காட்டிலும் வேளான் தொழிலே சிறந்த தொழில். அதுவே எல்லாத்தொழில் செய்பவர்களுக்கும் உணவைத் தருகிறது. மழை என்னும் வளம் செல்வத்தின் வளம் குறையுமானால், உழவர்கள் கலப்பைக் கொண்டு உழமாட்டார்கள்.

ஏரின் உழாஆர் உழவர் புயலென்னும்
வாரி வளங்குன்றிக் கால். கு-14

என்று தொழிலின் சிறப்பை சங்க கால மக்கள் வேளாண் தொழில் செய்ததை தொல்காப்பியர்

" வேளாண் மாந்தர்க்கு உழுதூண் அல்லது
இல்லென மொழிப பிறவகை நிகழ்ச்சி
வேந்துவிடு தொழிலின் படையும் கண்ணியும்
வாய்ந்தனர் என்ப அவர்பெறும் பொருளே"

என்று வேளாண் தன்மையை தொல்காப்பியரும் புலப்படுத்தியுள்ளர். மேகத்திலிருந்து மழைத்துளி விழுந்தால் அல்லாமல் பசுமையான புல்லின் தலையையும் காணமுடியாது என்பதை

விசும்பின் துளிவீழின் அல்லாமற் றாங்கே
பசும்பின் தலைகாண்ப அரிது. கு-16

என்கிறார் வள்ளுவர்.

அவ்வாறு நீர் நிறைந்த வயல் வெளிகளில் விளைந்த நெல் மணிகளின் வனப்பை குன்றூர்க் கிழார் மகன் கண்ணத்தனார் கீழ்வரும் புறநானூற்றுப்பாடல் வரிகளில் விளக்கியுள்ளார்.

தண்புனல் பரந்த பூசல் மண் மறுத்த
மீனின் செறுக்கும் பிறர் அகன்றலை நாடே - புறம் (7)

ஏர்பரந்த வயல் நீர்பரந்த செருவின்
நெல்மலிந்த மனைப் பொன்மலிந்த மருகின் - புறம் (335)

பதினாறாம் நூற்றாண்டில் தோன்றிய அறிவியல் வளர்ச்சிகள் மக்களிடத்தில் பல இயற்கை உண்மைகளை விளக்கி சமுதாய மாற்றத்திற்கு வித்திட்டது. கடல் பரப்பில் ஏற்படும் ஆவியாதல் மாற்றம் மூலமாக மேகங்களில் நீர் தேக்கிவைக்கப்பட்டு பின் மழை பொழிவு தோன்றுவதை வள்ளுவன், தன் காலத்திலே அறிந்து

"நெடுங்கடலும் தன்நீர்மை குன்றும் தடிந்தொழிலி
தான்நல்கா தாகி விடின். கு-17

என்று உணர்த்தியுள்ளார்.

மழை தவறாது பெய்வதால் தான் இந்த உலக உயிர்கள் வாழ்ந்து வருகின்றன. ஆகையால் அந்த மழை உயிர்களுக்குச் சாவா மருந்து (அமிழ்தம்) என்று சொல்லத் தக்கது.

வான்நின்று உலகம் வழங்கி வருதலால்
தான் அமிழ்தம் என்றுணரல்பாற்று. கு-11

உண்பவர்க்கு நல்ல உணவுகளை உண்டாக்கி அவற்றை உண்ணுகின்ற வாக்குத் தானும் உணவாக மழை அமைகிறது. என்கிறது பின்வரும் குறள்

துப்பார்க்குத் துப்பாய துப்பாக்கித் துப்பார்க்குத்
துப்பாய தூஉம் மழை.கு-12

எவ்வாறு கைம்மாறு கருதாமல் பெய்யும் மழைக்கு உயிர்கள் என்ன கைம்மாறு செய்கின்றனர், அவற்றை எதிர்பார்த்து மழை பெய்வதில்லை என்பதை வள்ளுவர்

கைம்மாறு வேண்டா கடப்பாடு மாரிமாட்டு
என்ஆற்றங் கொல்லோ உலகு. கு-211

இவ்வாறு பல வகையில் பயன்படும் நீரை மக்கள் திறம்பட சேமித்து பயன்படுத்தியுள்ளனர் என்பதை "இடையுடைப் பெருமழை எய்தா ஏகப் பிழையா விளையுள் பெருவளம் சுரப்ப மழைபிணித்து ஆண்ட மன்னவன்" என்று சிலப்பதிகாரத்திலும் நீரின் பயன்பாட்டை குறிக்கின்றது.

இருபுனலும் வாய்த்த மயலயம் வருபுனலும்
வல்லரணும் நாட்டிற்கு உறுப்பு கு-737

என்று நீரை வகைப்படுத்தி கீழ்நீர், மேல்நீர் எனப்பட்ட இரு தண்ணீரும் வாய்ப்புடைய மலையும், அதிலிருந்து வருகின்ற நீரும். அழியாத கோட்டையும் நாட்டிற்கு உறுப்புகளாகும்.

நீர் நாட்டினைக் காக்கும் அரண் வகைகளுள் ஒன்றாக உள்ளது என்பதை நற்றிணைப் பாடலில் 'தேர் வண் சோழர் குடந்தை வாயில் மாரிஅம் கிடங்கின் ஈரியமலர்ந்த" -379 என்றும் 'அன்பகத் தில்லா உயிர்வாழ்க்கை வன்பாற்கண்' மனத்தில் அன்பில்லாத மக்கள் இல்லறத்தில் நன்கு வாழ்தல் என்பது வலிய பாலைநிலத்தில் உலர்ந்த மரம் தளிர்த்தல் போன்றதாகும். போன்ற தன்மைகளை நீரின் அளவைக் கொண்டு மலரின் தண்டு அமைவதை உவமையாகக் கூறி மக்களிடையே ஊக்கமுடைமையை பின் வரும் குறளில் வலியுறுத்தினார்.

வெள்ளத் தனைய மலர்நீட்டம் மார்ந்தர்தம்
உள்ளத் தனைய துயர்வு. கு-595

மக்கள் தொகைப் பெருக்கத்தால் நம் நாட்டில் நீரின் தேவை அதிகமாகிறது. அதேசமயம் நம்முடைய நீரின் வளங்கள் குறைவாக இருக்கின்றது. ஆகையால் நமக்குக் கிடைக்கும் ஒவ்வொரு சொட்டு நீரையும் பாதுகாக்க நாம் நடவடிக்கை மேற்கொள்ள வேண்டும்.

பஞ்ச பூதங்களில் ஒன்றான நீர் நீர்ம சுழற்சி அடைந்து சூழலினை ஆளுகை செய்கின்றது. உயிரினங்களின் வாழ்விடமாகவும் உயிர் ஊற்றாகவும் செயல்படும் நீர் நாட்டின் பொருளாதார வளமைக்கும் வலிமைக்கும் முக்கிய காரணியாகத் திகழ்கின்றது. மக்களின் அகப்புற வாழ்வியலும் நீரின் ஆளுமைக்கும் உட்பட்டே அமைகின்றது. இத்தகைய நீர், நீர் ஆதாரங்களை வள்ளுவர் வாக்கினைப் போல் காப்பது நம் கடமை ஆகும்.

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(பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்)

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15 பகுதி-1 Part -1

பாரதியின் பார்வையில் சமூகம்

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உதவிப்பேராசிரியர், தமிழ்த்துறை, தேசியக் கல்லூரி (தன்னாட்சி),
திருச்சிராப்பள்ளி - 620 001, தமிழ்நாடு, இந்தியா

முன்னுரை

வெள்ளையர் ஆதிக்கத்தின் விடாப்பிடியில் சிக்கித் தவித்த இந்திய மக்கள் ஆங்கிலேயரின் அடக்குமுறையில் ஒடுக்கப்பட்டனர். அதோடு இந்திய நாட்டின் அனைத்துத் துறைகளும் ஆங்கிலேயர் வசம் இருந்தன. இந்நிலையில் தான் சமுதாயத்தில் போராட்ட இயக்கங்களும் புரட்சிகளும் வெடித்தன. இந்திய நாட்டு மக்களிடம் ஆங்கிலேய ஏகாதிபத்தியத்தை எதிர்க்கின்ற தன்மை ஏற்படவும், சமூகத்தில் விழிப்புணர்வு அடையவும் உரிமைக்கீதம் எழுப்பியவர் மகாகவி பாரதியார். இவர் அந்நியச் சமூகத்தினரிடம் காணப்பட்ட சாதிப்பாகுபாடு, தீண்டாமை, வறுமை, மொழிப்பாகுபாடு, தனிமனித ஒழுக்கச் சிந்தனைகள், ஆன்மீகம் ஆகியவற்றால் தனது படைப்புகளின் வாயிலாக அவற்றையெல்லாம் கண்டு சீர்குலைந்த சமுதாயத்தைச் சீர்திருத்துவதற்குப் பாரதி மேற்கொண்ட புரட்சிக்கரக் கருத்துக்களை எடுத்துக் கூறுவதாக இக்கட்டுரை அமைகிறது.

சமூகம் - விளக்கம்

சமூகம் என்பது ஒவ்வொரு மனிதனும் ஏனைய மனிதர்களிடம் கொண்டிருக்கின்ற சிக்கலான சமூக உறவு முறைகளைக் கொண்ட தொடர்பாகும். மனிதன் கொள்கின்ற தொடர்புகளை எல்லாம் சமூகத் தொடர்புகளாகவிட முடியாது. ஏனெனில் இது மாறிக்கொண்டும், வளர்ந்து கொண்டும் இருக்கின்ற தன்மையைப் பெற்றிருக்கின்றது. ஆகவே இன்றைய வாழ்வின் அடிப்படையே சமூகமாகும்.

'சமூகம்' என்ற சொல் தம்முள் உறவுகளை ஏற்படுத்திகொள்ளும் மக்கள் அனைவரையும் குறிக்கும். ஆண்கள், பெண்கள், குடும்பங்கள், தொழிலாளர்கள், முதலாளிகள், இனங்கள், சங்கங்கள், குடிகள் ஆகிய மனிதச் சேர்க்கைகள் எல்லாம் சமூகம் என்றே சொல்லுகிறோம்.

சமூகமானது நாட்டுக்கு நாடு, மொழிக்கு மொழி வேறுபட்டதன்மை உடையதாகும். அதன் பண்பாடு, நாகரிகம் போன்றவை மக்களிடம் மாறுபட்டு விளங்கும் தன்மையுடையது. அவ்வகையில் நமது இந்தியச் சமுதாயம் ஒவ்வொரு காலத்தில் ஒவ்வொரு விதமான போக்கினைக் கொண்டு மாற்றம் பெற்று வந்துள்ளது. இவ்விதமானப் போக்கினைக் கண்ட மகாகவி கருத்துக்களைக் கூறியுள்ளார்.

இந்தியச் சமூகச்சூழல்

இந்திய வரலாற்றில் கி.பி. 1819 ஆம் நூற்றாண்டுகளில் ஏற்பட்ட அரசியல் மாற்றங்கள் சமயம், சமூகம், பண்பாடு, பொருளாதாரம் ஆகிய துறைகளில் மாறுதல்களை ஏற்படுத்தின. பிற்போக்கான சமுதாயம், அதில் ஏழ்மை, அறியாமை, மூடநம்பிக்கை அவற்றால் பிறந்த தீய பழக்கங்களும் மிகுந்துள்ளன. என்ற கருத்துப் பரவல் எழுந்தது. இத்தகைய நிலைகளில் இந்திய நாடு ஆங்கிலேயருக்கு அடிமைப்பட்ட காலமாக இருந்தது. இந்திய மக்களிடம் மூடப்பழக்க வழக்கங்களும், அறியாமைத் தன்மையும் குறைவில்லாமல் இருந்தது. சமூகத்தில் வகுப்புச்சண்டை, சாதிபேதங்கள்,

பொருளாதார ஏற்றத்தாழ்வுகள், தீண்டாமைக் கொடுமைகள் மக்களை அலைக்கழித்தன. இத்தகைய ஏற்றத்தாழ்வுகளை, முரண்பாடுகளைக் கண்டு நெஞ்சம் பொறுக்காத பாரதியார், தான் வாழ்ந்த சமூகத்தை சீர்மைபடுத்தும் நோக்கில் பல வழிகளைக் தமது படைப்புகளில் கூறியுள்ளார். பாரதி அவர் காலத்தில் நிலவிய எந்தப் பிரச்சினைக்கும் அப்பால் சென்று ஒதுங்கிவிடாமல் முடிந்தவரையில் தன் சிந்தனையாலும் செயலாலும் சமுதாயத்திற்கு கருத்துகளை கூற விழைந்திருக்கிறான் என்று பி.யோகேசுவரன் கூறுகிறார்.

பாரதியின் சமூக சீர்திருத்தப்போக்கிற்கு, அவர்காசியில் வாழ்ந்த வாழ்க்கையே தொடக்கமாக அமைந்தது எனலாம். அங்கு தோன்றிய சீர்திருத்த கருத்துக்களுக்கு உருக்கொடுத்து ஒளியேற்றியவர் அன்னை நிவேதிதா தேவி ஆவார். அன்னை நிவேதிதா தேவி அவர்களின் தொடர்பும், பல ஞானியர்களின் தொடர்பும் பாரதியாரின் உலகளாவிய சீர்திருத்த நோக்கத்திற்குத் துணை நின்றிருப்பதாகக் கொள்வர். பாரதியின் இத்தகைய சீர்திருத்தம் பல்வேறு வகையில் ஏற்றத்தினைப் பெற்றுள்ளது.

சாதி

இந்தியச் சமூக அமைப்பில் மக்களிடம் சாதி முக்கியமான இடத்தைப் பெற்றுள்ளது. யாதும் ஊரே யாவரும் கேளிர், ஒன்றே குலம் ஒருவனே தேவன், சாதிகள் இல்லையடி பாப்பா, என்று இலக்கியம் படைத்த புலவர்கள் தங்களுடைய எண்ணத்தை கூறினர். இதுபோன்று மனிதன் வாழவேண்டும் என்று விரும்பினர். ஆனால் மனிதன் ஒன்றுபட்டு வாழத் தவறிவிட்டான். தமிழர்களின் நிலையை கண்ட இலக்கிய கால புலவர்கள் பாடிச்சென்றாலும் மனித சமூகம் தழைத்தோங்கும் வகையில் சாதிப்பாகுபாட்டை களைத்து, தன்னுடைய எழுச்சி மிக்க கருத்துக்களை மக்களிடம் கூறியவர் மகாகவி பாரதியார்.

சாதி என்பது தமிழ்ச் சொல் அன்று. ஜாதி என்ற வடமொழிச் சொல்லே சாதி என்று தமிழில் வழங்குகிறது. என்று சாமி சிதம்பரனார் குறிப்பிடுகின்றார்.

நமது பாரதத்தில் முக்கியமாக் காணப்படும் சாதி சமய வேற்றுமைகள் மறைந்து ஒன்றுபட்ட ஒரு தாய் மக்களாக மாறி வாழ வேண்டும் என்பதை பாரதியாரின் விருப்பமாயிருந்தது. சங்க காலம் தொட்டே சமூகப்பாகுபாடு மக்களிடம் இருந்தது.

வேற்றுமை தெரிந்த நாற்பால் உள்ளும்
கீழ்ப்பால் ஒருவன் கற்பின்
மேற்பால் ஒருவனும் அவன் கண்படுமே

என்று புறநானூற்றுப் பாடல் வழி அறியப்படுகிறது. தொழில் அடிப்படையில் தமிழ்நாட்டில் சாதிப்பிரிவுகளும் தோன்றின.

பாரதி வாழ்ந்த காலத்தில் இச்சாதிப் பிரிவினைகள் இந்திய மக்களிடம் மேலோங்கி இருந்தது. ஆங்கிலேயரிடம் அடிமைப்பட்டிருந்த நிலையிலும் சாதிப்பாகுபாடு பேசிச் திரிந்த மூடரைக் கண்டு மனம் வெறுத்தார். இத்தகைய இழிநிலையை மகாகவி

சாதிப் பிரிவுகள் சொல்லி- அதில்
தாழ்வென்றும் மேலென்றும் கொள்வார்
நீதிப்பிரிவுகள் செய்வார்- அங்கு
நித்தமும் சண்டைகள் செய்வர்

என்று தனது பாடல்வரிகளில் உயர்வு, தாழ்வு என்ற அடிப்படையில் சாதிப்பாகுபாட்டை வளர்த்துக்கொண்டு ஒற்றுமையின்மையால் சமூகத்தினர் பிளவுண்டு வாழ்வதைக் கூறுகிறார்.

நாட்டு மக்கள் அனைவரும் தொழில்களை மாண்புறச் செய்து ஒற்றுமையுடன்

வாழவேண்டும். இத்தகையில் வாழும் போது அவர்களின் அடிமை வாழ்வு அகன்றுவிடும் என்பதை

ஜாதிக் கொடுமைகள் வேண்டாம்- அன்பு
தன்னில் செழித்திடும் வையம்

என்று பாரதி சமூகத்திற்கு கூறும் போது அடிமை வாழ்வு அகன்று, நிலையான வாழ்வில் செழித்திடுவதற்கான கருத்தினை வெளிப்படுத்துகிறார்.

இந்தியச் சமூகத்தினர் ஒவ்வொருவரும் தன் குலப்பெருமையைப் பேசும்போது நாட்டில் மக்களிடம் பிளவு பாகுபாடு ஏற்பட்டு சமூகம் சீர்குலையக் காரணமாக இருக்கின்றன. இந்திய சமூகத்தினர் சாதிப் பற்றினையும், சத்திய வாழ்வினையும் கடைபிடிக்க வேண்டும். அப்போது சமூகம் சீர்மை பெறும். இல்லையெனில் மக்களுக்கு துன்பம் ஏற்படும் இவற்றினை தனது கட்டுரையில்

இன்றைய இந்து சமூகத்திலே தாழ்த்தப்பட்ட குலத்தைச் சேர்ந்த ஒருவன் எவ்வளவுதான் அறிவுச் செல்வம் பெற்றவனாக இருந்தாலும் அவனைப் பிராமணனாகச் சமூகம் ஏற்காது. ஆயின் கல்வியறிவு அற்ற நிர்மூடனாக ஒருவர் பிராமணக் குலத்தில் பிறந்துவிட்டால் அவன் பிராமணக் குலப் பெருமைக்கு உள்ளாகிறான். உலகில் வெற்றியும் வேறுபாடுகளும் இருப்பது இயற்கையே. ஆயின் வேறுபாடுகள் கட்டாயம் ஏற்றத்தாழ்வுகளாக விளங்குவது மடமை என சாதி ஏற்றத்தாழ்வினால் மக்களிடம் உண்டாகும் பிரிவினை நிலையினைக் கூறுகிறார்.

இந்தியச் சமூகத்தினரிடம் உயர்வு தாழ்வு என்ற பாகுபாடு, குலத்தாலும், நிறத்தாலும், நிலை நாட்டுவதைத் தவிர்த்து, அனைவரும் நீதிநெறியோடு செயல்படுவதை 'பாப்பா' பாட்டில்

சாதிகள் இல்லையடி பாப்பா! - குலத்
தாழ்ச்சி உயர்ச்சி சொல்லல் பாவம்

எனக் கற்பிக்கிறார். சாதி அடிப்படையில் உயர்வு தாழ்வுகள்; இருப்பதை

வெள்ளை நிறத்தொரு பூனை - எங்கள்
வீட்டில் வளருது கண்டீர்,
பிள்ளைகள் பெற்றப் பூனை அவை
பேருக்கொரு நிறமாகும்

என்று இந்து சமூகத்தினரிடம் பிளவு பட்டு வளர்ந்து வந்ததை பாரதியார் தனது பாடலில் கூறியுள்ளார்.

மக்களின் மேலோர், கீழோர் என்ற பாகுபாட்டை தவிர்த்து ஒற்றுமையுடன் செயல்பட வேண்டும், மத நல்லிணக்கக் கொள்கையை நாம் அனைவரும், கடைபிடித்து சிறந்த பாரத சமுதாயமாக உருவாக்க வேண்டும் என்பதை பாரதியார் தனது கருத்துக்களாக கூறியுள்ளார்.

சமய வளர்ச்சி

இந்தியச் சமூகத்தினரிடம் குழுநிலையிருந்து உலகளாவிய நிலை வரைக்கும் சமயம் வளர்ந்துள்ளதைக் காண்கிறோம். நாட்டில் எத்தனை சீர்திருத்த இயக்கங்கள் தோன்றினாலும், அரசாங்கம் எத்தனை சட்டங்கள் இயற்றினாலும் சமய உண்மைகள் மக்களின் உள்ளத்தில் ஆழப்பதிந்து கொண்டுதான் இருக்கின்றன.

பூமியிலேயே கண்டம் ஐந்து
மதங்கள்கோடி

என்று பாரதியார் கூறுகிறார். மனித சமுதாயத்தின் சக்தியாக சமயம் உள்ளது. இறைவன் எல்லோரையும் எல்லா உயிர்களையும் படைத்தவன் - எல்லோருக்கும் பொதுவானவன் என்பதை மனதில் எண்ணிக் கொண்டு உலகளாவிய அளவில் சமத்துவ நிலையை அடைய வேண்டும் என்று பாரதியார் கூறுகிறார்.

மொழிப் பாகுபாடு

பேசுவது ஒரு கலை. இப்படிப்பட்ட அறிவார்ந்த கருவி, மனித குல மேம்பாட்டின் மாபெரும் சக்தி ஆகும். மொழியின் உதவியின்றி மனிதனால் வாழ இயலாத நிலையில் மொழியே மக்களின் மனத்தைப் பிரதிபலிக்கும் கண்ணாடி என்று உளவியலார் கூறுவர். மக்களால் போற்றப்படும் இத்தகைய தாய்மொழி வாழ்விழந்து, சிறப்பு குன்றுமானால்; அது மக்களின் குற்றமே என்று திரு.வி.க. கூறுவார்.

மேலும் தாய்மொழி வாழ்விழந்தால் தரைமோதி மாய்தல் நலம் போய்க் கடலில் விழுதல் நலம், பொலிதருமோ உடலுயிரோடு என்று தாய்மொழி மக்களின் அடிப்படைத் தேவையைக் கூறுகிறார்.

மொழியின் துணைகொண்டு ஒருமைப் பாட்டை வளர்த்த பாரதி தமிழ், ஆங்கிலம், வடமொழி இந்தி, பிரெஞ்சு முதலான பலமொழிகள் கற்றறிந்தவர். தாய்மொழியின் மீது பற்றுகொண்டு தமிழை வளரச் செய்தார். அதோடு மட்டுமல்லாமல் மொழியின் துணைகொண்டு ஒருமைப் பாட்டினை வளர்த்த பாரதியார்.

யாமறிந்த மொழிகளிலே
தமிழ்மொழிபோல்
இனிதாவது எங்கும் காணோம்

என்று கூறும்போது தாய்மொழியின் மீது கொண்டிருந்த உண்மையான மொழிப்பற்றினை அறிய முடிகிறது. இந்திய மக்களிடம் தாய் மொழி நிலைப் பெற வேண்டும் என்பதை

சொல்லில் உயர்வு தமிழச்சொல்லே-அதைத்
தொழுது படித்திடடி பாப்பா

என்று பாடுகிறார். தமிழர் தாய்மொழியில் கல்வி கற்பிக்கப்பட வேண்டும். மேலும் அவர்கள் தொழில் படிப்பையும் கற்றுக் கொண்டு அடிமை வாழ்வினை அகற்றுதல் வேண்டும்.

ஏழ்கடல் வைப்பினும் தன் மணம் வீசி
இசை கொண்டு வாழியவே

என்று மகாகவி பாடுகின்றபோது தமிழர் தாய் மொழியை முதன்மை மொழியாகக் கொண்டு புகழ் பரப்பி வாழ வேண்டும் என்கிறார்.

ஆன்மிகம்

மனிதச் சமூகம் சராசரி வாழ்க்கையிலேயே சதிராட்டம் நடத்திக் கொண்டிருக்கிறது. நிலையில்லாத உலகையும், வாழ்வையும், இளமையையும், பொருளையும் நிலையானது என்றெண்ணி போரிட்டுக் கொண்டிருக்கிறது. ஒற்றுமையின்மை என்ற போர்க்குணத்தோடு விவேகமற்ற செயல்பாடுகளோடும் செயல்பட்டுக் கொண்டிருக்கிறது. இதனால் மக்களிடம் ஒற்றுமையும், அமைதியும், சமத்துவமும் மறைந்து மிருகத்தனமான எண்ணங்கள் செய்வடிவம் பெறுகின்றன. அதன் காரணத்தால் உலகெங்கும் பரந்து பட்ட நிலையில் வாழக்கூடிய மனித இனம் சுயநலத்தின் மேலீட்டால் அமைதியிழந்து வாழ்ந்து கொண்டிருக்கிறது.

இதன் அடிப்படையில் உலகம் நாடு, இனம், மொழி, முதலாளி வர்க்கம், தொழிலாளி வர்க்கம் என்ற அளவில் பல்வேறு கூறுபாடுகளில் பிளவுபட்டு காணப்படுகிறது.

இத்தகைய சூழ்நிலையில் மதங்களும் விமர்சிக்கப்படுகின்றன. ஒரு விதத்தில் மதம், மனிதச் சமூகத்தைப் பிரிக்கிறது என்று குற்றம் சொன்னாலும் மற்றொரு விதத்தில் மனிதவர்க்கத்தை ஒன்று சேர்த்து அறிவூட்டி அமைதி நிலவ வழிவகுக்கிறது. அமைதியும் அறிவும், நிலைபெற அது ஒரு கட்டமைப்பாகவே செயல்படுகிறது. எந்த ஒரு மதமும் மனிதனை மனிதன் துன்புறுத்துவதை அடிமைப்படுத்துவதை, அடிப்படைத் தேவைகளைத் தர மறுப்பதை ஏற்கவில்லை. மாறாக மனிதச் சமூகத்திடமும் மற்ற

உயிர்களிடத்தும் அன்பு செலுத்தவே வற்புறுத்துகின்றன. அந்தந்த மதத்தில் வேத நூல்கள் அன்பையும், அறத்தையும், கல்வியையும், நன்னெறிகளையுமே வலியுறுத்துகின்றன.

கடமையைச் செய் பலனை எதிர்பார்க்காதே என்னும் வாக்கிற்கேற்ப ஒவ்வொரு மனிதனும் தூய்மையான அன்பு மனத்துடன் செயல்பட வேண்டும். இந்த நிலையில் இறைவனைக் காண நான்கு வழிகள் இருக்கின்றன.

கர்ம மார்க்கம், ஞான மார்க்கம், பக்தி மார்க்கம், யோக மார்க்கம் ஆகிய நான்கு மார்க்கங்களையும் ஒருவன் கடைபிடிக்க வேண்டியதில்லை. இந்நான்கு முறைகளில் பக்தி மார்க்கம் மட்டும் யாவரும் எளிதில் கடைபிடிக்கக் கூடியது. கடவுளிடம் உண்மையான பக்தி செலுத்துவது என்பது கடவுளால் படைக்கப்பட்ட இவ்வுலகில் உள்ள உயிர்களிடம் அன்பு செலுத்துவதுதான் என்று அறிஞர்கள் கூறுகின்றன.

'இறைவன் ஒன்றே, என்னும் பொது நெறியைச் சைவ சமயக்குறவர்களும் கற்பித்துள்ளனர். ஆயினும் இறைவனைப் பல வடிவங்களில் சமூகத்தினர் பேசும் மூடத்தனத்திற்கு எதிராகப் பறைசாற்றியவர் வள்ளலார். அவர்களின் வழித்தோன்றலாக நின்ற பெருமை பாரதிக்கு உரியதாகும். இவர் இறைமை பற்றிக் கூறுமிடத்து,

ஆணாய் பெண்ணாய் அலியாய் உள்ள
தியாதுமாய் விளங்கு மியற்கைத்
தெய்வமே

என்கிறார். 'அறிவே இறைவன்' என்ற பெரிய உண்மையையும் அவர் பல இடங்களில் கூறுகிறார்.

இந்து மதம் அறுலகை உட்கூறுகளைக் கொண்டது. அவை சைவம், வைணவம், சாக்தம், காணபத்தியம், ஐந்திரம், கௌமாரம் என்பனவாகும். இவ்அறுவகைச் சமயங்களில் சிவன், கண்ணன், முருகன், சக்தி, கணபதி, ஆகிய கடவுளரை ஒரே பரம்பொருளில் பல வடிவங்களாகக் கொண்டு வழிப்பட்ட பொதுமைவாதி என்று பாரதியைக் கூறலாம். ஆயினும் சக்தி வழிபாடு அவருடைய வாழ்வில் மிகுந்திருந்தது. பக்தியால் மதங்கள் மனிதனுக்கிடையே வேறுபடுவதால் மனிதனின் உயர்ந்த இலட்சியங்கள் நிறைவேறுவதில்லை. இதனைப் பாரதியார்

நல்லதோர் வீணை செய்தே - அதை
நலங்கெடப் புழுதியிலே றிவதுண்டோ
சொல்லடி சிவசக்தி - எனைச்
சுடரெனு மறிவுடன் படைத்துவிட்டாய்
வல்லமை தாராயோ - இந்த
மாநிலம் பயனுற வாழ்வதற்கே?

என்று சக்தியிடம் வேண்டுகிற பொழுது தன்னுடைய நலனுக்காகவும், குடும்ப நலனுக்காகவும் ஆற்றலைத்தராமல் 'தேச நலனுக்காக' ஒவ்வொரு மனிதனும் பொதுநல இலட்சியங்களை கடைபிடித்து சமூக உணர்வோடு வாழவேண்டும் என்கிறார். ஒவ்வொருவரிடமும் பக்திநெறியினை புகுத்துகின்ற போது ஒற்றுமையுணர்வு மேன்மையடைகிறது. அதோடு மட்டுமல்லாமல் தேசநலனுக்காக பாடுபடுகின்ற உயர்ந்த இலட்சயங்கள் பக்தியின் மூலம் நிறைவேற்ற முடியும் இவற்றை

சக்தி தனக்கே கருவியாக்கு -அது
சாதனைகள் யாவினையும் கூடும்

என்று பக்தியுணர்வினால் சமூகத்தினரிடம் ஒற்றுமையுணர்வு ஏற்படும் என்கிறார். இக்கருத்தினை வலியுறுத்தும் வகையில் தனது கட்டுரை ஒன்றில்

கடவுள் எங்கும் இருக்கிறாரே?
எல்லாம் கடவுள் தானே?

ஊருக்கு நடுவில் ஒரு கோவிலைக் கட்டி அதில் ஒரு கல்லையோ செம்பையோ நட்டு

அங்கேதான் எல்லோரும் வந்து கும்பிடவேண்டுமென்று நியமம் எதற்காக? என்றால் ஜனங்களுக்கு ஐக்கியம் ஏற்படுவதற்காக என்று கூறும் பொழுது மனிதன் மதப்பாகுபாட்டினால் ஏற்படும் தெய்வங்களில் இறையண்பையும், பொது வழிபாட்டின் மூலம் ஒற்றுமையுணர்வையும் காணலாம் என்று பாரதி கூறியுள்ளார்.

இந்திய நாட்டினரிடம் எந்த இடர்பாடும் காணாமல் மகிழ்வுடனும், பரிபூரண தையத்துடனும், வாழ வேண்டுமானால் பக்தி உணர்வு அடிப்படைத் தேவையாகிறது என்பதைக் கூறும் மகாகவி மக்கள் அனைவரும் ஒன்றுகூடி தியானம் செய்தால் சோர்வும், தைரியமும் விலைவிக்கத்தக்க எண்ணங்களுக்கு இடம் கொடுக்காமல் வாழமுடியும் இவற்றினைப் 'பாப்பா பாட்டில்' பாரதியார்

தெய்வம் நமக்குத் துணை பாப்பா- ஒரு
தீங்கு வரமாட்டாது பாப்பா

என்று பாடுகிறார்.

இந்திய மக்களிடம் பல தெய்வங்கள் உலகில் உள்ளதாக எண்ணிக் கொண்டு, பேதமையால் உழன்று, பிணக்குற்று வாழும்; பித்து மனப்பான்மைத் தகர்த்தெறிய வேண்டும். இவர்களிடம் பல நாமங்கள் இருப்பினும் 'ஒன்றே தெய்வம்' என்ற ஒரு மனத்துடன் செயல்பட வேண்டும்.

ஆயிரம் தெய்வங்களுண்டென்று தேடி
அலையு மறிவிலிகள் - பல
லாயிரம் வேதம் அறிவொன்றே
தெய்வமுன்
டாமெனில் கேளிரோ

என்று பாரதி கூறுகின்றார்.

மனிதன் மனிதனாக வாழ வேண்டுமெனில், இறைவன் மீது பக்தி கொள்ள வேண்டும். இறைத் தன்மையுடன் வாழ்ந்த பாரதியார், பராசக்தி, விநாயகர், நான்மணிமாலை, முருகன் பாட்டு, கண்ணன்பாட்டு, கண்ணம்மா பாட்டு, முதலானப் பாடல்களை வெகுவாகப் பாடியிருக்கிறார். பகவத்கீதையை மொழி பெயர்த்து எழுதியது அவரின் அளவற்ற இறைப்பற்றிற்கு அடையாளமாகிறது.

முடிவுரை

வெள்ளையர்களின் ஆதிக்கப்படியில் அடிமைப்பட்டு கிடந்த இந்திய மக்களின் துன்ப நிலையினைக் கண்ட மகாகவி, சமூகத்தினரிடம் நிலவிய சாதி, சமய, மொழிப்பாகுபாடு, ஆன்மிகம் போன்றவற்றின் வேறுபாட்டில் சீர்குலைந்து காணப்பட்ட மக்களின் நலனைப்பெற விழைந்தார். சமூகத்தில் இந்திய மக்களிடம் அறியாமை உணர்வு நீங்கி, விடுதலை உணர்வு பெற்று ஒற்றுமையுணர்வோடு வாழ வேண்டும் என்கிற அவசியத்தை வலியுறுத்துவதோடு அதற்கான வழிமுறைகளையும் தனது கருத்தாக படைப்புகளில் மகாகவி கூறியுள்ளார் என்பதையும் இக்கட்டுரையில் கண்டு தெளிந்தோம்.

நூல்கள்

1. சாமி சிதம்பரனார் - பழந்தமிழர் வாழ்வும் வளர்ச்சியும்
2. சீனி விசுவநாதன் (தொ.ஆ) பாரதியார் கட்டுரைக் களஞ்சியம்
3. திரு.வி.க.வின் உரிமை வேட்கை
4. பாரதியார் கவிதைகள் (பூம்புகார் பிரசுரம்)
5. பாரதியார்- மகாகவி பாரதியின் உரைநடை வரிசை கட்டுரைக்கோவை, மணிமேகலைப் பிரசுரம்
6. புலியூர் கேசிகன் (உ.ஆ.) - புறநானூறு
7. மிழலைத் தொண்டன்-மகாகவியின் இலக்கியத்தில் பக்தி நெறி
8. பி.யோகீசுவரன்- பாரதியின் சமுதாயப்பார்வை.

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மொழிபெயர்ப்பும் ஒலிபெயர்ப்பும்

முனைவர் ச.ஈஸ்வரன்
இணைப்பேராசிரியர், தலைவர், தமிழாய்வுத்துறை, தேசியக் கல்லூரி (த), திருச்சிராப்பள்ளி - 1,
தமிழ்நாடு, இந்தியா

முன்னுரை

பிற மொழிகளில் உள்ள சிறந்த படைப்புகளை நம் மொழியில் மரபிற்கேற்பப் பெயர்த்தல் மொழிபெயர்ப்பாம். மூலத்தைப் படிக்கத் தூண்டும்படி, எளிய நடையில் மொழிபெயர்ப்பு இருத்தல் நன்றாம்.

பிறமொழிச் சொற்களை முதலில் ஒலிபெயர்ப்பர். பின்னர் படிப்படியாக அதன் அச்சொல்லின் செயல்பாட்டிற்கேற்ற சொல்லை உரிய மொழியில் மொழிபெயர்ப்பர். பழகப்பழக ஒலிபெயர்ப்புச் சொல் நீங்கி மொழிபெயர்ப்பு நின்று நிலைபெறும்.

ஒலிபெயர்ப்புக் குறைந்து மொழிபெயர்ப்பு அதிகரிக்கும் போதுதான் மொழிபெயர்ப்பாளரின் பணி பலரால் பாராட்டப்பெற்று ஏற்கப்பெறும். ஒரே சொல்லைப் பலர் மொழிபெயர்த்திருந்தாலும் எளிய, இனிய, பொருத்தமான மொழிபெயர்ப்பே நின்று நிலைபெறும்.

1.1 எளிமை

'Smile of Beauty' என்பதை 'அழகின் சிரிப்பு' எனவும், 'Hearty Welcome' என்பதை 'இனிய வரவேற்பு' எனவும் ஒலிபெயர்க்காது எளிய சொற்களால் மொழிபெயர்த்துள்ளனர்.

'No admisson without permission' என்பதைப் 'பெர்மிஷன் இலாது உள்ளே நுழைய அட்மிஷன் இல்லை' என முன்பு ஒலிபெயர்த்தனர். பிறகு, 'அனுமதியின்றி உள்ளே வராதீர்' என மொழிபெயர்த்துள்ளனர்.

1.2 ஆக்கம்

பாரசீகக் கவிஞர் உமர்கயாமின் பாட்டல்களைக் கவிமணி தேசிக விநாயகம் பிள்ளை, பின்வருமாறு தமிழில் பெயர்த்துள்ளார்.

'A flask of wine, a book of verse and thou' எனும் அடியை,

'கையில் கம்பன் கவியுண்டு, கலசம் நிறைய மதுவுண்டு' என்று பெயர்த்துள்ளார். புதிய சொல் ஆக்கமே செய்துள்ளார்.

'Cowards die many times before their death but a valiant never taste of death but once' எனும் ஜூலியஸ்சீசர் நாடக வாக்கியங்களைப் பின்வருமாறு விபுலாநந்த அடிகள் ஆக்கம் செய்துள்ளார்.

'அஞ்சினார்க்குச் சதா மரணம் அஞ்சாத நெஞ்சத்து ஆடவர்க்கு ஒரு மரணம்'

என்றவாறு பெயர்த்துள்ளார்.

1.3 வழக்கத்தில் நிலைபெறல்

'Candidate' என்ற சொல்லை 'அபேட்சகர்' என்று பெயர்த்தனர். பின்னர் நாவலர் நெடுஞ்செழியன் அவர்கள் 'வேட்பாளர்' என்று பெயர்த்தார். அச்சொல்லே இன்று வழக்கில் உள்ளது.

'Radio' என்ற சொல் 'ரேடியோ' என ஒலிபெயர்க்கப்பட்டது. பின் 'வானொலி' என அறிஞர் இராஜாஜியால் மொழிபெயர்க்கப் பட்டு அச்சொல்லே இன்று வழக்கில் நின்று நிலவுகிறது. 'Culture' என்ற சொல்லை ரசிகமணி டி.கே.சி - 'பண்பாடு' என்று பெயர்த்தார்.

Cell phone - செல்போன் - செல்பேசி - அலைபேசி - செல்லிடப்பேசி - கைபேசி என்றும், Governor - 'கவர்னர்' என்று முதலில் ஒலிபெயர்ப்பாகவும் பின்னர் 'ஆளுநர்' என்று மொழிபெயர்ப்பாகவும் ஆக்கம் செய்யப் பெற்றுள்ளது.

1.4 சூழல்

மொழிபெயர்க்கும் பொழுது சூழலையும் மனதில் கொள்ளல் நன்றாம். Very young child பச்சைப்பிள்ளை, Cold Water - பச்சைத்தண்ணீர், Fertile Green Field - பச்சைவயல், Growing tree- பச்சைமரம், Vulgar words - பச்சையான பேச்சு, Green saree - பச்சைப்புடவை.

A badly written book is oly a blunder, but a bad translation of a good book is a crime

என்பதற்கேற்ப மோசமான நூலை விட தவறாக மொழிபெயர்க்கப்பட்ட நூல் குற்றநூலாகக் கருதப்பெறும்.

1.5 வழக்கம்

சிற்சில சொற்களைப் பெயர்க்கும்போது நம்மொழி வழக்கை ஒட்டிப் பெயர்க்க வேண்டும்.

Kerals, Maharastra, Karnataka என்பதை - கேரளா, மகராஷ்டிரா, கர்நாடகா என்று பெயர்க்காது கேரளம், மகராஷ்டிரம், கர்நாடகம் என்று 'அம்' விகுதி சேர்த்துப் பெயர்த்தல் வேண்டும்.

Kollai - கொலை, கொள்ளை, Kadal - கடல், காதல் இச்சொற்களை முன், பின் பயன்பாடு பார்த்துப் பெயர்க்க வேண்டும்.

1.6 நன்றி

கண்டுபிடித்தோர் பெயர்களை நன்றி மறவாது அப்படியே ஒலிபெயர்ப்புச் செய்தலே சிறப்பானதாம்.

Ampier - ஆம்பியர், Volt - வோல்ட், Ohm - ஓம், Hery - ஹென்றி.

1.7 பொது

பொதுவான சொற்களை ஒலிபெயர்த்தலே வழக்கில் உள்ளது. Logratham - இலாக்கிருதம், Sine - சைன், Cosin - கொசைன், Tangent - டேன்ஜன்ட்

Petrol - பெட்ரோல், பீரோ, (கம்பெனி - நிறுவனம்), சிமெண்ட் இவைகளுக்குச் சரியான மொழிபெயர்ப்புச் சொற்கள் வேண்டும்.

1.8 ஒரு சொல் பல துறைகள்

ஒரே சொல் பல அறிவியல் துறைகளுக்கும் பொதுவாக வழங்கிவரும். அவை பயன்படுத்தும் துறைகளைப் பொருத்துப் பொருள் அமையும். (துறைகள் அடைப்புக்குறிக்குள்)

1. Cell - உயிரணு (உடலியல்), மின்கலம் (இயற்பியல்) சிறை (பொது)
2. Scale - செதில் (உயிரியல்), அளவுகோல் (இயற்பியல்)

1.9 மரபுத்தொடர்

மரபுத் தொடரைப் பெயர்க்கும் போது கவனமுடன் பெயர்த்தல் வேண்டும்.

He kicked the bucket

'அவன் வாளியை எட்டி உதைத்தான்' - தவறு, அவன் இறந்து போனான் - சரி.

1.10 பாரதியின் பெயர்ப்பு

பாரதியார் தம் இதழில் சோவியத் யூனியன் கிளர்ச்சியைக் கலகம் என்றோ, கிளர்ச்சி என்றோ கூறாது, 'புரட்சி' என்று பெயர்த்தார். கம்யூனிஸ்ட் என்ற ஒலிபெயர்ப்புச் சொல்லைப் 'பொதுவுடைமைக்கட்சி,' 'பொதுவுடைமை' என்று பெயர்த்தார். (தீபம், இதழ் தொகுப்பு எண். 1975)

1.11 ஒலிபெயர்ப்பு - இன்றைய நிலை

சூப்பர் ஸ்டார், லாண்டரி, ஓட்டல், சூப்பர் மார்க்கெட், ஜீனியர் போஸ்ட், ரிப்போர்டர், வெஜிடபிள் சூப், பாஸ்ட், சர்ட், டைரக்டர், ஹெட், கம்ப்யூட்டர், ஹாஸ்பிடல், மார்க்கெட், கலைக்டர், மேக்கப், டிக்கெட், டிரைவர் என்றவாறே பயன்படுத்துகிறோம்.

சிட்டியில், காலனியில், அப்பார்ட்மெண்டில், பிளாக்கில், புளோரில் இருக்கிறோம்.

பேஸ்ட்டால் பல் துலக்கி, ஹேர் ஆயில் தடவி, சோப்பால் குளித்து பிளேடால் ஷேவ் செய்து, டிபன், லஞ்ச் சாப்பிட்டு டூட்டிக்கு ஸ்கூட்டர், காரில் செல்கிறோம். பேங்க்கும் போஸ்ட் ஆபீஸிக்கும் போகிறோம்.

வீட்டு வாசலில் 'வெல்கம்' (Welcome) 'இன் - அவுட்' என்றும், திருச்சியை டிரிச்சி, தஞ்சையை டான்ஜூர் என்றும் உரைக்கிறோம்.

இனி, இவ்வாறு இல்லாது மொழிபெயர்த்தல் நன்றாம். இயன்றவரை தமிழில் எழுதுதல் சிறப்பானதாம்.

1.12 உருவாக்கம்

Pilot - வலவன், Aeroplane - வானுவூர்தி, Photograph - ஒளிப்படம், Gas - வளியம் X-Ray - ஓ கதிர்,

அப்பீல் (மேல் முறையீடு) சம்மன் (அழைப்பாணை) ஜட்ஜ் (நடுவர்) கமிட்டி (குழு) பட்ஜெட் (வரவு செலவு பட்டியல்) டெண்டர் (ஒப்பந்தக் குறிப்பு) என்றவாறு ஒலிபெயர்ப்பிலிருந்து சொற்கள் மொழிபெயர்க்கப் பெற்றுள்ளன.

ஜீவாலை (சுடர்) பிளாஸ்டிக் (குழைமம்) பிராணவாயு (உயிர்வளி, உயிரகம்) என்றவாறு ஆக்கம் செய்யப் பெற்றுள்ளன.

1.13 கவிதை மொழிபெயர்ப்பு

கவிதையை மொழிபெயர்க்கக் கூடாது, மொழிபெயர்க்க இயலாது என்கிறார் தாகூர்.

'Learning a Language through translation is loving a girl through an agent' கவிதையை மொழிபெயர்ப்பது என்பது, 'ஒரு பெண்ணை வேறு ஒரு நண்பன் மூலம் காதலிப்பதற்குச் சமம்' என்கிறார் தாகூர்.

சான்று,

தாயும் ஞாயும் யாராகியரோ
எந்தையும் நுந்தையும் எம்முறைக் கேளிர்
யானும் நீயும் எவ்வழி அறிதும்
செம்புலப் பெயல் நீர் போல
அன்புடை நெஞ்சம் தாம் கலந்தனவே'
(குறுந். பா. 40)

Your mother and my mother
how are they related?
your father and my father
what are they too one another/
you and I
how do we know each other
like the rain and red earth
our loving hearts are mingled as one'
(எம். சண்முகம்பிள்ளை & David E, Luden)

1.4 ஒலி பெயர்க்கப்பட வேண்டிய சொற்கள்

மொழிபெயர்ப்பில் சரியான சொல் அகப்படாத நிலையில் அதனை ஒலிபெயர்க்கலாம். பன்னாட்டுப் பொதுச் சொற்களை அப்படியே ஏற்கலாம். இயன்ற வரையில் இலக்கண விதிகட்கு உட்பட்டு ஒலிபெயர்ப்புச் செய்ய வேண்டும்.

வேற்று ஒலிகளைக் குறிக்கப் பின்வரும் மூன்று முறைகளைக் கையாளலாம்

i) ஒத்த ஒலிகளைப் பயன்படுத்தல் (thaiamin தையாமின்)

ii) கிரந்த எழுத்துக்களைப் பயன்படுத்தல் (சல்ஃபர்)

iii) புதிய குறியீடுகளை உருவாக்குதல் (சல்ஃபைட்டு)

1.15 புதிய சொற்களுக்கான பெயர்ப்பு : (மின் பொறிகளின் தமிழ்ப்பெயர்கள்)

பின்வருமாறு, நடைமுறையில் காணப்பெறும் புதிய சொற்களுக்கான மொழிபெயர்ப்பு செய்யப்பெற்றுள்ளது

Whats App	-	புலனம்
Face Book	-	முகநூல்
Youtube	-	வலையொளி
We chat	-	அளாவி
WI FI	-	அருகலை
Blue tooth	-	ஊடலை
Battery	-	மின்கலம்
Broad band	-	ஆலலை
On line	-	இயங்கலை
3D	-	முத்திரட்சி
2D	-	இருதிரட்சி
Scanner	-	வருடி
Laser	-	சீரொளி
Sim Card	-	செறி வட்ட்ட
Projector	-	ஒளி வீச்சி
Charger	-	மின்னூக்கி
Selfie	-	தம்படம்
Thumb drive	-	விரலி
Print Screen	-	திரைப்பிடிப்பு

இவ்வாறாகப் பெயர்க்கப்பெற்றுள்ளன.

1.16 மொழிபெயர்ப்பு - சில மைல்கற்கள்

i) லார்டு லிட்டன் பிரபுவின், The Secret way' யைத் தழுவி திரு. சுந்தரம்பிள்ளை அவர்கள், 'மனோன்மணீயம்' (நாடகம்) உருவாக்கினார்.

ii) பக்கிம்சந்திரருடைய புதினமாகிய 'ஆனந்தமாடத்தில்' இடம்பெற்றுள்ள பாடலை 'வந்தேமாதரமாகத்' தமிழில் மகாகவி பாரதியார் பெயர்த்துள்ளார்.

iii) புறநானூறு, திருக்குறள், திருவாசகத்தை ஜி.யூ.போப் அவர்கள் ஆங்கிலத்தில் பெயர்த்துள்ளார்.

iv) நம்மொழி நூல்கள் (சங்கு, நீதி, பக்தி, இக்காலப் புனைகதைகள்) ஆங்கிலம், இந்தி, கன்னடம், மலையாளம், தெலுங்கு, வங்காளம், பிரஞ்சு, ஜெர்மன், குஜராத்தி, பஞ்சாபி உள்ளிட்ட மொழிகளில் பெயர்க்கப் பெற்றுள்ளன.

v) மூலமொழிகளில் (Source Language) உள்ளனவற்றைப் பெயர்ப்பு மொழியில் (இலக்குமொழி) (Target Language) மாற்றித் தரும் மொழிபெயர்ப்புப் பணி தொடர வேண்டும்.

vi) மூலத்தைப் (Matter) பெயர்க்கலாம். முறையினைப் (Manner) பெயர்க்க முடியுமா? உள்ளதை உரைக்கலாம். ஆனால் உணர்வினை (ளுநளெந) உணரமுடியுமா? எனவே நல்ல மொழிபெயர்ப்பு மூலத்தைப் படிக்கத் தூண்டும்படி இருத்தல் நல்லதாம்.

vii) மேடைப்பேச்சு மொழிபெயர்ப்பே சிறிது கடினமானது. அதிலும் சிறப்புற நம் புலமையை வளர்த்துக் கொள்ள வேண்டும். வானொலி, தொலைக்காட்சி, இதழ்கள் தரும் சொற்களுக்கு உரிய மொழிபெயர்ப்பு முறையினைக் கேட்டும், படித்தும் உணர்ந்தால் நமக்கும் மொழிபெயர்ப்புப் பணி எளிதாக நிறைவேறும்.

முடிவுரை

புதிய புதிய சொற்கள் தமிழில் பெயர்க்கப்பெற வேண்டும். நிறையப் பிறமொழி நூல்களைப் படித்து நம் மொழி மரபிற்கேற்பப் பெயர்த்தல் நன்றாம்.

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கம்பன் கவிதையில் சூழல்கள்

*முனைவர் க.முருகேசன், *உதவிப்பேராசிரியர், தமிழ்த்துறை, தேசியக் கல்லூரி, (தன்னாட்சி), திருச்சிராப்பள்ளி – 01, தமிழ்நாடு, இந்தியா, 9976225551.

கவிதை இலக்கியங்களில் பேரிலக்கியமாகத் திகழ்வது காப்பியமாகும். அதனால் பெரிதும் வளர்ச்சியுற்ற கலை வடிவம் எனலாம். அது வீரயுகத்தில் தோன்றியதாகத் திறனாய்வாளர்கள் கருதுகின்றனர். அவ்யுகத்தில் மிகுதியும், உடல் வலிமையும், அழகும், ஆளுமையும், வீரமும், பேராண்மையும், ஈகைப் பண்பும் வாய்ந்த ஒருவன் தலைசிறந்து விளங்கினான். இத்தகைய பெருமை மிக்க அவனை அக்கால மக்கள் வியந்து பாராட்டிப் புகழ்ந்தனர். போற்றத்தக்க பண்புகளைப் பாடல்களில் புகழ்ந்து பாடலாயினர். நாளடைவில் அப்பாடல்கள் கதை வடிவில் வளர்ச்சியுற்றன. முடிவில் அவையே காப்பியப் பாடல்களாக உருவாக்கம் பெற்றன.

"காப்பிய இலக்கியம் பல தலைமுறைகளில் படிப்படியாகச் செம்மைப் படுத்தப்பட்டதாகும். பொதுவாக வழக்கிலிருந்த பழமையான கவிதைகளிலிருந்தும் பக்தி கையறுநிலை, இயன்மொழி ஆகியவைகளைப் பொருளாகக் கொண்ட பாடல்களிலிருந்தும் காப்பியம் வளர்ச்சி எய்தியதாகும். இவ்வளர்ச்சி நுண்ணறிவுத் திறனையும் கற்பனையின் விரிவையும் குறிப்பதாகும் என்று டபிள்யூ.பி.கெர் (W.P.Ker) கூறுகிறார்.

வீரஉணர்வினை முதன்மையாகவும் விளங்கித் தோன்றும் பண்பாகவும் கொண்டு முதலில் காப்பியங்கள் தோன்றின. இவைகளைத் தொன்மைக் காப்பியங்கள் (Primitive EPICS) அல்லது நம்பகமான காப்பியங்கள் (Authentic EPICS) என மேனாட்டுத் திறனாய்வாளர்கள் வகைப்படுத்துவர்.

இவற்றை இயற்கைக் காப்பியங்கள் (Natural EPICS) என்றும் கூறுவர். பிற்காலக் காப்பியங்களில் செயற்கைப் பண்புகள் அமைந்துள்ளன. எனவே அவைகள் செயற்கை அல்லது இலக்கியக் காப்பியங்கள் (Artificial or Literary EPICS) எனப்படும்.

சங்ககாலம் தமிழகத்தின் வீர யுகமாகும். அக்காலத்தில் தோன்றிய நம்பகமான காப்பியம் என்று கொள்ளத்தக்க பேரிலக்கியம் ஒன்றும் கிடைக்கவில்லை. அக்காலத்தில் இராமாயணம்,

பாரதம், தகடூர் யாத்திரை ஆகிய இலக்கியங்கள் இருந்ததாக கருதப்படுகிறது. அவ்விலக்கியங்களின் பாடல்கள் சிலவற்றைப் பிற்கால உரையாசிரியர் உரைகளில் குறிப்பிட்டுள்ளனர்.

இவ்விலக்கியங்கள் உரையிடையிட்ட பாட்டுடைச் செய்யுட்களாக உள்ளன. இதனை,

"தொன்மை தானே சொல்லுங் காலை

உரையொடு புணர்ந்த பழமை மேற்றே" (தொல்.செய்யுளியல் நூ - 235)

தொல்காப்பியம் கூறும் 'தொன்மை' இலக்கணத்திற்கு இவ்விலக்கியங்கள் பொருந்துபவையாக உள்ளன.

உலகில் விளங்கும் மகாகாவியங்களில் கம்பராமாயணமும் ஒன்று. தமிழ் மொழிக் கண் பல்லோராலும் போற்றப்படும் காவியமும் இதுவேயாகும். கம்பர் தம் காவியத்தை இயற்ற வான்மீகியின் இராம காதையை முதனூலாகக் கொண்டார். வான்மீயின் அடிப்படைத் தத்துவத்தை மாற்றாமல் தம் காவியத்தைக் கம்பர் வடித்துள்ளார். ஆனால் தமிழகத்தின் பண்பாடு, காலச்சாரம் ஆகியவற்றுக்கேற்ப ஓரளவு மாற்றமும் செய்துள்ளார்.

ஐம்பெருங்காப்பியங்களின் கருத்துக்களைக் கம்பர் ஆங்காங்கே கையாண்டிருக்கின்றார். கம்பருடைய காவியத்தில்,

"நிலத்திற் கிடந்தமை கால்காட்டும்; காட்டும்

குலத்திற் பிறந்தார் வாய்ச்சொல்" (திருக்குறள் - 959)

ஒரு பூமியினுடைய வளத்தை அப்பூமியில் தோன்றிய பயிர்களின் வளமையைக் கண்டும் வலிமையைக் கண்டும் அறிதல் போலக் கம்பர் கவிதையிலுள்ள உயிர்நாடியான சொற்களைக் கொண்டு, அவருடைய உயர்ந்த மனப்பாங்கையும், தூய எண்ணத்தையும் அறியலாம். 'சூழல்' என்ற சொல்லாக்கத்திற்கு சூழ்கை, சுற்றுப்புறம், மணற்குன்று, கூட்டம், அவதாரம், சூழ்ச்சி, வழிவகை உள்ளிட்ட பொருள் தொடர்களை அகராதி சுட்டுகிறது.

கம்பரின் காப்பிய வளர்ச்சிக்குச் சூழலியல் சிந்தனைகள் எவ்வாறு வழிவகை செய்கின்றதென்பதை இக்கட்டுரையில் ஆய்வோம்.

"மன ஆற்றலின் துடிப்புகள் தான் இருப்பதிலேயே மிகவும் சிறந்தவை அதனால் அவை இருப்பதிலேயே அதிக சக்தி வாய்ந்தவையாக விளங்குகின்றன" என்பார் சார்லஸ் ஹானல். அத்தகைய மன ஆற்றல் நிரம்பிய கம்பர் அவ்வாற்றலின் வெளிப்பாடாக தம் பாத்திர வார்ப்பில் நேர்த்தியை மிக அழகியலோடு கையாளும் வல்லண்மையைப் பெற்றுத் திகழ்கிறார்.

மகாப் பிரளய காலத்தில் எல்லா உலகங்களையும் தன் வயிற்றில் அடக்கிப் பிரளயம் நீங்கியதும் அவற்றை முன்பு போல் உமிழ்ந்து வெளிப்படுத்துகின்ற கடவுளாகிய திருமாலைக் கோசலை தன் வயிற்றினின்று ஈன்றார். இராமனுடைய பிறப்பின் நோக்கத்தையும், சூழலையும் கையாளும் கம்பர்,

"ஒருபகல் உலகெலாம் உதரத் துள்பொதிந்(து)

அருமறைக்கு உணர்வரும் அவனை, அஞ்சனக்

கருமுகில் கொழுந்தெழில் காட்டும் சோதியைத்

திருஉறப் பயந்தனள் திறங்கொள் கோசலை"

(திருஅவதாரப் படலம், பாலகாண்டம்)

தம் பாடலில் நயமுடன் நவில்கிறார்.

தவம் செய்வோர்க்கு காமம், வெகுளி நேர்ந்து தவத்தைக் குலைப்பதுபோல் அரக்கர் வந்து இடையூறு செய்கின்றனர். போர் செய்து அரக்கரை வெல்லும்படி விசுவாமித்திரர் உன் புதல்வர் நால்வரினும் கரிய நிறத்தை உடைய இராமனைத் தருவாயாக என்று இராமனைக்

கேட்டது. எமன் வந்து உன் உயிரைக் கொடு என்று கேட்பது போல தரசதனுக்குப்பட்டது. இச்சூழலை,

"தருவனத்துள் யான் இயற்று தவவேள்விக்கு
இடையூறாத், தவம் செய் வோர்கள்
ஒருவனைத்தந் திடுதிஎன, உயிர்இரக்கும்
கொடுங்கூற்றின் உளையச் சொன்னான்"

(கையடைப் படலம், பாலகாண்டம்)

காப்பியத்தின் உயிரோட்டத்திற்குப் பயன்படுத்துகிறார் கவிச்சக்கரவர்த்தி.

முனிவர் சபிக்கும் சாபத்தைப் போன்ற இராமனது அம்பு, தாடகையின் வயிரமலை போன்ற மார்பில் பட்டுஉருவி, அற்பர்களுக்கு அறிஞர்கள் கூறும் நற்கருத்துக்கள் அவர்கள் மனத்தில் தங்காது ஓடி விடுவது போல் ஓடிவிட்டது இக்கருத்தை வலியுறுத்த ஏற்றதொரு சூழலை ஆழமான உவமைச் சொற்களால் அமைக்கிறார் கம்பர். அதனை,

"சொல்லுக்கும் கடிய வேகச் சுடுசரம் கரிய செம்மல்
.....
கல்லுக்கும் நெஞ்சில் தங்காது அப்புறம் கழன்று; கல்லாப்
புல்லர்க்கு நல்லோர் சொன்ன பொருள்எனப் போயிற்று; அன்றே"

(தாடகைவதைப்படலம், பாலகாண்டம்)

விளக்குகிறார்.

உலகத்தில் செத்த பிணம் என்று சொல்லத் தக்கவர் கையை ஏந்திப் பிச்சை எடுப்பவரே. கொடையாளர்கள் இறந்தபோதிலும் புகழுடம்பால் சாகாது நிற்பவராவர் இக்கருத்தை வெளிப்படுத்திய விதத்தால் கொடையின் இலக்கணத்தை வெளிப்படுத்துகிறார். அதனை,

"மாய்ந்தவர் மாய்ந்தவர் அல்லர்கள்; மாயாது
.....
ஈந்தவர் அல்லது இருந்தவர் யாரே?" (வேள்விப்படலம், பாலகாண்டம்)

என்கிறார். மேலும்,

"ஈயென இரத்தல் இழிந்தன்று அதனெதிர்" (புறநானூறு)

இப்புறநானூற்றுப் பாடல் கருத்தோடு வேறுபட்ட தன்மையுடையவராகத் திகழ்கிறார் கவிவலவர்.

மிதிலை நகரின் பல வளங்களையும் கண்டு சென்ற மூவரும் அரச வீதியில் சென்றபோது அரண்மனையில் மேல் நிலையில் இருந்த சீதையை, இராமன் நோக்க அவளும் இராமனை நோக்கினாள் இச்சூழலை நேர்த்தியாகக் கையாளும் கல்வியில் பெரியன் கம்பன் தலைவன், தலைவி பார்வையின் மூலம் பேசுந் திறமிக்கவர்களாகப் படைத்துள்ளார். இதனை,

"எண்அரு நலத்தினாள் இனையன் நின்றுழி
.....

உண்ணவும் நிலைபெறாது உணர்வும் ஒன்றிட
அண்ணலும் நோக்கினான்; அவளும் நோக்கினாள்"
(மிதிலைக் காட்சிப் படலம், பாலகாண்டம்)

படம் பிடித்துக் காட்டுகிறார். இக்கருத்தை,

"கண்ணொடு கண்இணை நோக்குஒக்கின் வாய்ச்சொற்கள்
என்ன பயனும் இல." (திருக்குறள் - 1100)

வள்ளுவத்தின் பயனாக கம்பர் இதனைக் கையாள்கிறார் என்றால் அக்கூற்று பொருத்தமானதாகும்.

இராமனுக்கு மணிமகுடம் சூட்டும் வேளையில் கைகேயியின் அரண்மனைக்கு வந்த தசரதன் அவளைத் தேற்றப்புக, அவள் "முன்பு ஒருநாள் நீர் எனக்குக் கொடுத்த வரங்கள் இரண்டில், ஒன்றால் பரதன் முடிசூடவும் மற்றொன்றால் இராமன் வனம் போகவும் வேண்டும்" என்று கேட்டு நின்றாள். காப்பியத்தின் ஒட்டுமொத்த உயிர்ப்பையும் கைகேயியின் பாத்திரத்தில் ஏற்றி கையாளும் கம்பர்,

"ஏயவரங்கள் இரண்டில், ஒன்றி னால்என்
சேய்உலகு ஆள்வது, சீதைகேள்வன் ஒன்றால்
போய்வனம் ஆள்வது எனப்புகன்று நின்றாள்;
தீயவை யாவையினும் சிறந்த தீயாள்"
(கைகேயி சூழ்வினைப்படலம் அயோத்தியா காண்டம்)

கைகேயியின் மன வோட்டத்தினைப் பதிவுசெய்கிறார்.

"கைகேயி தசரதனிடம் பெற்ற வரத்தைப் பற்றி இராமனிடம் கூறுமிடத்தில் அரசன் கட்டளை என்று கூறுவாள். இதற்குப் பதில் கூறும் இராமன் சூழலைப் புரிந்துகொண்டு அன்னையே! உனது கட்டளையென்றால் நான் மறுப்பேனா? என் தம்பி பெற்ற செல்வம் நான் பெற்றதல்லவா? எனக்கு இதன் மேலும் வேறு நன்மை என்ன இருக்கமுடியும்? இக்கட்டளையைத் தலைமேற்கொண்டேன்; இதோ இப்படியே காட்டுக்குப் போகின்றேன்; உம்மிடம் உத்தரவு பெற்றுக் கொள்கிறேன்" என்று இராமன் பதிலுரைப்பதாக அமையுமிடத்தில்,

"மன்னவன் பணிஅன் றாகில் நும்பணி மறுப்ப னோஎன்
பின்னவன் பெற்ற செல்வம் அடியனேன் பெற்ற தன்றோ?
என்இனி உறுதி அப்பால்; இப்பணி தலைமேற் கொண்டேன்
மின்ஒளிர் கானம் இன்றே போகின்றேன்; விடையும் கொண்டேன்"
(கைகேயி சூழ்வினைப் படலம், அயோத்தியா காண்டம்)

பெற்ற அன்னையைக் காட்டிலும் வளர்த்த அன்னைமீது வைத்திருக்கும் அன்பினைப் வெளிப்படுத்துகிறது.

இராமன் இலக்குவனைச் சமாதானப்படுத்துமிடத்தில் தம்பியே! ஓர் ஆற்றில் தண்ணீர் இல்லா விட்டால் அ.்.து அந்த ஆற்றின் குற்றமன்று. அதுபோல நான் காடுபோக வேண்டியிருந்தது இந்த நகர் செய்த குற்றமன்று; நம்மைப் பெற்று வளர்த்த கைகேயியின்

குற்றமும் அன்று; பரதன் குற்றமும் அன்று; நமது விதி செய்த குற்றமேயாகும். ஆதலால் யாரோடு கோபம் கொள்கிறாய்? என்று கூறுமிடத்தில் அதனை,

"நதியின் பிழைஅன்று நறுப்புனல் இன்மை, அன்றே
பதியின் பிழைஅன்று பயந்து நமைப் புரந்தாள்
மதியின் பிழைஅன்று; மகன்பிழை அன்று; மைந்த
விதியின் பிழை; நீ இதற்குஏன் கொல்வெகுண்டது என்றான்"

(நகர் நீங்கு படலம், அயோத்தியா காண்டம்)

கானகம் ஏகிய சூழலுக்கு விதியின் பிழைதான் காரணம் எனும் இராமன் சிறந்த மனோதிடம் கொண்டவனாக விளங்குகிறான்.

'வேத நாயகனாக இராமன் அனுப்பிய தூதன்யான் அவன் பணிந்த சொற்களை உன்னிடம் கூறுவதற்காக வந்தேன்' என்கிறான் இதைக்கம்பர்,

"பூதநாயகன், நீர் சூழ்ந்த புவிக்குநா யகன்இப் பூமேல்
சீதைநா யகன், வேறுள்ள தெய்வநா யகன், நீசெப்பும்
வேதநா யகன்மேல் நின்ற விதிக்குநா யகன்தான் விட்ட
தூதன்யான்; பணித்த மாற்றம் சொல்லிய வந்தேன்; என்றான்"

தம் கவியால் சூழலையும் முக்கடவுளும் எனையணுக அஞ்சாதே; எனக் கேட்கின்றான். இவற்றிற்கு விடை அங்கதன் கூற்று வழி நிறுவுகிறார்.

உவமைகள் எவ்வளவு வேண்டுமானாலும் கூறலாம். ஆனால் அவைகள் பொருத்தமுடையனவாக இருத்தல் வேண்டும். கம்பர் காட்டும் உவமைகள் மிகப் பொருத்தமாக அமைகின்றன. கைகேயியினுடைய இரக்கமற்ற தன்மையினால் தான் இப்பூவுலகில் இராமாயணம் என்னும் அமுதம் பருகக் கிடைத்ததாகக் கம்பர் தனிக்கவியில் கூறுகிறார்.

அயோத்தி நகரை விட்டுப் பிரியும் இராமனின் பிரிவுத் துயரைப் பொறுத்துக் கொள்ளாத தயரதனைப் போல் அங்கிருந்த பசுக்களும், கன்றுகளும், யானை குதிரைகளும், பறவைகளும் அழுதன. சோலைகளும், அவற்றில் மலர்ந்த மலர்களும் அழுவதைப்போல் வாடிநின்றன. தண்ணீரும் அழுவதைப்போல் தெளிவின்றி காணப்பட்டதென்பதைத் தம் கவியில்,

கிள்ளை யொடுபூவை அழுத கிளர்மாடத்து
உள்உறையும் பூசை அழுத, உருஅறியாப்
பிள்ளை அழுத, பெரியோரை என் சொல்ல;
வள்ளல் வனம்புகுவான் என்றுரைத்த மாற்றத்தால்

(அயோத்தியா காண்டம், நகர்நீங்குபடலம்)

அ.·றிணை உயிர்களும் இராமனின் பிரிவுத் துயரைத் தாளாது அழுத காட்சியை நேர்த்தியாகப் பதிவு செய்கிறார்.

அயோத்தியை விட்டு வனத்திற்குச் செல்லும் இராமன் தன்னோடு வரவேண்டாம் என்றும் தம் இளவல் இலக்குவனிடம் கூறினான். அம்மொழி கேட்ட இலக்குவன் இராமபிரானே! ஒரு குளத்தில் தண்ணீர் இருக்குமானால் அங்கே மீனும் நீலோத்பலமும் இருக்கும். பூமி இருக்குமானால் அதிலிருந்து உண்டாகும் பொருள்கள் எல்லாம் இருக்கும். அதுபோல நானும்

சீதையும் உயிர் வாழ்ந்திருப்பது யாரால் என்று நினைக்கிறீர்? என்று தன்னை வனத்திற்கு வரவேண்டாமென்ற இராமனிடம் கூறுவது போல் கம்பர் தம்கவியில்,

நீர்உள எனின்உள மீனும் நீலமும்:
பார்உள எனின்உள யாவும் பார்ப்புறின்
நார்உள தனுஉளாய்! நானும், சீதையும்
ஆர் உளர் எனில்உளேம் அருளுவாய் என்றான்
(அயோத்தியாகாண்டம், நகர்நீங்கு படலம்)

பதிவு செய்கிறார்.

கோதாவரியின் கரையில் சீதையும் இராமனும் உலாவும் நிலையில் அங்கு இயற்கையாக நிகழும் நிகழ்வொன்றில் சூழலை மிக அழகாகப் பதிவு செய்கிறார்.

ஓதிமம் ஒதுங்கக் கண்ட
உத்தமன், உழையன் ஆகும்
சீதைதன் நடையை நோக்கிச்
சிறியதோர் முறுவல் செய்தான்
மாதவன் தானும், ஆண்டு
வந்து நீர்உண்டு மீளும்
போதகம் நடப்ப நோக்கிப்
புதியதோர் முறுவல் பூத்தாள்
(ஆரணியகாண்டம், பஞ்ச வடிப்படலம்)

இக்கவியில் கம்பர், அங்கே விளையாடும் அன்னங்களின் நடையையும் தன்னோடு வரும் சீதையின் நடையையும் ஒப்புமை நோக்கி இராமன் சிறிய முறுவல் செய்தான். சீதை, அங்கே நீருண்டு செல்லும் ஆண் யானைகளின் நடையையும் தன்னோடு உலாவும் இராமனின் நடையையும் ஒப்புமை நோக்கி இதுவரையும் சிரித்திராத சிரிப்பைச் சிரித்தாள் என்று குறிப்பிடுகிறார்.

கவிஞர்கள் தங்கள் கவிதைகளிலும் காவியங்களிலும் பல உவமைகளைப் புகுத்தியிருக்கிறார்கள். தங்கள் கருத்துக்களை மக்கள் எளிதில் புரிந்து கொள்ளவே உவமைகளைக் கையாள்கிறார்கள். கம்பர் தம் காவியத்தில் நூற்றுக்கணக்கான உவமைகளைக் கையாண்டிருக்கிறார். மிகச்சிறந்த ஒப்புவமைகள், சிறப்புவமைகள், இல்பொருளுவமைகள் முதலியவற்றைக் கம்பர் காவியத்தில் நாம் காணலாம்.

எண்ணற்ற வாழ்க்கைத் தத்துவங்களைக் கம்பர் தம் காவியத்தில் விளக்க எண்ணினார். அவைகளை எளிதில் விளங்கச் செய்ய உவமைகளைக் கருவியாகக் கொண்டார். ஆரணிய காண்டத்தில் சூர்ப்பணகைப் படலத்தில் அவள் அழகிய உருவமெடுத்து வருகின்ற சூழலை உவமை நயத்தால் நேர்த்தியாக கையாள்கிறார். அவள் மின்னல் கொடியைப்போல் அழகியவடிவம் எடுத்துக் கொண்டு மயில் போலும் தோற்றத்தோடு அன்னமென நடந்து வருவதை,

பஞ்சுஒளிர் விஞ்சுகுளிர் பல்லவம் அனுங்கச்
செஞ்செவிய கம்ளும் திகர் சீறடிகள் ஆகி,

அம்சொல்இள மஞ்ஞைஎன, அன்னம்என, மின்னும்
வஞ்சிஎன நஞ்சம்என, வஞ்சமகள், வந்தாள்
(ஆரணியகாண்டம், சூர்ப்பணகைப் படலம்)

சந்த நயத்தோடு நடந்து வருவாகப் புனைகிறார்.

கல்வியினால் ஏற்படும் சிறப்பையும், புகழையும் விளக்கும் கம்பர், கல்லாமையினால் ஏற்படும் தீங்கையும் அற்புதமாகக் காட்டுகிறார். கல்போன்ற கரிய நிறமுடைய தாடகையின் மீது இராமபிரான் அம்பெய்துகிறார். இராமபாணம் தாடகையின் மார்பை ஊடுருவச் சென்ற விதத்தைக் கம்பர் அழகாக விளக்குகிறார்.

சொல்லுக்கும் கடிய வேகச் சுடுசரம் கரிய செம்மல்
அல்ஒக்கும் நிறத்தி னாள்மேல் விடுத்தலும், வயிரக் குன்றக்
கல்லொக்கும் நெஞ்சில் தங்காது அப்புறம் கழன்று; கல்லாப்
புல்லர்க்கு நல்லோர் சொன்ன பொருள்எனப் போயிற்று
(பாலகாண்டம், தாடகை வகைப்படலம்)

என்னும் உவமை மூலம் அழகாகச் சித்தரிக்கிறார். கல்லாதவர் நெஞ்சில் நல்லோர் அறிவுரை தங்காது கழிவதைப்போல இராமபிரான் அம்பும் ஊடுருவச் சென்றது. கல்லாமையின் இழிநிலையைத் தம் காப்பியத்தின் கதையோட்டத்திற்கு ஏற்ப பலவிடங்களில் பதிவுசெய்கிறார்.

ஈகையும் கல்வியும் மனிதப் பண்புகளில் எவ்வளவு உயர்ந்தது என்பதைக் காட்ட எண்ணிய கம்பர் இவ்விரண்டின் சிறப்பையும் கூறுகிறார். இவ்விரண்டும் குறைந்திருப்பதனால் விளையும் பெருந்தீங்கையும் அற்புதமாகப் படம் பிடித்துக் காட்டுகிறார். கல்வியற்றவன் மனம் இருண்டுதான் இருக்கும். அவனிடத்தில் கண்ணோட்டத்தையோ அருட்குணத்தையோ முழுதும் காண முடியாது. கல்விக்கேள்விகளில் குறைந்த ஒருவனும் ஈகையென்னும் நற்பண்பு பூண்டு நல்லவிதமாக மக்களுடன் வாழ முடியுமானால் அந்த அருட்சிந்தனை தூய்மையான பால்நிறைந்த குடத்தில் ஒதுதுளி பிரை விழுந்தால் எப்படி அந்தப் பாலின் தன்மை மாறிவிடுகிறதோ, அதைப்போல நற்குணங்கள் உடையவர்கள் சிறிய கெட்ட குணத்தினால் தங்கள் மனம் திரிந்து விடுகின்றனர். அதனால் அவர்கள் அதர்மத்தின் குறியீடாக்குகிறார்.

எத்தகைய துன்பமான சூழ்நிலை வந்தாலும் முகமலர்ச்சியுடன் மனதார பணிபுரிய வேண்டும் என்ற உயரிய தத்துவத்தைக் கம்பர் இராமன் வாயிலாக எடுத்தியம்புகிறார். இராமனின் இப்பண்பை இத்துடன் நிறுத்திவிடவில்லை. பின்பும் உணர்த்துகிறார். சீதை அசோகவனத்தில் சிறைப்படுத்தப்படுகிறாள். சீதையின் கற்பு மனம் இராமனை நினைத்துருகின்றது. இராமனின் செயலைத் தம்மனக்கண்முன் நிறுத்தினாள். இச்சூழலைக் கம்பர் நேர்த்தியாகச் சித்தரித்திருக்கிறார்.

மெய்த்தி ருப்பதம் மே(வு)என்ற போதினும்
இத்தி ருத்துறந்து ஏ(கு) என்ற போதினும்
சித்தி ரத்தின் அலர்ந்தசெந் தாமரை
ஒத்து ருக்கும் முகத்தினை உன்னுவாள்

இராமன இன்பத்துள் இன்பம் விழையவில்லை. ஆகவே துன்பத்துள் துன்பமும் உறவில்லை மனித இனம் முழுவதும் இக்கொள்கையைக் கடைபிடிக்க வேண்டுமென்பதே கம்பரின் உயர் லட்சியமாகும். இதையே நடையின் நின்று உயர் நாயனாகிய இராமன் வாயிலாக உலகிற்கு அறிவிக்கிறார்.

கருணைக் கடலாகிய இராமன் தனக்கு ஒன்றும் செய்ய மாட்டான் என்று தக்க காரணங்களைக் காட்டிக் கூறிவிட்டு வாலி போருக்குப் புறப்பட்டான். இலக்குவன் தன் அண்ணன் இராமனிடம் வாலி – சுக்ரீவன் போரில் தலையிடுவது தகாது என்று இயம்புகிறான். ஆனால் இராமன் விலங்குகளின் ஒழுக்கங்கள் தம்மைக் கட்டுப்படுத்தாது என்று கூறி மறைந்திருந்து வாலியின் மேல் அம்பு தொடுக்கிறான். தன் நெஞ்சில் பாய்ந்த அம்பைக் கையினால் பற்றிய வாலி அதில் இராம நாமம் பொறிக்கப்பட்டிருப்பதைக் காண்கிறான். இராமன் மேல் கொண்டிருந்த பெருமதிப்பெல்லாம் தாழ்வடைத் துயர் உழந்து அழிந்து சோர்கிறான். இரவி குலத்தின் அறநீதி இராமனால் தவறிவிட்டது என்று கூறி நகைக்கிறான். இராமன் மேல் சினமுற்று 'என் உற்றாய்! என் செய்தாய்!' எனப் பலவாறு ஏசத் தொடங்குகிறான். சூரியக் குலத் தோன்றலாகிய தசரதன் வாய்மையும் மரபையும் நிலைநிறுத்த உயிரையே விட்டான். பரதன் தன் தாயின் வரத்தால் கிடைத்த அரசெல்லாம் முறையற்றது என்று கூறி அதை உரியவரிடமே சேர்ப்பிக்க முயல்கிறான் அன்னவர்க்கு மைந்தனும், அண்ணனுமான நீ பிறந்தாயே? என்று வாலி இகழ்வதைக் கூறும் கவி அழகானது.

வாய்மையும் மரபும் காத்து மன்உயிர் துறந்த வள்ளல்
தூயவன் மைந்தனே! நீ! பரதன்முன் தோன்றி னாயே?
தீமைதான் பிறரைக் காத்துத் தான் செய்தால் தீங்கன் றாமோ?
தாய்மையும் அன்றி, நட்பும் தருமமும் தழுவி நின்றாய்

(வாலிவதைப் படலம்)

பிறருக்கு நேரும் இடையூற்றைக் காத்துத் தான் மட்டும் இன்னல் இழைத்ததால் அது அறநெறியாகுமா? என்று வாலியின் கூற்று வழி மனத்தை உருகச் செய்யும் விதத்தில் கம்பர் அமைத்துள்ளார்.

இராவணன் சீதையைக் கவர்ந்து வந்து சிறையில் வைப்பதற்கு முன்னமே தன் மனமாகிய சிறையில் வைத்தான்; அவனுடைய உள்ளம், வெப்பத்தையுடைய வெயிலில் ஒரு பாறையின் மேல் வைத்த வெண்ணையைப் போல உருகிற்று இக்கருத்தை,

மயில்உடைச் சாய லாளை
வஞ்சியா முன்னம், நீண்ட
எயில்உடை இலங்கை நாதன்
இதயமாம் சிறையில் வைத்தான்
அயில்உடை அரக்கன் உள்ளம்
அல்வழி மெல்ல மெல்ல
வெயில்உடை நாளில் உற்ற
வெண்ணெய் போல் உருகிற்(று) அன்றே

(ஆரணிய காண்டம் - இராவணன் துன்புறு படலம்)

என்று குறிப்பிடுகிறார். இக்கருத்தோடு ஒத்த கருத்துடைய சங்க இலக்கியப் பாடலில்,

இடிக்கும் கேளிர்! நும்குறை ஆக
நிறுக்கல் ஆற்றினோ நன்றுமன் தில்ல
ஞாயிறு காயும் வெவ்அறை மருங்கில்
கைஇல் ஊமன் கண்ணின் காக்கும்

வெண்ணெய் உணங்கல் போலப்

பரந்தன்று, இந்நோய் நோன்று கொளற்கு அரிதே!

(குறுந்தொகை : 58)

கருத்தோடு ஒத்த கருத்துடையதாக அமைந்துள்ளது.

கடலால் சூழப்பட்ட இலங்கையிலே, கற்பினுக்கு அணிகலனாகிய பிராட்டியரை என் கண்களால் நேரே கண்டு வந்தேன். வேத நாயகனே! இனிப் பிராட்டியரைப் பற்றிய ஐயமும் துயரும் நீங்குவீராக என்று இராமனிடம் அனுமன் பணிகிறான். இக்கருத்தை,

கண்டனென் கற்பினுக்கு அணியைக் கண்களால்

தென்திரை அலைகடல் இலங்கைத் தொன்னகர்

அண்டநா யக! இனித் துறத்தி ஐயமும்

பண்டுள துயரும் என்று அனுமன் பன்னுவான்

(சுந்தரகாண்டம், திருவடி தொழுத படலம்)

தம்சொல்லாற்றலால் அனுமனுக்குச் 'சொல்லின் செல்வர்' என்ற அடைமொழியோடு அவருடைய தொண்டறத்தினை வெளிப்படுத்துகிறார்.

ஒரு நாட்டில் தோன்றிய மகா கவிகளைப் பொருத்துத்தான் அந்நாட்டில் உயர்பண்புகள் வளரும் என்பர். கம்பர் மிகச் சிறந்த மகா கவியாகத் திகழ்பவர். தம் பாத்திர வார்ப்பு மூலம் முன்னுதாரணமான மாந்தர்களைப் படைத்து அவர்களின் கூற்றுவழி கதையின் சூழலுக்குத் தேவைப்படும் இடங்களில் எல்லாம் மிகச் சிறந்த உவமைச் சொல்லாடல் மூலம் காப்பியத்தை அழகுறச் செய்கிறார். சூழலினால் எந்தெந்த இடங்களில் காப்பியச் சுவை மிகுந்திருந்தமையை இக்கட்டுரை நமக்குத் தெளிவாக்குகிறது.

பார்வை நூல்கள்:

1. இளம்பூரணர் (உரையாசிரியர்), தொல் - பொருளதிகாரம்.
2. கருத்திருமன் P.G. கம்பன் கவியும் கருத்தும்.
3. குமாரசாமி PSV (தமிழில்) இரகசியம்.
4. சுப்பிரமணியன் ச.வே. மெய்யப்பன் தமிழ் அகராதி.
5. ஞானமூர்த்தி தா.ஏ. இலக்கியத்திறனாய்வியல்.
6. வரதராசன். மு. திருக்குறள் தெளிவுரை.

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பல்லவி பதிப்பகம்

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க. முருகேசன்

சங்க இலக்கியங்களில் நிர்வாகவியல் மேலாண்மைக் கோட்பாடுகள்

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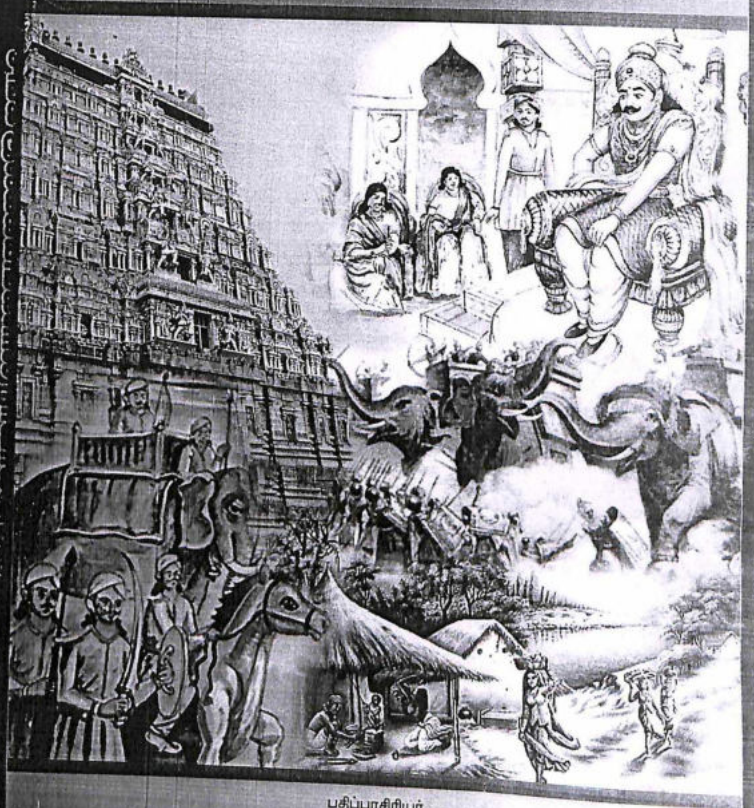
ADMINISTRATIVE MANAGEMENT THEORIES IN SANGAM LITERATURE



பதிப்பாசிரியர்
முனைவர் க. முருகேசன்

சங்க இலக்கியங்களில் நிர்வாகவியல் மேலாண்மைக் கோட்பாடுகள்

பல்கலைக்கழக நிதிநல்கைக் குழுவின் நிதியுதவியுடன்
கொங்குநாடு கலை அறிவியல் கல்லூரித் தமிழ்த்துறை
மற்றும்
முனைவர் மா. ஆறுச்சாமி ஆராய்ச்சி நிறுவனம்
இணைந்து நடத்தும்

இரண்டு நாள் தேசியக் கருத்தரங்கம்

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முனைவர் க. முருகேசன்

Estd 1973

தமிழ்த்துறை
கொங்குநாடு கலை அறிவியல் கல்லூரி
(தன்னாட்சி)

தேசிய மதிப்பீடு, மீள் தர நிர்ணயக் குழுவின் 'A' தகுதி வழங்கு
தனிச்சிறப்புத் திறன் கல்லூரித் தகுதியும், நட்சத்திரத் தகுதியும் வழங்கு
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சங்க இலக்கியங்களில் நிர்வாகவியல் மேலாண்மைக் கோட்பாடுகள்

(தேசியக் கருத்தரங்கம்)

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டாக்டர் சி.ஏ. வாசுகி
செயலர் மற்றும் இயக்குநர்
கொங்குநாடு கலை அறிவியல் கல்லூரி (தன்னாட்சி)
கோயம்புத்தூர் - 641 029.

அணிந்துரை

சீரிளமைத் திறம் குன்றாத தமிழ்மொழி எண்ணிலடங்காச் சிறப்புகளைப் பெற்றது. உலகின் மூத்தமொழி என்ற பெருமைக்கு உரியது. இத்தகைய தமிழ்மொழியின் வளமைக்குச் செழுமை சேர்ப்பன சங்க இலக்கியங்கள். காதலால் இருவர் கருத்தொருமித்து ஆதரவு பட்டு வாழ்கின்ற அகத்தையும், வாளெடுத்துப் பகை முடிக்கும் புறத்தையும் வண்ண ஓவியமாய்த் தீட்டி வைத்தவர்கள் சங்கத்துச் சான்றோர்கள். இரண்டாயிரம் ஆண்டுகளுக்கு முன்பே அகத்துக்கும் புறத்துக்கும் இலக்கணம் வகுத்து அதிலிருந்து சிறிதும் பிறழாமல் வாழ்ந்தவர்கள் தமிழர்கள் என்று எண்ணும்போது தமிழனின் சீர்த்த நாகரிகமும் கூர்த்த மதியும் புலனாகின்றது.

சங்க இலக்கியம் என்னும் கடலில் வானியல், உளவியல், சமூகவியல், அறிவியல், வணிகம், பண்பாடு, பழக்கவழக்கங்கள், பக்தி, நிர்வாகம் ஆகிய முத்துக்கள் நிறைந்துள்ளன. இவற்றுள் சங்க இலக்கியத்தில் இடம்பெற்றுள்ள நிர்வாகவியல் மேலாண்மைச் சிந்தனைகள் பல இன்றைக்கும் பொருந்துவனவாக உள்ளன. நிர்வாகவியல் அறிஞர்கள் கூறும் திட்டமிடுதல், ஒருங்கிணைத்தல், செயற்படுத்தல் உள்ளிட்ட நிர்வாகவியல் நெறிமுறைகளைச் சங்க இலக்கியத்தில் காணமுடிகிறது. எந்த ஒரு செய்தியாக இருப்பினும் அதனை யார் சொல்ல வேண்டும், அச்செய்தி யாரிடமிருந்து யாருக்குச் செல்ல வேண்டும் என்பதெல்லாம் நிர்வாகத்தில் கவனத்துடன் கையாளப்பட வேண்டியவையாகும். இத்தகையதொரு நிர்வாக முறைக்குச் சான்றாகச் சங்க அகப் பாடல்களில் இடம்பெற்றுள்ள அறத்தொடு நிற்றல் என்னும் துறை அமைந்துள்ளது. தலைவன் மீது தலைவி கொண்ட காதலை முதலில் தலைவி தன் தோழியிடம் கூறுவாள், தோழி செவிலியிடம் கூறுவாள், செவிலி நற்றாயிடம் எடுத்துரைப்பாள், நற்றாய் தலைவியின் தந்தைக்கும் உடன்பிறந்தார்க்கும் உரைப்பாள். இந்த முறை எந்தச் சூழலிலும் மாறாது.

செல்வச் செழிப்பு மிக்க தந்தையின் இல்லத்தில் தேன் கலந்த சுவை மிகுந்த பாலைப் பொற்குவளையில் பருகிய பெண் தன் உள்ளம் கவர்ந்த தலைவனோடு இல்லறம் நடத்த விரும்பி உடன்போக்கு மேற்கொள்கிறாள். தலைவனது குடியோ வறுமையானது. அந்த நிலையிலும் தலைவி, தன் தந்தையின் வீட்டில் உள்ள

யாண்டுவளன் ஆயினும் அரியேன் ஒரும்
புலிசோர்ந்து போகிய இல்வுளை போல
என்ற வயிறோ இதுவே
தோன்றுவன் மாதோ போர்களத் தானே" *(புறம்-86)*

என்ற பாடல்வரிகளில் சிறிய வீட்டில் நின்மகன் எங்கிருக்கிறான் என வினவுகிறாய். என் மகன் எங்கிருக்கிறான் என யான் அறியேன். புலி தங்கியிருந்து நீங்கிய கற்குகையைப் போல அவனைப் பெற்ற வயிறோ இது! அவன் போர்க்களத்தில் தோன்றுவான். என்று அவளது மகனின் வீரத்தை விளக்குவதோடு மறக்குடியின் மாண்பும் விளக்கப்படுகிறது.

நிறைவுரை

வாழ்வின் உயிரும் உடம்புமாய் இருப்பவை அன்பும் உண்மையுமே. இவை இல்லையேல் வேறொன்றும் இல்லை என்பதாம் மனித இனம் நலம் பெறவும் முன்னேறவும் இலக்கியங்கள் துணை நிற்கின்றன. என்பதோடு மட்டுமல்லாமல் வரலாற்றின் வெளிச்சத்தில் இலக்கியங்களை வாசித்து மகிழவும் உலக உயர்நெறிகளை உலகறியச் செய்வதற்கும் புறநானூறு மிகச் சிறந்த உதாரணமாகும். புறத்தை மட்டும் பேசாமல் மக்கள், மன்னன் வாழ்வியலைப் பேசும் புறநானூறு விடியலின் திசைகளையும் காட்டுகின்றது. தன் மக்களையும், நாட்டையும் உயிரும், உடம்புமாய்க் கருதுபவனே சிறந்த மன்னன் என்பதைப் புறப் பாடல்கள் நமக்குத் தெளிவுறுத்துகின்றன. இப்படி நம் மூதாதையர் வாழ்ந்த வாழ்க்கையைப் பெருமையுடன் கூறும் புறநானூற்றைப் படிக்கும் எவருக்கும் புதிய சிந்தனைகள் புலரும், புதிய வழித்தடங்கள் புலருவதையும் காணலாம். எனவே, எண்ணிய எண்ணியபடி பெறுவோம் எது வேண்டுமோ அதைப்பெறுவோம்.

45. புறநானூற்றில் மேலாண்மைச் சிந்தனைகள்

முனைவர் இரா. இரவிச்சந்திரன்
இணைப்பேராசிரியர், தமிழாய்வுத்துறை
தேசியக்கல்லூரி (தன்னாட்சி)
திருச்சிராப்பள்ளி - 620 001.

முன்னுரை.

பண்டைத்தமிழர்கள் காதலையும் வீரத்தையும் இருகண்களாகப் போற்றினர். அவையே அகம்,புற இலக்கியங்கள் தோன்றுவதற்குக் காரணங்களாக அமைந்தன. அக இலக்கியங்கள் தலைவன் தலைவியரின் உள்ளம், காதலைப் பற்றி எடுத்துரைத்ததோடு களவு, கற்பு வாழ்க்கையையும் எடுத்துக் கூறியுள்ளன. புற இலக்கியங்கள் வீரம், கொடை, நிர்வாகத்திறம் ஆகியவற்றைக் கூறுகின்றன. இத்தகைய சிறப்புக்களைக் கூறும் புற இலக்கியங்களில் ஒன்றான புறநானூற்றில் காணக்கிடக்கின்ற மேலாண்மைச் சிந்தனைகளை வெளிக்கொணர்வதே இக்கட்டுரையின் நோக்கமாக அமைகிறது. அவற்றை இக்கட்டுரையின் கீழ்க்காண்போம்.

"ஒருமுறையாக அமைக்கப்பட்ட நிறுவனத்தில் வேலையைப் பிறரிடமிருந்து செய்து வாங்கும் கலையே மேலாண்மை" என்கிறார் ஹாரல் கூன்ட்ஸ். ஒரு செயலைச் செய்து முடிக்க திட்டமிடுதலும் ஒருங்கிணைத்தலும் அவசியமாகும். மன்னராட்சியில் இவை சிறப்பாக நடைபெற்றமைக்குப் புற இலக்கியங்களே சான்றாகின்றன. மன்னர் நீர் நிலைகளைப் பெருக்கி மக்களை வளமாக வைத்திருத்தலையே மேலாண்மை என்கிறோம்.

"**நீரின்றி அமையாது உலகு**" என்று வள்ளுவர் கூறுவது போல இந்த உலகம் நீர் இல்லாமல் வாழ முடியாது. இத்தகைய நீரைப் பெருக்கி நாட்டை வளமாக்கினர் நம்முன்னோர்கள்.

"நீர்இன்றி அமையா யாக்கைக்கு எல்லாம்
உண்டி கொடுத்தோர் உயிர்கொடுத்தோரே
உண்டி மதற்றே உணவின் பிண்டம்
உணவெனப் படுவது நிலத்தொடு நீரே" *(புறம்: 18)*

என்ற புறநானூற்றுப் பாடல் வழியும் இது வெளிப்படுகிறது. வள்ளுவர் கூறும் கருத்துப்படி நீர் உணவுப் பொருள்களை உற்பத்தி செய்ய உதவுவதோடு மட்டுமல்லாமல் உணவாகவும் இருந்து வருகிறது என்பது வெளிப்படுகிறது. இத்தகைய நீரை மழைக்காலங்களில் தேக்கி வைக்க ஏரி, குளம், அணைகள் போன்றவற்றைக் கட்டினர்.

"காடுகொன்று நாடாக்கிக்
குளம் தொட்டு வளம் பெருக்கிப்
பிறல் நிலை" *(பட்டினப்பாலை: 283-286)*

என்ற பாடலின்வழி குளம்வெட்டி நீரைப் பெருக்கி நாட்டை வளமாக்கினர் என்பது வெளிப்படுகிறது. இதனையே புறநானூறும்,

"நாடா கொன்றோ காடா கொன்றோ
அவளா கொன்றோ மிசையா கொன்றோ

எவ்வழி நல்லவர் ஆடவர்
அவ்வழி நல்லை வாழிய நலனே" *(புறம்: 187)*

என்று குறிப்பிடுகிறது. நாடாக இருந்தாலும், காடாக இருந்தாலும், பள்ளமாக இருந்தாலும், மேடாக இருந்தாலும், எங்கு நல்ல ஆடவர் வாழ்கின்றாரோ அங்கு நிலமும் வளமாக இருக்கும் என்பதை மேற்கண்ட புறநானூற்றுப் பாடல் எடுத்துரைக்கிறது. இங்கு ஆடவர் என்பதற்கு ஆள்பவர் என்னும் பொருளையே உணர்த்துகிறது என்பது ஆய்வாளரின் கருத்தாகும்.

"மண்திணிந்த நிலனும்
நிலன் ஏந்திய விசும்பும்
விசும்பு தைவரு வளியும்
தீமுரணிய நீரும் என்றாங்கு
ஐம்பெரும் பூதத்து இயற்கை போல"

என்ற புறநானூற்றுப் பாடல் இந்த உலகம் பஞ்சபூதங்களால் ஆனது என்பதை வெளிப்படுத்துகிறது. இவை உலகம் தோன்றியபோதே தோன்றினாலும் அவற்றை ஆக்க சக்திக்குப் பயன்படுத்தி ஆள்பவன் மனிதனே. நீரைத் தேக்கி வைத்து அவற்றை வேளாண்மைக்குப் பயன்படுத்தி வளத்தைப் பெருக்கினான்.

"உணவெனப் படுவது நிலத்தொடு நீரே
நீரும் நிலனும் புணரியோர் ஈண்டு
உடம்பும் உயிரும் படைத்திசி னோரே
நிலன்நெறி மருங்கின் நீர்நிலை பெருக்கத்"

என்பதிலிருந்து நீர்வளத்தைப் பெருக்க வேண்டும். அப்பொழுதுதான் நாடு செழிக்கும் வளம் பெருகும் என்பது வெளிப்படுகிறது.

புறநானூற்றில் நீர்வள மேலாண்மை மட்டுமின்றி அரசர்களின் நிர்வாக மேலாண்மையும் இடம்பெற்றுள்ளதைப் பாடல்கள் வழி காணமுடிகிறது.

"நெல்லும் உயிரன்றே நீரும் உயிரன்றே
மன்னன் உயிர்த்தே மலர்தலை உலகம்" *(புறம்: 186)*

என்ற புறநானூற்றுப் பாடல்வழி மன்னன் நெல்லும் நீரும் உயர்வதைப் போல வளமான ஆட்சியை மேற்கொண்டுள்ளான் என்பது வெளிப்படுகிறது. "மன்னன் எவ்வழியோ மக்கள் அவ்வழி" என்பது இங்கு நினைவு கூறத்தக்கதாகும்.

"பாஅல் புளிப்பினும் பகல் இருளினும்
பாஅல் வேதநெறி திரியினும்
திரியாச் சுற்றமொடு முழுதுசேண் விளங்கு" (புறம்: 2)

என்ற பாடல்வழி அறநெறி தவறாமல் ஆட்சி செலுத்தினர் என்பதை உணரமுடிகிறது. அரசவையில் திறன்மிக்க நல்ல ஆலோசனைகளைக் கூறும் அமைச்சர்கள், புரோகிதர்கள், அந்தணர்கள், புலவர்கள் நிர்வாக மேலாண்மையை மேற்கொள்ள முடிந்தது என்பதைப் பழம்பாடல் உணர்த்துகிறது. மேலும் மன்னர்கள் அறநெறி காத்தனர் என்பதை,

"ஆவும் ஆனியர் பார்ப்பன மக்களும்
பெண்டிரும் பிணியுடை யீரும் பேணித்
தென்புல வாழ்நர்க்கு அருங்கடன் இறுக்கும்" (புறம்: 9)

என்ற புறநானூற்றுப்பாடல் வலியுறுத்துகிறது. மேலும் தன் நாட்டின் எல்லையை விரிவுபடுத்துவதற்காக பிற நாட்டு மன்னர்களுடன் போரிட்டு வெற்றிபெற்று நாட்டையும் நாட்டு மக்களையும் காத்தனர் என்பதை,

"இன்னா ஆகப் பிறர் மண்கொண்டு
இனிய செய்திநின் ஆர்வலர் முகத்தே" - (புறம்: 12)

என்ற பாடல் கூறுகிறது. அவற்றின் வழி மன்னன் பிறநாட்டின்மீது படையெடுத்து நாட்டின் செல்வத்தைப் பெருக்கினான் என்பதும் மக்களைக் காக்கும் மேலாண்மைப் பண்பும் இங்கு வெளிப்படுவதைக் காணமுடிகிறது. **"படைகுடிகூழ் அமைச்சு நட்பு அரண்"** என்று வள்ளுவர் கூறுவதுபோல அனைத்தையும் பெற்றுத் திகழ்பவனாக மன்னர் இருக்க வேண்டும். அதுவே அரசருக்குரிய சிறந்த மேலாண்மையாகும்.

"முறைசெய்து காப்பாற்றும் மன்னவன் மக்கட்கு
இறையென்று வைக்கப் படும்" - (குறள்: 388)

என்ற குறள்வழி நல்லமுறையில் நீதி வழங்கி மக்களைத் துன்பத்திலிருந்து காக்கும் மன்னனைத் தெய்வமாக மதிக்கப்படுவர் என்பதை எடுத்துரைக்கிறார். இவ்வகையான நல்லாட்சி மேலாண்மையையே மக்கள் விரும்புவர். சங்ககால மன்னர்கள் மேன்மையான ஆட்சி புரிந்துள்ளனர் என்பதற்கு புற இலக்கியங்கள் சான்றாக விளங்குகின்றன.

மன்னர்கள் மக்களைத் தன்குடியாட்சியின் கீழ் வைத்து ஆட்சிசெய்தார்கள். மக்களும் மன்னராட்சியில் மகிழ்ச்சியோடு வாழ்ந்தனர். இவற்றிற்குக் காரணம் சிறந்த மேலாண்மையே ஆகும். இலக்கியங்கள் அன்றைய கால நிகழ்வுகளை எடுத்துக் கூறுகின்ற ஆவணங்களாகும். மேற்கோள் காட்டப்பட்டுள்ள பாடல்கள்வழி சங்ககாலத்தில் மன்னர்கள் நீர்வளத்தினைப் பெருக்கி நிர்வாக மேலாண்மையைச் செய்துள்ளனர் என்பதை அறியமுடிகிறது.

கொங்குநாடு கலை அறிவியல் கல்லூரி

(தன்னாட்சி)

தேசிய மதிப்பீடு மீள் தர நிர்ணயக்குழுவின் "A" தகுதி பெற்றது)

பல்கலைக்கழக நிதிநல்கைக் குழுவின் தனிச்சிறப்புத்திறன் தகுதியும், நட்சத்திரத் தகுதியும் பெற்றது)

கோயம்புத்தூர் – 641029, தமிழ்நாடு.

சான்றிதழ்

பல்கலைக்கழக நிதிநல்கைக்குழுவின் நிதியுதவியுடன்

கொங்குநாடு கலை அறிவியல் கல்லூரித் தமிழ்த்துறை

மற்றும்

முனைவர் மா. ஆறுச்சாமி ஆராய்ச்சி நிறுவனம்

இணைந்து நடத்திய

இரண்டு நாள் தேசியக் கருத்தரங்கம்

சங்க இலக்கியங்களில் நிர்வாகவியல் மேலாண்மைக் கோட்பாடுகள்

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பல்கலைக்கழக நிதிநல்கைக்குழுவின் நிதியுதவியுடன் எமது கல்லூரித் தமிழ்த்துறையில் நடைபெற்ற தேசியக் கருத்தரங்கில் முனைவர் இரா. இரவிச்சந்திரன் இணைப்பேராசிரியர், தமிழாய்வுத்துறை நேசியக்கல்லூரி, நிலச்சி அவர்கள் பழநாளாற்றில் மேலாண்மைச் சிந்தனைகள் என்னும் தலைப்பில் ஆய்வுக் கட்டுரை வழங்கிச் / கருத்துரை வழங்கிச் / பங்கேற்றுச் சிறப்பித்தார் எனச் சான்றளிக்கப்படுகிறது.

முனைவர் க. முருகேசன்
கருத்தரங்க ஒருங்கிணைப்பாளர்

முனைவர் வே. பாலசுப்பிரமணியம்
முதல்வர்

டாக்டர் சி.ஏ. வாசுகி
செயலர் & இயக்குநர்

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சங்க இலக்கியங்களில் நிர்வாகவியல் மேலாண்மைக் கோட்பாடுகள்

ADMINISTRATIVE MANAGEMENT THEORIES IN SANGAM LITERATURE

பதிப்பாசிரியர்
முனைவர் க. முருகேசன்

29. பட்டினப்பாலை கூட்டும் நிர்வாகவியல் சிந்தனைகள்

முனைவர் ப. சுமதி
உதவிப்பேராசிரியர், தமிழாய்வுத்துறை
தேசியக் கல்லூரி, (தன்னாட்சி)
திருச்சி -1.

முன்னுரை

சங்க இலக்கியங்கள் கி.மு.மூன்றாம் நூற்றாண்டிலிருந்து கி.பி.மூன்றாம் நூற்றாண்டு வரையிலான 600 ஆண்டுகளில் தோன்றின என அறிஞர் பலர் கருதுவர். இந்நெடிய காலப் பகுதியில் பல்வேறு சமூக மாற்றங்களை இலக்கியங்களின் வாயிலாகக் காண முடிகிறது. நாட்டை ஆளும் வேந்தனின் போர் நிலையிலிருந்து மக்கள் வாழும் வாழ்க்கை வரை அரசாட்சி செய்யும் அரசரின் நாடு, நகர், வணிகம், போர் புரிந்த முறையை சங்க இலக்கியங்கள் எடுத்து இயம்புகின்றன. அரசாட்சி நடத்தும் வேந்தனின் நிர்வாகக் கோட்பாடு சங்கக் கால சமூகத்தில் சமனிலைச் சமூகத்தை உண்டாக்கியது. உடைமைச் சமூகத்திற்கு உரிய வேந்தர் தம்மின மக்களோடு ஒன்றுக் கூடியும் வாழ்ந்தனர். பத்துப் பாட்டினுள் பட்டினப்பாலையில் சோழ வேந்தன் கரிகாலப் பெருவளத்தானின் ஆட்சி நிர்வாகவியல் காவேரிப்பூம்பட்டினத்தில் மேன்மை பொருந்திய நிலையில் இருந்ததனை எடுத்துரைப்பது இக்கட்டுரையின் முக்கிய நோக்கமாக அமைகிறது.

வாணிகம்

ஒரு நாட்டின் நன்மைக்கு உழவர், வணிகர், சான்றோர் என்னும் முத்திறத்தார் வேண்டப்படுகின்றனர் என்பது திருவள்ளுவர் கருத்தாகும் இதனைத் திருக்குறளில்

"தள்ளா விளையுளும் தக்காரும் தாழ்விலாச்
செல்வரும் சேர்வது நாடு"

என்னும் குறள் "தாழ்விலாச் செல்வர்" என்னும் தொடர் வணிகரைக் குறிப்பதாகும். நாட்டில் ஓரிடத்தில் உண்டாகும் விளைபொருள்களை எல்லாம் அவை உண்டாகத பிற இடங்களுக்கு அனுப்புதலும் பலநாட்டுப் பண்டங்களை விற்றலும் வணிகர் தொழிலாகும். இத்தொழிலால் நாட்டில் செல்வம் வளரும். "மன்னர் பின்னோர்" என்றும் "இளங்கோக்கள்" என்றும் இவ்வணிகர் அரசரோடுப் பாராட்டப் பெறும் சிறப்பு பெற்றனர். இவர்கள் யானை மீதும் குதிரை மீதும் ஏறிச்செல்வது உண்டு. "எட்டி" முதலியப்பட்டங்களும், பொற்பூகளும் அரசரால் இவர்களுக்கு வழங்கப் பெறுவது உண்டு சங்கக் காலத்தில் வாழ்ந்தத் தமிழர்கள் அயல்நாட்டினரோடு மேற்கொண்டிருந்த வணிக நிர்வாகத் தொடர்பு முறையினைப் பட்டினப்பாலையில் கூறுகின்றன. காவிரிப் பூம்பட்டினத்தை ஆட்சி புரிந்தக் கரிகால் பெருவளத்தானின் வணிக முறையினை

"பல் ஆயமொடு பதிபழகி
வேறு வேறு உயர்ந்த முதுவாய் ஒக்கல்

சாறு அயர் மூதூர் சென்று தொக்காங்கு
மொழிபல பெருகிய பழிதீர் தேஎத்துப்
புலம்பெயர் மாக்கள் கலந்தினி துறையும்
முட்டாச் சிறப்பின் பட்டினம்"

என்ற பட்டினப்பாலை பாடல் வரிகள் பிறநாடுகளிலிருந்து அறிவு மிக்க பலமொழிப் பேசும் மக்கள், பலர் காவிரிப் பூம்பட்டினத்தில் வந்து வழித்தடங்களை அமைத்துக் கொண்டு இங்குள்ள மக்களுடன் இணைந்து மகிழ்ச்சியாக வாழ்க்கை நடத்தினர். இத்தகையப் பட்டினத்தில் தலைமைப் பண்புடைய சோழமன்னன் சிறப்புடன் ஆட்சி புரிந்து வந்த நிலையைக் கூறப்படுகின்றன.

நவமணிகளை விற்ற வணிகர் முதல் பிட்டு அப்பம் விற்ற வணிகர் வரை வாணிகம் புரிந்து வந்த எல்லாரும் நடுவு நிலை தவறாது வாணிகம் நடத்தினர். தாம் பொருளை வாங்கியதற்குக் கொடுத்த விலையையும், அப்பொருள் விற்பதால் தமக்கு வரும் இலாபத்தையும், வெளிப்படையாகக் கூறி வாணிகம் செய்தனர்.

இத்தகைய உயர் பண்புச் சோழ மன்னன் கரிகால் பெருவளத்தான் ஆட்சி செய்யும் காவிரிப்பூம்பட்டினத்தில் மக்கள் வாணிகம் புரிந்த இருந்ததைக் காண முடிகிறது. இதனைப் பட்டினப்பாலையில் கடியனர் உருத்திரங்கண்ணனார்

"நடுவுநின்ற நன்னெஞ்சினோர்
வடுவஞ்சி வாய்மொழிந்து
தமவும் பிறவும் ஒப்பநாடிக்
கொள்வதூஉம் மிகைகொளாது
கொடுப்பதூஉம் குறைகொடாது
பல்பண்டம் பகர்ந்து வீசும்
தொல் கொண்டித் துவன்றிருக்கை"

என்று கூறுகிறார். தமிழர்கள் கடல்வழியாக மரக்கலங்களைப் பயன்ப் படுத்தி பிறநாட்டினரோடு வணிகத்தில் ஈடுபட்டனர். ரோமாபுரிக்கும் - தமிழகத்திற்கும் உள்ளத் தொடர்பை பெரிபுளுஸ் பிளினி, தாலமி போன்றோர் குறிப்பிட்டுள்ளனர். உள்நாட்டு வணிகரும், வெளிநாட்டு வணிகரும் ஒன்றாகக் கலந்து இனிதாக வாழும் நகரமாகக் காவிரிப்பூம்பட்டினம் விளங்கியிருந்தது. இந்நகரத்தினை ஆட்சி செய்யும் சோழ மன்னன் வணிகச் சிறப்பினைப் பட்டினப்பாலையில்

"வெள்ளை உப்பின் கொள்ளை சாற்றி
நெல்லொடு வந்த வல்வாய்ப் பஷறி'

என்ற பாடல்வரிகளில் உப்பு வணிகர்களான உமணர்கள் தாங்கள் கொண்டு வந்த உப்பினை விலைபேசி விற்றுவிட்டு அதற்குப் பதிலாக நெல்லை ஏற்றிக் கொண்டு வாழ்ந்த நிலையை எடுத்துக் கூறுகிறது.

தமிழர்கள் கடல்வழியாக மரக்கலங்களைப் பயன்படுத்தி பிற நாட்டினரோடு வாணிகத்தில் ஈடுபட்டனர். கடலைக் குறிப்பிடுவதற்கு பரவை, ஆழி, புணரி, ஆர்கலி, முந்நீர், ஓடம், கலம், மரக்கலம், தோணி, மிதவை, கப்பல், நாவாய், மரம், திமில், அம்பி முதலிய மரக்கலத்தைப் பற்றியச் சொற்களும் சங்க இலக்கியங்களில் காணப்படுகின்றன. நாட்டின்

கரையோரங்களுக்குச் செல்வதற்கு ஓடங்களையும் அயல்நாட்டின் வணிகத்திற்கு நாவாய்களையும் பயன்படுத்தி உள்ளனர்.

அரச வேந்தனின் ஆட்கள் வெளியிலிருந்து நகருக்குள் வரும் பொருள்களுக்கு வரிவாங்கும் வழக்கத்தினை மேற்கொண்டன. "உல்கு" என்பது "வரி" அதனையே பின்னாளில் "சுங்கம்" என வழங்கினர். அரசனுடைய ஆட்களே நடுநிலையிலிருந்து உண்மையாக நடந்துச் சுங்கம் வசூலித்தனர். இந்தச் செயலினைப்பட்டினப்பாலையில்

"மாஅ காவிரி மணம் கூட்டும்
தூஉ எக்கர்த் துயில் மடிந்து
வால்இனர் மடல்தாழை
வேல்ஆழி வியன்தெருவில்
நல்லிறைவன் பொருள் காக்கும்
தொல்லிசைத் தொழில் மாக்கள்
காய்சினத்த கதிர்ச் செல்வன்
தேர்பூண்ட மாஅபோல
வைகல்தொறும் அசைவு இன்றி
உல்குசெயக் குறைபடாது"

என்றப் பாடல் வரிகள் காவிரிப் பூம்பட்டினத்தில் ஆட்சிப் புரியும் சோழ மன்னன் இருப்பிடத்தில் வணிகம் புரிவரிடம் சுங்கம் வாங்குவோர் உறங்கும் போதுக் கூட தங்கள் கடமையில் கண்ணும் கருத்துமாய் நடந்து கொண்டனர் அரசனுடையப் பண்டகச்சாலைத் தெருவில் குவிந்திருக்கும் அப்பண்டங்களைப் பிறர் கவராமல் பாதுகாப்பதில் வல்லவர்களாக இருந்தனர். அவர்கள் கதிரவன் தேரில் பூட்டிய குதிரைகள் போல அயராது வணிக இருப்பிடத்தைச் சுற்றி வருவார்கள். சளைக்காமல் வாங்க வேண்டியச் சுங்கங்களை வாங்கிக் கொண்டே இருந்தார்கள் என்பதனை கரிகால் பெருவளத்தானின் ஆட்சியில் வணிக நிர்வாகத்தினைப் பட்டினப் பாலையின் வாயிலாக அறிய முடிகிறது.

அரசனின் போர்முறை

சங்க காலத்தில் தமிழ் மக்களும், மன்னர்களும் வீரத்தின் அடிப்படையாகத் தோன்றும் போரை மிகப் பெருமையாக மதித்தனர். தமிழர் மறப்போரிலும் அறம் வழுவாதிருந்தனர். நாட்டைப்பிறர் படையெடுத்து வரும் போது அதைக் காக்க வேண்டியக் கடமையை எண்ணி வீரர் போருக்குப் புறப்படுவர். அந்த வீரமகன் ஒழுக்கமுள்ள மகனாக விளங்கும்படி அவனுக்கு நல்நடை வழங்க வேண்டிய கடமை வேந்தனுக்கு உட்பட்டிருந்தது. இவற்றின்

"ஈன்று புறந்தருதல் என்தலைக் கடனே
சான்றோன் ஆக்குதல் தந்தைக்குக் கடனே
வேல்வடித்துக் கொடுத்தல் கொல்லற்குக் கடனே
நன்னடை நல்கல் வேந்தற்குக் கடனே - புறம் (312)

என்றப் புறநானூறு வரிகள் வீரமகன் போருக்குப் புறம்படும் போது வேல் முதலியப்படைக்கலங்களை திருத்தமாகச் செய்துக் கொடுக்க வேண்டும். இத்தகையச் செயலுக்கு அரசன் தகுந்தனவற்றை அறநெறியோடு ஆட்சியினை வழிநடத்த வேண்டும்.

பட்டினப் பாலையில் கரிகால் பெருவளத்தான் தன் நாட்டு வீரர்களுடன் பகைவர்கள் மேல் சினம் கொண்டு வாள் முதலான கருவிகளுடன் யானைகளோடும், குதிரைப்படையோடும் விருப்பமுடன் போருக்குச் சென்றான்.

சோழவேந்தனின் போர்முரசு ஒலிக்கும் போது போர்ப் பாசறையே நடுக்கம் கொண்டது. பகை நாடுகள் போர்களத்தில் அழிந்தன. வெற்றிக் கொண்ட அரசன் பாதுகாப்பு அரண்கள் சூழத்தொடர்ந்து படை நடத்திச் சென்றதை பாலையில்

"முடியுடைக் கருத்தலை புரட்டு முன்றாள்
உகிருடை யடிய ஓங்கெழில் யானை
வடிமணிப் புரவியொடு வயவர் வீழப்
பெருநல் வானத்துப் பருந்துலாய் நடப்பத்
தூறிவர் துறகற் போலப் போர்வேட்டு"

என்றப் பாடல்வரிகள் திருமாவளவனின் போர் சிறப்பினைக் கூறுகின்றது. சங்கக் காலத்தில் மன்னன் வீரத்துடன் திகழ்ந்ததையும், நிர்வாகம் புரிந்தத் தன்மையையும் காட்டுகின்றது.

ஆட்சிமுறை

குடிமக்களுக்ககாகவே அரசாட்சி என்பது அக்கால மன்னர்க் கருத்தாக இருந்தது. குடிமக்களின் கருத்தறிந்து அதற்கேற்ப ஆட்சிபுரிய பேரவைகள் இருந்தன. அவை ஐம்பெருங்குழு எண்பேராயம் என்பவையாகும். அமைச்சர், புரோகிதர், தானைத்தலைவர், தூதர், சாரணர் என்பவர் ஐம்பெருங் குழுவினராவர். இவருள் புரோகிதர் என்பவர் பிற்காலச் சோழர் ஆட்சியிலிருந்த அரசகுருமார் போன்றவராக இருந்தனர்.

ஐம்பெருங்குழுவினரையும் கொண்டு அவைக் கூட்டித்தக்கவற்றை ஆராய்ந்து மன்னன் தன்நாட்டை அறநெறிப் பிறழாது அரசாட்சி நடத்தினான். இவற்றால் மக்கள் அரசனை இறைவனாகப் போற்றினர். இக்கருத்தினை

"முறைசெய்து காப்பாற்றும் மன்னவன் மக்கட்கு
இறையென்று வைக்கப்படும்"

என்றுத் திருவள்ளுவர் திருக்குறளில் கூறியுள்ளார். பட்டினப்பாலையில் பெரியதும்பிக்கை உடைய யானை தன் தந்தங்களால் பகைநாட்டை சிதைத்து வெளியேறிப் பெண்யானையைச் சென்றடைந்துப் போல திருமாவளவன் பகைவரின் வலிமையான வாள் படையை வெற்றி கொண்டு அரசப்பதவியினை அடைந்தான். இவ்வீரத்தினை

"பெருங்கை யானை பிடிபுக் காங்கு
நுண்ணிதன் உணர நாடி நண்ணார்
செறிவுடைத் திண்காப்போறிவாள் கழித்து
உருகெழு தாயம் ஊழினெய்திப்"

என்று பட்டினப்பாலையில் கடியலூர் உருத்திரக் கண்ணனார், சோழவேந்தன் அரசாட்சி நடத்திய முறையினைக் கூறியுள்ளார். அதனோடு அரசப் பெருமகன் ஆட்சிமுறையில் சோழநாடு வளமும், செழுமையும் பெற்றிருந்த வளத்தினையும் பட்டினப்பாலையில்

"காடு கொன்று நாடாக்கிக்
குளந்தொட்டு வளம் பெருக்கிப்
பிறங்குநிலை மாடத் துறந்தை போக்கிக்
கோயிலொடு குடிநிறீஇ
வாயிலொடு புழையமைத்து"

என்ற வரிகள் கூறிகின்றன. திருமாவளவன் சோழநாட்டில் காடாக இருந்தப்

பகுதிகளை எல்லாம் அழித்து மக்கள் வாழும் இடங்களாக மாற்றினான். தூர்ந்து போன குளங்களைத் தூர்வாறி நீர் வளம் பெருக்கி நாட்டின் செல்வ வளத்தைப் பெருக்கச் செய்தான். நீண்ட தூண்கள் உடைய மாடங்களைக் கொண்ட உறையூரைச் சோழ நாட்டின் தலைநகராக்கினான். கோயில்கள் எழுப்பிப் பழமையானக் குடிகளை அதனதன் முறைமையில் நிலைநிறுத்தி தன் வலிமையான ஆட்சிமுறையை நிருவகித்து வந்துள்ளான் இத்துடன் மக்கள் மனதில் நீங்காது இறைத்தன்மையுடைய அரசப் பெருமகனாகத் திருமாவளவன் திகழ்ந்ததையும் அறிய முடிகிறது.

பட்டின மக்களின் வளமான வாழ்வு

முடிமன்னர் மூவரும் தத்தம் நாட்டின் அரசியல் நிகழ்வதற்குரிய தலைநகரங்களைச் சிறந்த முறையில் அமைத்திருந்தனர். காவிரிக் கடலோடு கலக்குமிடத்தில் காவிரிப்பூம்பட்டினம் சோழர்களின் தலைநகரமாகவும் மக்களின் வளமான நகரமாகவும் விளங்கியது. மன்னர்களுக்கு இத்தலைநகரம் மதில் முதலிய அரண்களுடன் அமைந்திருந்தன. அரசன் வாழ்ந்த அரண்மனை நகரத்தின் நடுநாயகமாகப் பொலிவுற்றது. அமைச்சர், படைத்தலைவர் வணிகர், பலதிறப்பட்டத் தொழிலாளர் முதலியோர் வாழ்வதற்கு ஏற்றப் பல்வேறுத் தெருக்கள் வரிசை வரிசையாக அமைக்கப்பட்டிருந்தன.

ஆங்காங்கே கோயில்களும், பொதுமன்றங்களும், சோலைகளும், குளங்களும் காணப்பட்டன. நகரத்து அழுக்கு நீரை வெறியே கொண்டு செல்லும் கால்வாய்கள், நிலத்தின் கீழே மறைவாக அமைத்திருந்தன. இத்தகையப் பட்டினத்தின் வளம், சோழ நாட்டு மக்களின் இன்ப வாழ்க்கை வளத்துக்கு பொருந்தியதாக இருந்தது.

"செல்லா நல்லிசை யமரர் காப்பின்
நீரின் வந்த நிமிர்பரிப் புரவியும்
காலின் வந்த கருங்கறி மூட்டையும்"

என்னும் பட்டினப்பாலை பாடல்வரிகள் எப்போதும் நிலைபெற்ற அரசரின் நற்புகழைத் தெய்வங்கள் காத்து வருவதால் பட்டினம் வாழ் மக்களின் தெருக்கள் எல்லாம் செல்வம் பெருகி அளவிடுவதற்கு அரிதாக விளங்கின. அவர்கள் கடலின் வழியே வாணிபம் செய்து வந்து மகிழ்ச்சிப் பொருந்திய வாழ்க்கை வாழ்ந்ததை உணர்த்துகின்றது. பட்டினத்தில் மக்கள் மணல் பரப்பில் பூக்களைத் தூவியும், மீனைப் பொரித்து விற்பனை செய்தும், இறைவழிபாடு நடத்தியும், கொடிகள் கட்டப்பட்டும். கள் விற்பனை செய்தும, பல்வேறுக் கொடிகள் நகரெங்கும் பறந்ததனால் கதிரவன் ஒளி அவற்றைக் கடந்துப் புக முடியாத அளவிற்கு வளத்துடன் வாழ்ந்தனர். இவற்றினை

"ஊன்பொரிக்கும் ஒலிமுன்றில்
மணற்குவைஇ மலர்சிதறிப்
பலர்புகுமனைப் பலிப்புதவின்
நறவு கொடைக் கொடியோடு
பிறபிறவு நனி விரைஇப்
பல்வே றுருவிற் பதாகை நீழல்
செல்கதிர் நுழையாச் செழுநகர் வரைப்பிற்"

என பட்டினப் பாலை வரிகள் மக்கள்குற்றங்கள் இல்லாத வாழ்க்கையினை திருமாவளவன் ஆட்சிக் காலத்தில் வாழ்ந்ததைக் கூறுகின்றன.

முடிவுரை

சங்கக் காலத்தில் வேந்தனின் நிர்வாகத் திறன் வீரநிலைக் காலவாழ்க்கையிலிருந்து மக்களின் வளம் பொருந்திய வாழ்க்கை வரை நற்பயனாக இருந்ததை அறியமுடிகிறது. காவிரிப் பூம்பட்டினத்தில் சோழ அரசனின், வாணிகம். போர்முறை அரசாட்சி நாட்டுமக்களின் வளமான வாழ்வு, சீர்குலையாத நிர்வாக மேம்பாட்டினையும் பட்டினப்பாலையில் கூறப்பட்டுள்ளன. சங்கச் சமூகத்தினின்று நாம் பெற வேண்டிய பின்பற்ற வேண்டிய நிர்வாகத்திறனையும், ஒருமைப்பாட்டு உணர்வையும் கூறியுள்ளது. அத்துடன் மக்களின் வாழ்க்கை எல்லா அமைப்புகளின் வளம் பொருந்தியதன்மைக்குச் சோழ வேந்தனின் நிர்வாகத் திறனின் மேம்பாட்டினை பட்டினப்பாலை வழி விளக்கப்பட்டுள்ளதை இக்கட்டுரையின் வாயிலாக கண்டுணர முடிகிறது.

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பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்

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திருஞானசம்பந்தரின் இறைமைச் சிந்தனைகள்

முனைவர் ச.ஈஸ்வரன்
இணைப்பேராசிரியர் மற்றும் தலைவர், தமிழாய்வுத்துறை,
தேசியக் கல்லூரி (தன்னாட்சி), திருச்சிராப்பள்ளி - 620 001, தமிழ்நாடு, இந்தியா

முன்னுரை

சோழ நாட்டில், சீர்காழியில் அந்தணர் குலகவுணியர் கோத்திரத்தில் அவதரித்தவர் திருஞானசம்பந்தர். மூன்றாம் வயதில் பிரமதீர்த்தக் கரையில், தோணியப்பரால் அம்பிகையின் ஞானப்பால் ஊட்டுவிக்கப் பெற்றமையால் தோடுடைய செவியன் எனத் தொடங்கும் திருப்பதிகம் பாடி அருளினார். இவரின் தேவாரப் பாடல்கள் பன்னிரு திருமுறைகளில் 1, 2, 3 திருமுறைகளாகத் தொகுக்கப் பெற்றுள்ளன. இக்கட்டுரையில் திருஞானசம்பந்தரின் இறைமைச் சிந்தனைகளைத் தொகுத்தறியலாம்.

1.1 திருவடி பற்றல்

நிலையற்ற இவ்வுடலைப் பேணல் நல்லதன்று. ஆதலால் இளமைக் காலம் தொட்டே இறைவன் திருவடியைப் போற்ற வேண்டும் என்கிறார் திருஞானசம்பந்தர்.

ஊனமர் ஆக்கை உடம்பு தன்னை
உணரிற் பொருளன்று
தேனமர் கொன்றையி னான் அடிக்கே
சிறுகாலை யேத்துமினோ.
(திருவலம்புரம், பதிகம் 4, ப.60)

இவரின் காலம் 7ஆம் நூற்றாண்டு. இவரின் திருப்பாடல்கள் திருக்கடைக்காப்பு எனும் வழங்கப்பெறும். இவரின் இயற்பெயர், ஆளுடையபிள்ளையார்.

1.2 இறைவனைச் சார்தலால் கிட்டுவன

திருச்சாய்க்காடு எனும் திருத்தலத்தில் வீற்றிருக்கும் இறைவனை, வணங்கியவர்கட்கு, 'மீண்டும் பிறவார், பேரின்பம் அடைவர்; வருத்தம் அடையார் பசியால் வருத்தம் உரார், பிணி அறியார்' என்கிறார் திருஞானசம்பந்தர்.

மண்புகுவார் வான் புகுவர் மனம்
இளையார் பசியாலும்
கண்புகார் பிணியறியார் கற்றாரும்
கேட்டாரும் விண்புகார்
(திருச்சாய்க்காடு, பதிகம் ப. 76)

1.3 நல்வினை பெறல்

நெஞ்சே! நீ நாளும் நினைந்து, இறைவனை வணங்கி, வாழ்நாளை அறிவார் யார்? என்பதை அறிந்து மலர்களைச் சுமந்து சென்று, அவன்புகழைச் செவியால் கேட்டும், திருப்பெயர்களைப் போற்றியும் வழிபட்டால் நல்வினை பெறலாம் என்கிறார் திருஞானசம்பந்தர்.

நீ நாளு நன்னெஞ்சே நினை
கண்டாய் ஆரறிவார்
சாநாளும் வாழ்நாளும்
சாய்க்காட்டெம் பெருமாற்கே
பூ நாளும் தலைசுமப்பப் புகழ்நாமம்
செவிகேட்ப
நாநாளும் நவின்றேத்தப் பெறலாமே
நல்வினையே
(திருச்சாய்க்காடு, பதிகம் 3, ப. 77)

1.4 மக்கட்பேறு கிட்டும்

திருவெண்காட்டு இறைவனை வேண்டி அத்தலத்தில் உள்ள முக்குள நீரில் நீராடி வழிபட்டால் வினைகள் வாரா. பேய்பற்றா. அஞ்ஞானம் அகலும். மக்கட்பேறு கிட்டும் அவரவர் விரும்பும் வரங்களைப் பெறுவர். ஐயம் வேண்டா என்கிறார் திருஞானசம்பந்தர்,

பேயடையா பிரிவெய்தும்
பிள்ளையினோடு உள்ள நினைவு
ஆயினவே வரம்பெறுவர்
ஐயுறவேண்டா ஒன்றும்
வேயனவே தோளுமைபங்கன்
வெண்காட்டு முக்குளநீர்
தோய்வினையார் அவர் தம்மைத்
தோவாவாம் தீவினையே'
(திருவெண்காடு, பதிகம் 2, ப. 90)

இப்பதிகத்தை மனமுருகப் பாடினால் மக்கட்பேறு கிட்டும் என்பது உறுதி.

1.5 ஆசைகளை அறுத்தல்

திருக்கலிக்காமூரில் (அன்னப்பன் பேட்டை) எழுந்தருளியிருக்கும் இறைவனைப் போற்றி வழிபட்டால், உடலில் வாழும் ஐவர்களான ஐம்புலன்களின் ஆசைகளை அறுத்து வாழ்தல் உறுதியாம் என்கிறார். திருஞானசம்பந்தர்,

மெய்வரை வான்மகள் பாசன்றன்னை
விரும்ப உடல் வாழும்
ஐவரை ஆசறுத்து ஆளும் என்பர்
அதுவும் சரதமே
(திருக்கலிக்காமூர், பதிகம் 2, ப. 121)

பராசரமுனிவர் பூசித்த தலம் திருக்கலிக்காமூர் ஆகும்.

1.6 துன்பமில்லை

திருக்கலிக்காமூரில் மறைகளால் போற்றப் பெறும் சிவனார் விளக்கமற இருப்பர். இச்சிவபிரானை நினைத்து வணங்க நிறை புகழ் ஒங்கும். நம்மை வருத்தும் துன்பமும் இல்லை. வினைகளும் விலகும் என்று உறுதியிட்டுப் பகர்கிறார் திருஞானசம்பந்தர்.

மறைவளரும் பொருள் ஆயினானை
மனத்தால் நினைந்து ஏத்த
நிறைவளரும் புகழ் எய்தும் வாதை
நினையா வினைபோமே
(திருக்கலிக்காமூர், பதிகம் 6, ப. 123)

இதன் வழி, இறையருளை மனம் ஒன்றி வழிபட, சிறப்புப் பெறலாம் என்பதை இப்பதிகம் வழி உணர வைக்கிறார் ஞானசம்பந்தர்.

1.7 மாயையினின்று விடுதலை

தில்லைப்பதியான் (சிதம்பரம்) சிற்றம்பலத்தில் வீற்றிருக்கும் பிறப்பற்ற பெருமானை, சடையானை, மறவாது எப்பொழுதும் நினைந்து வழிபடுபவர்கள் உலக மாயையினின்று நீங்கியவராய்த் திகழ்வார்கள்.

பிறப்பில் பெருமானைப் பின் தாழ் சடையானை
மறப்பிலார் கண்டீர் மையல் நீர்வாரே
(திருத்தில்லை, பதிகம் 2, ப. 13)

என்கிறார் திருஞானசம்பந்தர்

1.8 இறையருளைப் போற்றிப் பெறல்

திருமுதுகுன்றத்தில் (விருத்தாசலம்) வீற்றிருக்கும் பழமைநாதரைப் போற்றி வழிபடின் வாழ்வில் அனைத்து நலன்களும் பெறலாம் என்கிறார் ஞானசம்பந்தர். உலகில் இறப்பவர், பிறப்பவர், தவம் உடைய முனிவர் போன்றோர் வணங்கிப் போற்றுவது திருமுதுகுன்றமே ஆகும். ஆண்டுச்சென்று நாமும் அவ்விறைவனை வணங்குவோம் என்கிறார்.

சாவாதவர் பிறவாதவர் தவமே மிக
உடையார்
மூவாதபல் முனிவர் தொழு முதுகுன்று
அடைவோமே
(திருமுதுகுன்றம், பதிகம் 6, ப.168)

எனக் கூறுகிறார் திருஞானசம்பந்தர்.

1.9 நல்வாழ்வு வாழ

பெண்ணாடம் பெண் (தேவகன்னியர்), ஆ காமதேனு, கடம் ளையானை) எனும் கோயிலைத் 'தூங்காளை மடம்' என்பர். உடலை ஒடுக்குவதான பிணி, பிறவி, கேடுகள் போன்ற கொடிய துன்பத்தினின்று விடுபட்டு வாழ தூங்கானை மடம் செல்லல் நலம் என்கிறார் திருஞானசம்பந்தர்,

ஒடுங்கும் பிணி பிறவி கேடென்று இவை
உடைத்தாய வாழ்க்கை ஒழியத்தவம்
....
தொடங்கும் கடந்தைத் தடங்கோயில்
சேர் தூங்கானை மாடம் தொழுமின்களே
(பெண்ணாகடம், பதிகம் 1, ப. 200)

என உரைக்கிறார் ஞானசம்பந்தர்.

1.10 அஞ்செழுத்தின் சிறப்பு

பஞ்சாக்கரத் திருப்பதிகம் எனும் தலைப்பினில், 'செந்தமிழ் ஓம்பிய செம்மை வேதியர்க்கு அந்தியுள் மந்திரம் அஞ்செழுத்துமே' எனக் கூறித் திருப்பதிகம் பாடுகிறார் திருஞானசம்பந்தர்

தும்மல் இருமல் தொடர்ந்த போழ்தினும்
வெம்மை நரகம் விளைந்த போழ்தினும்
இம்மை வினையடர்ந்து எய்தும் போழ்தினும்
அம்மையினும் துணை அஞ்செழுத்துமே
(காழி, பதிகம், 6, ப. 309)

இதன் வழி, 'நமசிவாய' எனும் திருமந்திரத்தின் பெருமையை உணரமுடிகிறது.

1.11 நன்மை கிட்டல்

இன்று மகிழ்ச்சி தரும் நன்னாள். நாளை இதனினும் மகிழ்வு பூரிக்கும் புனித நாள் என்று எண்ணி மகிழும் பொய்மை வாழ்வை ஒழிமின். திருக்கோடிக்காவில் வீற்றுள்ள சிவபிரானை அடைந்தால் நன்மை கிட்டும் என்கிறார் திருஞானசம்பந்தர்.

இன்று நன்று நாளை நன்றென்று
நின்று இச்சையால்
பொன்றுகின்ற வாழ்க்கையைப்
போகவிட்டு போதுமின்
மின்தயங்கு சோதியான் வெண்மதி
விரிபுனல்
கொன்றை துன்று சென்னியான்
கோடிகாவு சேர்மினே
(திருக்கோடிக்கா, பதிகம் 1, ப. 447)

என்று பகர்கிறார் திருஞானசம்பந்தர்.

1.2 தீவினை தீண்டா

திருச்செங்கோடு (திருகொடி மாடச் செங்குன்றூர்) தலத்தில் எழுந்தருளியிருக்கும் இறைவனை வழிபடின் தீவினை தீண்டாது என்கிறார் திருஞானசம்பந்தர்.

அவ்வினைக்கு இவ்வினையாம் என்று
சொல்லும் அஃதறிவீர்
செய்வினை வந்து எமைத் தீண்டப்
பெறாதிரு நீலகண்டம்
(திருகொடி மாடச் செங்குன்றூர்,
பதிகம் 1, ப. 567)

1.3 சிந்தை பற்றி நிற்றல்

திருப்பாற்றுறையில் எழுந்தருளியிருக்கும் இறைவனையே சிந்தை பற்றி நின்றதாகத் திருஞானசம்பந்தர் குறிப்பிடுகிறார்.

பூவும் திங்கள் புனைந்த முடியினர்
ஏவின் அல்லார் எயில் எய்தார்
பாவம் தீர்புனல் மல்கிய பாற்றுறை
ஓவன் சிந்தை ஒருவரே.
(திருப்பாற்றுறை, பதிகம் 4, ப. 623)

'நீங்கி நில்லார் இடர்களையாய் நெடுங்கள மேயவனே' என்று (திருநெடுங்களம், பதிகம், 5, ப. 629) உரைக்கிறார் திருஞானசம்பந்தர். இப்பதிகத்தில் நின் திருவடி நிழல் அல்லாது வேறு யாதொன்றும் அறியாதார்களின் இடரையும் களைவீராக என்கிறார்.

தொகுப்புரை

இறையருளைத் தொழுது வாழ்ந்தால் சிறப்புற்றுத் திகழலாம் என்பதைத் திருஞான சம்பந்தரின் தேவாரப் பதிகங்கள் உரைக்கின்றன. இத்திருப்பதிகங்களை மனமுருக ஒன்றி நின்று படித்துச் சிறப்புப் பெறல் என்றுமே நலம் பயக்கும்.

துணை நின்ற நூல்

திருஞானசம்பந்தர், தேவாரம் (1,2,3 திருமுறைகள்) முதல் பகுதி, பி.ரா.நடராசன் (உ.ஆ.), உமா பதிப்பகம், சென்னை-1. முதற்பதிப்பு அக். 2004.

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ADMINISTRATIVE MANAGEMENT THEORIES IN SANGAM LITERATURE

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11. புறநானூற்றில் காணலாகும் நிர்வாகச் சிந்தனைகள்

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முன்னுரை

அரசியல் வித்தகர்களின் அரசியல் ஞானத்தை மேம்படுத்தும் அளப்பரிய தத்துவங்களைத் தன்னகத்தே கொண்டு விளங்கும் தன்னிகரற்ற நூல் புறநானூறு. நாட்டின் பொருளாதாரத்தை உயர்த்தும் புதிய தத்துவங்கள் புறநானூற்றிலே பொலிகின்றன. இன்றைய நிலையில் தனிமனித வாழ்வில் மட்டுமின்றி பொதுநல வாழ்விலும் சிக்கல்கள் எழும்போது அச்சிக்கல்களைப் போக்குகின்ற தீர்வுகள் பல புறநானூற்றிலே காணப்படுகின்றன. அவற்றைப் பற்றி இக்கட்டுரையில் காண்போம்.

கடமையை மறவாமை

உலகத்தில் உள்ள மக்கள் எல்லோரும் தம்தம் கடமைகளை அறிந்து அவற்றைச் செயலாற்ற வேண்டும். அவ்வாறு செயலாற்றினால் வையகம் செழிக்கும். வையத்தார் வாழ்வில் வளம் பெருகும் மனிதர்கள் இன்புற்று வாழ்வர்.

"**கடமையைச் செய் உரிமையைக் கேள்**" என அறிவுறுத்துவர் அறிஞர் பெருமக்கள். ஆதலால்தான் இன்றும் நம் நாட்டு மக்களை ஓட்டுப் போடுவதைத் தவிர்க்காமல் ஓட்டுப் போடச் சொல்வதும் அவ்வோட்டையும் பணம் பெறாமல் வாக்களிக்குமாறு தூண்டுவதும் இதுவே காரணமாகும்.

இவற்றையெல்லாம் சிந்தித்துத்தானோ என்னவோ பொன்முடியார் என்ற பெண்பாற் புலவர் சமுதாயத்தின் பல நிலைகளில் உள்ளவர்களின் கடமைகள் இவையெனக் காட்டும் நிலையில் பாட்டு ஒன்றினைப் பாடுகின்றார்.

"ஈன்று புறந்தருதல் என்தலைக் கடனே
சான்றோன் ஆக்குதல் தந்தைக்குக் கடனே..
களிறு எறிந்து பெயர்தல் காளைக்குக் கடனே"
- (புறநானூறு - 312)

மகனைப் பெற்று வளர்த்து விடுதல் தாயின் தலையாய கடமையாகும். அவனை நல்ல பண்புகளால் நிறைந்தவன் ஆக்குவது தந்தையின் கடமை. அவனுக்குத் தேவையான வேலினை வடித்துத் தருவது கொல்லற்குக் கடன். அவனுக்கு நல்லொழுக்கத்தினைக் கற்பிப்பது நாட்டினை ஆளுகின்ற வேந்தனுடைய கடமை. ஒளிபொருந்திய வாளினைக் கையில் ஏந்திச் சென்று தடுக்க முடியாத போரைச் செய்து பகைவர்களின் ஆண் யானைகளைக் கொன்று வெற்றியோடு திரும்புவது காளையாகிய அம்மகனுக்குக் கடமையாகும்.

இப்படி ஒருவரை ஒருவர் சார்ந்திருக்கின்ற சமுதாயத்தில் எதிர்பார்க்கும் கடமை அடிப்படையிலும் ஒருவரை ஒருவர் சார்ந்திருப்பதைக் காண முடிகிறது. சார்ந்திருக்கும் நிலைமை உணரும் வகையில் ஒவ்வொருவரின் கடமையையும் தெளிவாகத் தெரிவிக்கும் தீந்தமிழ்ப்புலவரின் திறம் போற்றுதற்குரியது.

அவ்வவ்வூர்களில் இருக்கும் பணியாளர்கள் அவ்வவ்வூர்களில் இருக்கும் மக்கள் வேண்டுவன செய்தல் வேண்டும் என்றும் அயலூர் சென்று பணி செய்வது குற்றமென்றும் முதற் குலோத்துங்க சோழன் காலத்தில் ஒரு கட்டுப்பாடு இருந்தது என்று திருபுவனையில் உள்ள கல்வெட்டு ஒன்று (A.R.NO.205 ழக 1919) கூறுகிறது.

இக்கல்வெட்டு காட்டும் கடமைக்கும் வழி வகுத்திருக்குமோ என்று கூட எண்ணத் தோன்றுகிறது. அதுபோல இன்று நம் நாட்டின் பொருளாதார முதுகெலும்பான விவசாயம் மெல்ல அழிந்துக் கொண்டு வந்திருக்கின்றன. காரணம் விவசாயிகளுக்கு அடிப்படைகளான நீர், நிலம் கிடைக்கப் பெறாமையே ஆகும். அதனால் அவர்கள் தங்கள் கடமையை ஆற்றாது போய்விடுகின்றன.

ஒருவன் பணியாற்றும் துறையில் அவன் புகழ் பெற்று ஓங்கித் திகழ வேண்டும். அவன் புகழ் பெற உரிய களத்தினை அமைத்து அதில் அவனை ஈடுபடுத்துதல் அரசு செய்ய வேண்டிய கடமையாகும். அக்களத்திலே பணி செய்யத் தேவையான கருவிகளையும், வசதிகளையும், சூழ்நிலையையும் ஏற்படுத்தித் தருதல் சமுதாயத்தின் பொறுப்பு! அரசு நன்னடை நல்க சமுதாயம் கடமையாற்ற தேவையான வசதிகளைச் செய்து தரல் வேண்டும்.

அக்கால மக்களின் கடமைகளினின்றும் மாறுபட்டிருக்கின்றனவே என்று கூட சிலர் கேட்கலாம். ஆனால் அடிப்படையில் கவிதையில் கருவாகப் பேசப்பட்டிருக்கிற கடமைகள் இன்றைய உலகிலும் மகனைப் பெற்றெடுத்து வளர்த்து சான்றோன் ஆக்கித் தருதல் பெற்றோர்க்குக் கடமை என்பதை யாரால் மறுக்க முடியும்? அம்மகன் பணி செய்வதற்கு ஏற்ற கருவிகளை அவன் சார்ந்திருக்கும் சமுதாயத்தின் ஒரு பிரிவினர் செய்து தர வேண்டிய கடமை கணினிக் காலம் என்ற இக்காலத்தும் மாறுபடவில்லை என்று கூறலாம்.

அவன் சமுதாயம் சார்ந்த சட்டதிட்டங்களை அறியச் செய்து அவன் பணி செய்வதற்கோர் களம் அமைத்து தருவது ஆட்சி செய்வோரின் அரிய கடமை என்பது காலத்தால் மறுக்கப்படுவது கிடையாது. ஆண் மகனை வைத்து இங்கே சொன்ன அனைத்துக் கடமைகளும் இன்றைய உலகில் பெண் மகளுக்கும் பொருந்தும் என்பதையும் அறியலாம்..

செல்வத்தின் பயன்

உலகில் உழைக்கும் தொழிலாளர்கள் வேலை நிறுத்தம் போன்ற கிளர்ச்சியில் ஈடுபடுகின்றார்கள் அதற்கு அடிப்படைக் காரணம் என்ன?

நாட்டில் பொருள் தட்டுப்பாடு உள்ளதே! இது எதனால் ஏற்படுகிறது? மக்களின் வாழ்க்கை மகிழ்ச்சி நிறைந்ததாக இல்லையே! அவர்களின் வாழ்க்கை எப்போது மகிழ்ச்சியால் நிரம்பும்? இவற்றையெல்லாம் ஆழமாகச் சிந்திக்கிறார் மதுரைக் கணக்காயனார் மகனார் நக்கீரனார். தேர்ந்து தெளிந்த அவர் உள்ளம் ஒரு செந்தமிழ்ப் பாடலாய் வெளிப்படுகிறது.

தெளிந்த நீரால் சூழப்பட்ட உலகம் முழுவதையும் மற்ற மன்னர்களுக்கு பொதுவாக இல்லாமல் தமக்கே உரியதாக வெண்கொற்றக் குடை நிழலில் ஆட்சி செய்து நாட்டைக் காத்து வரும் அரசன் இருக்கிறான். காட்டில் நடு இரவிலும் நண்பகலிலும் தூங்காமல் விரைந்து ஓடும் விலங்குகளை வேட்டையாடி வாழும் கல்வி அறிவில்லாத வேட்டுவன் இருக்கிறான். இவர்கள் இருவருமே கடுமையாக உழைக்கிறார்கள். பொருள் ஈட்டுகிறார்கள்! இவ்வாறு உழைப்பதும் பொருள் ஈட்டுவதும் எதற்காக? அடிப்படையில் இவ்விருவருடைய தேவைகளும் ஒரே நிலையில் தாம் உள்ளன? இவர்களின் அடிப்படைத் தேவைகள் தாம் யாவை? இவர்களுக்குத் தேவை உணவும் உடையும் மட்டுமே! அது கூட உயர்ந்த அரசன் என்பதால் பொன்னையும் மணியையும் உணவாக உண்டுவிட முடியுமா? ஒரு வேளைக்கு ஓராயிரம் கலம் உணவை உட்கொள்ள அவனால் தான் இயலுமா? இயலாது அல்லவா? அவன் உண்ணும் உணவும் அவனுடைய வயிற்றுப் பசியைப் போக்குவதற்குத் தானே! இல்லை வேட்டுவன் என்பதால் அவனுடைய வயிறு சிறியது அதற்குக் குறைந்த அளவே உணவு போதும் என்று சொல்ல முடியுமா? அவன் உட்கொள்ளும் உணவும் அவனுடைய வயிற்றுப் பசியைப் போக்குவதற்கே ஆகும்.

இவற்றையெல்லாம் கருத்தில் கொண்டு வேண்டுவன சிறிது, ஈட்டுவதோ பெரிது என்கிற நிலையினைப் புரிந்து மிகுந்து நிற்கும் செல்வத்தால் செய்ய வேண்டியது பிறருக்கு உணவும் உடையும் பிறவும் கொடுத்து மகிழும் அறமே ஆகும். எனவே அடிப்படைத் தேவைக்குமேல் உள்ளவற்றை இல்லாதவர்க்கு, வறியவர்க்கு, ஏழையர்க்கு எடுத்துக் கொடுங்கள்! அவ்வாறு கொடுக்காமல் தானே அவற்றையெல்லாம் அனுபவிக்க வேண்டும் என்று எண்ணினால் உலக வாழ்க்கையால் நாம் பெற வேண்டிய அறம், பொருள், இன்பம் நமக்குக் கிடைக்காது. அவற்றைப் பெறாமல் போனால் நாம் வாழ்வதற்குப் பொருளே இல்லை. எனவே சேர்த்த செல்வத்தால் பெறும் பயன் பிறருக்குத் கொடுத்திடல் வேண்டும்.

இப்பாடலை கருவாகக் கொண்டு தான் இன்றைய இந்திய அரசாங்கம் பிறருக்கு உதவாமல் பணக்காரர்களின் கையிலுள்ள கருப்புப் பணத்தை மக்களுக்கு உதவும் வகையில் செய்வதற்கே வருமானவரிகளிலும் பிற சங்கவரிகளிலும் மாற்றங்களை அவ்வப்போது ஏற்படுத்திக் கொண்டே இருக்கின்றது. அத்துடன் பொதுச் சேவை நிறுவனங்களுக்கும் வரிச் சலுகை வழங்கி வறியவர்களுக்கு உதவ செல்வந்தர்களை ஊக்குவிக்கின்றது.

"தெண்கடல் வளாகம் பொதுமை இன்றி
வெண்குடை நிழற்றிய ஒருமையோர்க்கும்...
செல்வத்துப் பயனே ஈதல்
துய்ப்பேம் எனினே தப்புன பலவே"
(புறநானூறு - 189)

இவைதாம் மக்களின் அடிப்படைத் தேவைகளைத் தீர்வு செய்யப் பணிக்கும் புதிய பொருளாதாரத் தத்துவமாகும் என்பதை புறநானூற்று வரிகள் எடுத்துரைக்கின்றது.

இவ்வரிகளை உணர்ந்து உள்ளத்தில் ஏற்று செயல்பட்டால் உண்மையில் முதலாளி - தொழிலாளி போராட்டங்கள் இல்லை. கிளர்ச்சிகள் இருக்காது. இருப்பவர்கள் இல்லாதவர்க்குக் கொடுப்பதால் பொருள் தட்டுப்பாடு பூவுலகில் தோன்றாது. இதனையே.

"இனியொரு விதி செய்வோம்! அதை
எந்த நாளும் காப்போம்
தனியொரு மனிதனுக்கு உணவிலை எனில்
சகத்தினை அழித்திடுவோம்!"

என்ற பாரதியின் சகத்தினை அழிக்கும் சாட்டையடி வரிகளிலும் கனன்று நிற்கும் கட்டளை இதுவேயாகும்.

கல்வியின் சிறப்பு

ஒரு நாடு நீர்வளத்தோடு நிலவளம் கொண்ட செல்வச் செழிப்போடு விளங்கினாலும் மக்கள் கல்வி அறிவு மிக்கவர்களாக இல்லாமல் போனால் சீரழியும் என்பதைத் தெளிவாக உணர்ந்த ஆசிரியப்படை கடந்த பாண்டியன்நெடுஞ்செழியன் தம் பாடலில் குறிப்பிடுகிறார். இவற்றை புறநானூறு வரிகள்,

"உற்றுழி உதவியும் உறுபொருள் கொடுத்தும்
பிற்றைநிலை முனியாது கற்றல் நன்றே...
வேற்றுமை தெரிந்த நாற்பாலுள்ளும்
கீழ்ப்பால் ஒருவன் கற்பின்
மேற்பால் ஒருவனும் அவன் கண்படுமே"
(புறநானூறு - 183)

என்று குறிப்பிடும் போது ஒருவர் ஒரு பொருளை பெற்றுக் கொள்ளும் போது பொருளைக் தருவோர் உயர்ந்தவராகவும் பொருளைப் பெறுவோர் தாழ்ந்தவராகவும் கருதப்படுவர் அல்லவா? அப்படியாயின் பொருளைத் தரும் மாணவன் உயர்ந்தவனாகவும் ஆசிரியர் தாழ்ந்தவராகவும் அல்லவா கருதப்பட வேண்டும்? கல்வி கற்றிட பொருள் தரும்போது மாணவன் உயர்ந்தவனாகக் கருதப்படக் கூடாது. அவன் வழிபாட்டு நிலையிலே வழங்குவதால் அங்கு அவன் உயர்ந்தவனாகக் கருதப்பட மாட்டான். இவற்றையெல்லாம் கருத்தில் கொண்டே பாண்டியன் ஆசியப்படை கடந்த நெடுஞ்செழியன் "பிற்றை நிலை முனியாது கற்றல் நன்றே" என்கிறான். அதாவது பொருளை வழங்குவதால் உயர்ந்தவன் என்று எண்ணாமல் வழிபடுகின்ற நிலையினின்று மாறாது கல்வி கற்றல் அழகானது என்பதே அவனுடைய உள்ளக் கிடக்கையாகும்.

இன்றைய நிலையில் கல்வித்துறையில் ஆசிரியர்க்கு உற்றுழி உதவுகிற பண்பும் உறுபொருள் கொடுத்து பிற்றை நிலை முனியாது கற்கும் சிறப்பும் அறவே இல்லாமல் போனதால் தான் கல்வி வணிகப் பொருளாக்கப்பட்டது. மாணவர்களும் ஒருமையுணர்வற்றவர்களாக ஆக்கப்பட்டனர்.

வேறுபாடு தெரியப்பட்ட (செய்யும் தொழிலால் வேறுபட்டிருக்கும்) நான்கு குலத்தில் கீழ்க் குலத்தில் பிறந்த ஒருவன் கல்வி பெற்றிருப்பானாயின் மேற்குலத்தில் பிறந்தவன்கூட கல்வியறிவுடையோன் கீழ்க்குலத்தான் என்று பாராது அவனுடைய கல்வியறிவை எண்ணி அவனிடத்தே சென்று வழிபடுவானாம்.

சாதி வேறுபாடுகள் கூட கல்வியால் காணாமல் போய்விடும் காட்சியைக் கனமான கவிதை வரிகளில் காட்டுகிறார் நெடுஞ்செழியன். அதனால்தான் நம் அரசாங்கம் கூட கல்வியை அனைவருக்கும் கொண்டு செல்ல முயற்சி செய்கிறது.

அறம் வழுவா வாழ்க்கை முறை

கொடுமைகளில் கொடுமை எது? எதைச் செய்தால் மீளவே முடியாத பாழ்நரகம் கிடைக்கும்! மன்னிக்க முடியாத குற்றம் எது? உய்வே இல்லாமல் ஒழிக்கும் பாவம் யாது? குற்றங்களிலே பெருங்குற்றம் எனப்படுவது எதனை? அற நூல்கள் என்ன கூறுகின்றன? இக்கேள்விகளுக்கு விடை நமக்குப் புறநானூற்றுப் பாடல் 34-ல் கிடைக்கிறது. விடையினை விளக்கமாக விளம்பி இருப்பவர் ஆலத்தூர்கிழார் என்னும் அருந்தமிழ்ப் புலவன். சோழன் குளமுற்றத்து துஞ்சிய கிள்ளி வளவனைப் போற்றிப் பாடிய நற்றமிழ்ப் பாடலில் நாம் தேடும் விடையினை நல்குகிறார் புலவர். எத்தகு கொடுமைகளைச் செய்த கொலையாளிகளுக்கும், பண்பற்ற செயல்களைச் செய்த பாவிகளுக்கும் கூட உய்வுதரும் உயர்ந்த வழி உள்ளதாம்!

ஆனால் செய்ந்நன்றி மறப்பது தான் செயல்களிலே மிகவும் தீமையானது. செய்ந்நன்றி கொன்றவர்களுக்கு உய்வே கிடையாது. அவர்களுக்கு மீள முடியாத நரகம்தான் சொந்தம். அவர்கள் நரகம் செல்வதிலிருந்து தப்பிக்கவே முடியாது. செய்ந்நன்றி கொன்ற சூரபத்மன் உய்வு பெற முடியாத வரலாறுதானே கந்தபுராணம். இதனை புறநானூறு வரிகள்

"ஆன்முலை அறுத்த அறனிலோர்க்கும்
மான் இழை மகளிர் கருச்சிதைத்தோர்க்கும்
குரவர் தப்பிய கொடுமையோர்க்கும்...
கொண்டல் மாமழை பொழிந்த
நுண்பல் துளியினும் வாழிய பலவே"
(புறநானூறு - 34)

சோழ மன்னன் கிள்ளிவளவனிடம் பெரும் செல்வத்தைப் பரிசாகப் பெற்றுச் செல்கிறார் புலவர் ஆலத்தூர்கிழார். அப்போது மன்னன் அவரிடம் **"என்னை நினைத்து மீண்டும் இங்கே வருவீர்களா?"** என்று கேட்க புலவர் - **பாணர்க்குத் தொலையாத செல்வத்தை வழங்கும் என்தலைவனாகிய கிள்ளிவளவன் வாழ்க!** - என வாழ்த்தி நான் பாடவில்லை எனில் ஒருவன் செய்ந்நன்றி கொன்றால் அவனுக்கு உய்வு இல்லை என அறநூல்கள் கூறியவாறு நான் வாழும் நாட்டில் சூரியன் முறைப்படி தோன்றாது. எனவே **"சான்றோர்கள் செய்த நல்வினையின் காரணமாக நாட்டிலே பெய்யும் மழைத்துளிகளின் எண்ணிக்கைகளை மிஞ்சிய ஆண்டுகள் நீ வாழ்வாயாக!"** எனச் சொல்லி வாழ்த்துகிறார்.

இப்புறப்பாடலில் எப்படிப்பட்ட கொடிய செயல்களைச் செய்த பாவிகளுக்கும் உய்வு உண்டு. ஆனால் செய்ந்நன்றி கொன்ற தீயவர்களுக்கு உயர்வு இல்லை. மேலும் நன்றி கொன்றவர்கள் வாழும் நாட்டில் சூரியன் முறைப்படித் தோன்றாது நீங்கி விடும். சான்றோர்கள் செய்த நல்வினைகளின் காரணமாகவே நாட்டில் மழை பெய்கிறது எனத் தனி மனிதனுக்கு அறத்தைச் சொல்லி அவ்வற வழியில் அவனை வாழச் செய்யும் பொன்னெறிகள் பொலிவதைப் பார்க்கிறோம்.

நிர்வாகத்திற்கு ஏற்றப் பணியாளர்கள்

இன்றைய சமுகத்தில் பலருக்கு பணியில் மன அழுத்தமும் பணிச் சுமையும் கூடுவதால் அவர்களுக்கு இதயத் துடிப்பு, இரத்தக் கொதிப்பு

போன்ற நோய்களுக்கு வழிவகுக்கிறது. நல்ல பணியாளர்கள் கிடைக்கப் பெறாதவர்களுக்கே இந்நிலை ஏற்படுகிறது. அது தனியாரோ அல்லது அரசு நிறுவனமோ அனைத்து ஊழியர்கள் மற்றும் அதிகாரிகளுக்கும் இது பொருந்தும்.

நல்ல பணியாளர்கள் கிடைக்கப்பெற்றால் ஒரு நிர்வாகிக்குக் கவலை இருக்க முடியுமா? கவலையுடன் அதன் காரணமாக வரும் தலைநரையும் தோன்றாமல் இருக்க நல்ல பணியாளர்களும் காரணமாக உள்ளார்களாம் என புறநானூற்றில் புகழ்கின்றார் பிசிராந்தையார். இதோ பாடல்!

"யாண்டு பல ஆக நரைஇல ஆகுதல்
யாங்கு ஆகியர்? என வினவுதிர் ஆயின்...
ஆன்று அவிந்து அடங்கிய கொள்கைச்
சான்றோர் பலர் யான் வாழும் ஊரே"
(புறநானூறு - 191)

என்று கூறும் பொழுது நல்ல பணியாளர் கிடைத்துவிட்டால் மேலாளருக்குக் கவலையே வராது என்று உணர்த்தும் புறநானூற்றுத் தத்துவம் காலத்தால் அழியாத கருத்துப் புதையல். மேலும்

"ஒல்லுவது ஒல்லும் என்றலும் யாவர்க்கும்
ஒல்லாது இல் என மறுத்தலும் இரண்டும் ..
இரப்போர் வாட்டல் அன்றியும் புரப்போர்
புகழ்குறை படுஉம் வாயில் அத்தை"
(புறநானூறு - 196)

இவ்வரிகளின் வழி இயன்றதை இயலும் என ஒப்புக் கொள்வதும், இயலாததை இயலாது என மறுத்துவிடுதலும் ஒரு மேலாளரின் புகழ் மேம்பட உதவும் என்பதும்இ அவ்வாறு தன்நிலை அறிந்து உணர்ந்திடாமல் இயன்றதை இயலாது என்றும், இயலாததை இயலும் என்றும் கொண்டு நிற்பது அவருக்கு இகழ்ச்சி தரும் என்ற கருத்து கூறப்பட்டுள்ளது.

தகவல் தொடர்பு சிந்தனைகள்

தகவல் தொடர்பு சிறப்புடையதாக விளங்கினால்தான் மேலாண்மை வெற்றியடையும் என்பது அனுபவம் காட்டும் உண்மை. கருதிய எண்ணத்தைத் தெளிவாக கருத்து பேதம் ஏற்படாத வண்ணம் ஐயம் திரிபு அற ரத்தினச் சுருக்கமாகச் சொல்ல வல்லவர்கள் உலகத்தையே வெல்லக் கூடிய ஆற்றல் மிகுந்தவர்கள். தகவல் பெறுபவர்களைத் தன்வயப்படுத்துகின்ற நிலையில் தான் விரும்பிய வகையில் பணியாற்றத் தூண்டும் வண்ணம் செய்தித் தொடர்பு அமைய வேண்டும். (Communication should be persuasive effective and inducing desired action)

புறநானூறு பாடிப் புகழ் கொண்ட பொற்றமிழ்க் கவிஞர்கள் செய்தித்தொடர்புக் கலையிலும் வல்லுநர்களாக விளங்கியதை அவர்களின் பாடல்களே சான்றாகி நமக்குப் புலப்படுத்துகின்றன. இக்கலையில் கை தேர்ந்தவர்களாக அவர்கள் விளங்கியதால் தான் அவர்களால் அரசனுக்கு அறிவுரை தந்து நாட்டில் பல மாற்றங்களைக் கொண்டு வர முடிந்தது. ஏன்? பல போர்களைக் கூட தடுத்து நிறுத்தி பைந்தமிழ்ப் புலவர்கள் சமாதான வெண்புறாக்களாக விளங்கி இருக்கிறார்களே!

ஔவையார் நம் கோவூர்கிழார் நம் தம் தமிழ்ப் புலமையாலும் கேட்டாரைப் பிணிக்கும் சொல் வன்மையாலும் போர்களை நிறுத்திய புகழ் வரலாறுகளைப் புறநானூற்றிலே நாம் காண்கிறோம்.

இவ்வாறே சோழன் குராப்பள்ளித் துஞ்சிய பெருநற்கிள்ளியும், பாண்டியன் வெள்ளியம்பலத்துத் துஞ்சிய பெருவழுதியும் போரிட முற்பட்டபோது காவிரிப் பூம்பட்டினத்துக் காரிக் கண்ணனார்

"நீயே தண்புனற் காவிரிக் கிழவனை" (புறநானூறு-58)

இங்ஙனம் புலவர்களின் செந்நாவளம் கொடிய போர்களையே தவிர்த்து நாட்டில் அமைதி ஏற்பட வழிவகுத்தது. எனில் நாவளத்தாலும் சொல்வன்மையாலும் மேலாண்மைத்துறையிலும் சாதனைகள் படைக்கலாம் என வரலாறு காட்டுகிறது.

"காய்நெல் அறுத்துக் கவளம் கொளினே
மாநிறை இல்லதும் .....
யானை புக்க புலம் போலத்
தானும் உண்ணான் உலகமும் கெடுமே"
(புறநானூறு - 184)

என்று பாண்டியன் அறிவுடைநம்பிக்குப் பிசிராந்தையார் பாடிய பாடலும் நம் உள்ளத்தில் பல மேலாண்மைச் சிந்தனைகளை விளைவிக்கிறது.

திட்டமிடுதலும் செயலாற்றுதலும் ஆகிய மேலாண்மைத் தத்துவங்கள் இப்பாடலில் படிமமாகப் பேசப்பட்டுள்ளது. பொருளினை எப்படிச் செலவழிக்க வேண்டும், எப்படி செலவழிக்க கூடாது, எப்படி செலவழித்தால் இலாபம் ஈட்டலாம் என்றெல்லாம் அறிவிக்கின்ற நிலையில் இப்புறப்பாடல் பல பொன்னான பொருளாதாரச் சிந்தனைகளையும் நம் மனத்தில் எழச் செய்கின்றது. அரசு ஊழியர்கள் பணிகளை நிறைவேற்ற கைக் கொள்ள வேண்டிய அணுகு முறைகளையும் இப்பாடல் எடுத்துக் காட்டுகிறது.

முடிவுரை

புறநானூற்றில் நேரடியாகவும் மறைமுகமாகவும் உய்த்து உணரும் வண்ணம் பேசப்பட்டிருக்கின்ற மேலாண்மைச் சிந்தனைகள் அளவற்றவை. அவற்றை உணர்ந்து செயலாற்றினால் நம் எல்லாப் பணிகளிலும் வெற்றி காணலாம் என்பதனை இக்கட்டுரையின் வழி அறியப்பட்டுள்ளது.

12. பாலைக்கலியில் காணலாகும் மேலாண்மைச் சிந்தனைகள்

முனைவர் ச. ஈஸ்வரன்
இணைப்பேராசிரியர் மற்றும் தலைவர், தமிழ்த்துறை
தேசியக்கல்லூரி (தன்னாட்சி)
திருச்சிராப்பள்ளி - 620 001.

முன்னுரை

150 கலிப்பாக்களைக் கொண்டது கலித்தொகை. ஒவ்வொரு திணையைப் பற்றியும் ஒவ்வொரு புலவராக ஐந்து திணைகள் பற்றியும் ஐந்து புலவர்களால் பாடப்பட்டது. பாலை-பெருங்கடுங்கோ, குறிஞ்சி-கபிலர், மருதம்-மதுரை மருதனிளநாகனார், முல்லை-சோழன் நல்லுருத்திரன், நெய்தல்-நல்லந்துவனார் ஆகியோர் பாடியுள்ளனர். கலித்தொகையைத் தொகுத்தவர் நல்லந்துவனார். "கற்றறிந்தார் ஏத்தும் கலி" எனப் புலவர்களால் பாராட்டப் பெறுவது கலித்தொகை. இந்நூலுக்கு நச்சினார்க்கினியர் உரை எழுதியுள்ளார். இனி, பாலைக்கலியில் காணலாகும் மேலாண்மைச் சிந்தனைகள் குறித்து ஆராயலாம். பாலைக்கலியில் 35 பாடல்கள் உள்ளன.

நெறிப்படுத்தும் மேலாண்மை

பாலையின் கொடுமையை இந்நூலைப் போல விரிவாகப் பிற நூல்களில் காணமுடியாது. பாலை வழியில் செல்பவர்களின் நாக்கு வறண்டு வீடுகின்றது. தண்ணீர் கிட்டவில்லை. துயரால் தடுமாறுகின்றார்கள். அப்போது அவர்களின் கண்களிலிருந்து கண்ணீர் வருகின்றது. அக்கண்ணீர் நாவை நனைத்துச் சிறிது ஆறுதல் அளிக்கிறதாம்.

"உள்நீர் வறப்பப் புலம் வாடு நாவிற்குத்
தண்ணீர் பெறாஅத் தடுமாற்று அருந்துயரம்
கண்ணீர் நனைக்கும் கடுமைய காடு."
(பாலைக்கலி, பாடல் எண்-5)

இத்தகைய காட்டில் ஆறலைக் கள்வர்கள் வாழ்கிறார்கள். அவர்கள் வழிச் செல்பவர்களை மறித்துக் கொள்ளை அடிக்கிறார்கள். கொள்ளை அடிப்பதற்குப் பொருள் இல்லை எனில், வழிச் செல்பவர்களைக் கொன்று அவர்களின் உடல்கள் துள்ளுவதைக் கண்டு மகிழ்கின்றார்கள். எனவே விழிப்புடன் பாதையில் செல்லுமாறு நெறிப்படுத்தும் மேலாண்மைத் திறத்தை இதன்வழி உணர முடிகிறது.

"கடுங்கண் மறவர் தாம்
கொள்ளும் பொருள் இலர் ஆயினும் வம்பலர்
துள்ளுநர்க் காண்மார் தொடர்ந்து, உயிர் வெளவலின்
புள்ளும் வழங்காப் புலம்பு கொள் ஆரிடை"
(பாடல்-3)

இக்காட்டில் பறவைகள் செல்லவில்லையாம்.

திருக்குறள்

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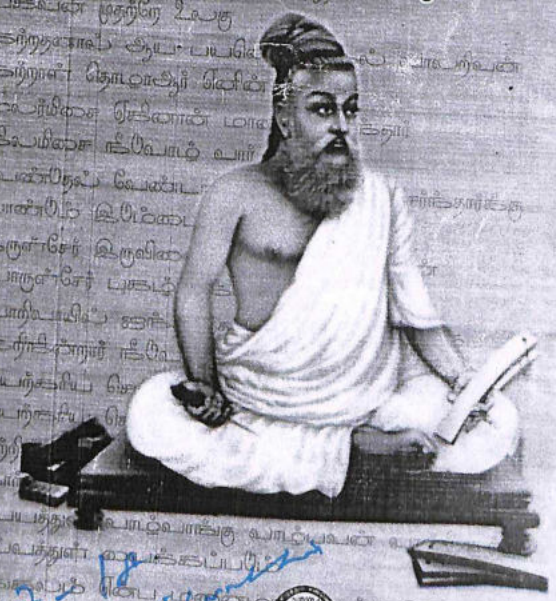
திருக்குறள் விழுமியங்கள்

முனைவர் கோ. தேவிபூமா

திருக்குறள் விழுமியங்கள்

தொகுப்பாசிரியர்
முனைவர் கோ. தேவிபூமா



மன்னர் திருமலை நாயக்கர் கல்லூரி (தன்னாட்சி)

பரிந்தோம்பிப் பற்றற்றேம் என்பர் விருந்தோம்பி வேள்வி தலைப்படாதார் விருந்தினரைப் பேணி, அந்தயாகத்தின் பயனைப் பெறும் பேறு அற்றவர் செல்வத்தைச் சிரமப்பட்டுக் காத்தும் அதனை இழக்கும் போது, எந்த துணையும் இல்லாதவராய்ப் போனோமே என்று வருந்துவர்.

உடைமையுள் இன்மை விருந்தோம்பல் ஓம்பா
மடமை மடவார்கண் உண்டு

செல்வம் உள்ள காலத்தில் ஏழ்மை என்பது விருந்தினரை உபசரிக்காததேயாகும் அது பேதையரிடம் உள்ள குணமாகும்.

செல்வநிலையில் உள்ள வறுமை என்பது விருந்தோம்புதலை போற்றாத அளியாமையாகும் அ.·.து அறிவிலிகளிடம் உள்ளதாகும், அவர்கள் பணம் இருந்தாலும் தரித்திரம் பிடித்தவர்களாவே கருதப்படுவர் என்று கூறுகிறார் வள்ளுவர்.

மோப்பக் குழையும் அனிச்சம் முந்திரிந்து
நோக்கக் குழையும் விருந்து

எல்லா மலரினும் மெல்லியதாகியது அனிச்சப்பூ இந்த அனிச்சப்பூ முகர்ந்தவுடன் வாடிவிடக்கூடியது. அதுப்போல் சற்று முகங்கோணி வரவேற்றாலே விருந்தினர் வாடிவிடுவர் என்று வள்ளுவர் கூறுகிறார்.

முடிவுரை

விருந்தோம்பல் என்பது தமிழர் பண்பாடு விருந்தினர்களை எப்படி உபசரிப்பது எவ்வாறு நடந்து கொள்வது போன்றவற்றை விருந்தோம்பல் அதிகாரத்தால் வள்ளுவப் பெருந்தகை விக்கியுள்ளார். இன்றைய கால கட்டத்தில் விருந்தோம்பல் என்றால் என்ன? என்று கேட்கும் சமூகத்தில் வாழ்ந்து கொண்டிருக்கிறோம். உபசரிப்பு வரவேற்றல், உபசரித்தல், பிறரிடம் பழக இனிமையாக நடந்து கொள்ளுதல், சுயநலம் பாராதிருத்தல், பிறர்நலம் வேண்டுதல், தன்னை வருத்தி பிறரை வாழ்வித்தல், இல்லறத்தின் சிறப்பே விருந்தினருக்கு இன்முகத்தோடு உபசரித்தல் போன்றவற்றை எடுத்துக் கூறியிருப்பது இக்காலம் மட்டுமல்ல எக்காலமும் பொருந்துவதாகும்.

63. தனக்குவமை இல்லாதான்

முனைவர் இராம.மாணிக்கவாசகன்
உதவிப்பேராசிரியர், தமிழாய்வுத்துறை,தேசியக்கல்லூரி, (தன்னாட்சி)
திருச்சிராப்பள்ளி

திருக்குறள் ஒரு வாழ்வியல் நூல். இது உலகப் பொதுமறை என்று போற்றப் பெறுகின்றது. திருவள்ளுவதேவர் வாய்மை என்கிற பழமொழி என்று அருணகிரி நாதரால் பாராட்டப்பெற்ற நூல். அறிஞர் பெருமக்களால் வியக்கத்தக்க கருத்துக்கள் திருக்குறளில் ஏராளமாக இருக்கின்றன. சைவ சித்தாந்தக் கருத்துக்கள் பலவும் இந்நூலில் இடம்பெற்றுள்ளன. இங்கே எடுத்துக் கொள்ளப் பெற்ற பொருள் தனக்குவமை இல்லாதான் என்பதாகும். இத்தொடர் சிவபெருமானைக் குறிக்கின்ற முறைமைபற்றி இக்கட்டுரையில் விளக்கமாகக் காணலாம்.

உலகத்திலேயே சில பொருள்களுக்கு உவமை கூற முடியாது. வாழைப்பழம் விற்கின்ற வியாபாரி ஒருவன் இது தேன் போன்று இனிக்கும் என்று கூறுவான். ஆனால் தேன் விற்கின்ற ஒருவன் அந்த தேனுக்கு ஏதேனும் உவமை கூறுவானோ என்றால் அ.·.து ஒருகாலத்திலும் இல்லை. ஏனென்றால் தேனுக்கு நிகரான பொருள் எதுவும் இல்லை. இதேபோன்று சிவபெருமானுக்கு நிகராக இன்னொருவரைக் காட்ட இயலாது. இதனால் சிவபெருமானுக்கு 'ஒப்பிலி' என்றும் தனக்குவமையில்லாதான் என்று திருநாமங்கள் உண்டாயின. 'சமான ரஹிதம் விபும்' என்றபடி சிவ பெருமான் சமான மற்றவராக விளங்குகின்றார். இக்குறட்பாவின் கருத்தைத் திருநாவுக்கரசு சுவாமிகள் 'ஒப்புடையனல்லன் ஓர் உவமன் இல்லி' என்று எடுத்துரைக்கின்றார். 'அம்மையே அப்பா ஒப்பிலா மணியே' என்பது திருவாசகம். ஒப்புனக்கில்லா ஒருவனே என்பதும் திருவாசகம். மணிவாசகப் பெருந்தகை சிவ பெருமானுக்கு உவமை கூறுதற்காகப் பல பொருள்களையும் ஒப்பிட்டு முடிவில் உவமை ஏதும் இன்மையால் உனக்கு நீயே ஒப்புடையனாகிறாய் என்று பகர்கின்றார்.

"என்னை அப்பா அஞ்சல் என்பவர்
இன்றி நின்று எய்த்தலைந்தேன்
மின்னை ஒப்பாய் விட்டுதி கண்டாய்
உவமிக்கின் மெய்யே
உன்னை யொப்பாய் மன்னும்
உத்தரகோச மங்கைக் கரசே
அன்னை யொப்பாய் எனக்கு அத்தனொப்பாய்
என் அரும் பொருளே"

நீத்தல் விண்ணப்பம்.

திருமூலர் திருமந்திரத்தில் சிவனுக்குச் சமமான தெய்வத்தைத் தேடினாலும் கிடைக்கவில்லை என்று பேசுகின்றார்.

"சிவனோ டொக்கும் தெய்வம் தேடினும் இல்லை
அவனோ டொப்பர் இங்கு யாவரும் இல்லை
புவனம் கடந்தன்று பொன்னொளி மின்னும்
தவனச் சடைமுடி தாமரை யானே"

"அப்பனை நந்தியை ஆரா அமுதினை
ஒப்பிலி வள்ளலை ஊழி முதல்வனை
எப்பரிசாயினும் ஏத்துமின் ஏத்தினால்
அப்பரிசு ஈசன் அருள்பெற லாமே"

சிவதருமோத்தரம் என்னும் நூலில் அகத்தியர் முருகனிடம் பாடம் கேட்டுக் கொண்டே வருகின்றார். அப்போது முருகப் பெருமான் இதுவரை எனக்குத் தெரியாத கருத்து ஒன்று இருக்கிறது என்றார். அகத்தியர் அதுபற்றி வினவுகிறார். அதற்கு முருகப் பெருமான், நான் இதுவரை படித்த நூல்களில் சிவபெருமானோடு மற்றவர்களையும் சேர்த்துச் சமம் என்று கூறுபவர்களுக்குப் பரிகாரம் என்பதே கிடையாது என்றார்.

"காரகன் தனை காயம்
காசினி காறும் காக்கும்
பார்கன் தனையும் பாரில்
படைத்திட பட்ட யாவும்
ஆரகன் அதிகன் என்னாது
அவர்த்தமக் கொப்பென் பார்கள்
நாரகர் பரிகா ரத்தை
நவிற்று நூல் அறியோம் நாமே"

காரகன் - பிரம்மா
பாரகன் - திருமால்
ஆரகன் - உருத்திரன்

இந்த மும்மூர்த்திகளுள் சிவனே ஒருவனாக எண்ணுதல் பாவம். இக்கருத்தைத் திருவாசகத்தில்,

"மூவரென்றே எம்பிரா னொடும் எண்ணி
விண்ணாண்டு மண்மேல்
தேவரென்றே இறுமாற்று என்ன பாவம்
திரிதவரே"

என்று பாடுகிறார்.

பிரம்மா, விஷ்ணு இவர்களையும் சிவபெருமான் படைத்து காத்து அழித்தலால் இந்த இருவருக்கும் மேற்பட்டவன் சிவனே ஆவான். மும்மூர்த்திகளுள் ஒருவராக எண்ணி பிரம விஷ்ணுக்களைப் பரம்பொருளாக எண்ணி வழிபாடு செய்பவர்கள் நரகத்தில் சென்று விழுவார்கள். அங்கிருந்து அவர்கள் மீள முடியாது. அவர்கள் அப்படி வழிபடுவதால் எங்களுக்கும் நரகம் உண்டாகிறது என்று பிரமன் தக்களுக்கு உபதேசிக்கின்றார்.

"நம்மையும் பரமென் றுன்னி
நாதனிற் சிறப்புச் செய்யும்
வெம்மைகொள் நெஞ்சர் தீரா
விழுமவெந் நிரயம் வீழ்வர்
தம்மைய.. தெடுதல் செய்யா
சமம் எனப் புகல்கிற் போர்கள்
எம்மையும் பாவமென்னும்
இருவ்கடற் படுப்ப ரன்றே" – கந்த புராணம்.

ஆகவே உயிர்வர்கங்களாகிய பிரமன் முதலான தேவர்கள் வேறு சிவமாகிய கடவுள் வேறு. இக்கருத்தையே வள்ளுவர் பெருந்தகைச் சிவ பெருமானைத் தனக்குவமை இல்லாதவன் என்று சிறப்பித்துள்ளார். இப்பெருமானைச் சார்ந்து வழிபாடு செய்யும் ஆன்மாக்களுக்கு மனக்கவலை இருக்காது. சாராதவர்கள் மனக்கவலையை மாற்ற முடியாமல் வருந்துவர். எனவே மகிழ்ச்சியாக வாழ எல்லாம் வல்ல இறைவனைச் சார்ந்து வாழுங்கள் என்று இப்பாடல் மூலம் விளக்கப்படுகின்றது.

"தனக்குவமை இல்லாதான் தான்சேர்ந்தார்க் கல்லால்
மனக்கவலை மாற்றல் அரிது"

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சான்லாக்ஸ் பன்னாட்டுத் தமிழியல் ஆய்விதழ்

காலாண்டிதழ்

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பொருளடக்கம்

கம்பராமாயணத்தில் பிற இலக்கிய வகைக்கூறுகள்

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அறிமுகம்

முன்னர் தோன்றிய இலக்கியமே பின்னர் இலக்கியங்களின் தோற்றத்திற்கு ஒரு மூலக்காரணமாக அமையும் என்றால் அது மிகையாகா. எந்த ஓர் இலக்கிய வகையும் திடீரென்று தோன்றுவதற்கு இயலாது. ஓர் இலக்கிய வகை தோன்றுவதற்குமுன் அவ்விலக்கிய வகையின் மூலக்கூறுகள்,அதற்கு முன் உள்ள இலக்கணம், இலக்கியம் ஆகியவற்றில் வித்தாகப் பதிவுசெய்யப்பட்டு அமையும். அந்த வகையில் கம்பராமாயணம் என்ற ஒரு காப்பியத்தில் (இதிகாசத்தில்) காணப்படும் பிற இலக்கிய வகைக்கான கூறுகளை இனங்கண்டு எடுத்துரைப்பதே இக்கட்டுரையின் நோக்கமாக அமைகிறது.

இலக்கிய வகை பற்றிய அறிஞர் கருத்துக்கள்

ஒரு நாட்டின் சமுதாய, பொருளாதார,அரசியல் சமயச் சூழல்களுக்கேற்பக் காலந்தோறும் பல்வேறு இலக்கியங்கள் தோன்றி வளர்கின்றன. அத்தகைய இலக்கியங்கள் அவற்றின் அமைப்பு, பொருள், யாப்பு முதலியவற்றின் அடிப்படையில் பல்வேறு வகைகளாகப் பாகுபாடு செய்வர். அவற்றை இலக்கிய வகைகள் என்பர்.

"இலக்கிய வகைகளின் தோற்றத்தில் மூன்று நிலைகளை குறிப்பிடுவர் கி.ராசா"[1]

1. இலக்கிய மூலக்கூறு எனும் தோற்ற நிலை.
2. இலக்கிய மூலக்கூறுகள் சான்றுப் பாடல்களைப் பெற்று வகைமைகளாக இயங்கும் நிலை.
3. இலக்கிய வகைமைகள் வகைகளாக உருவாகும் நிலை.

"அனைவராலும் ஒப்புக் கொள்ளப்பெற்ற வடிவத்தாலும், கருத்தாலும் ஒப்புமைகளை உடைய நூல்களின் தொகுதிக்கு ஓர் இலக்கிய வகை எனப்பெயரிடலாம் என்று ஆல்பர்ட் ஜோல்டு கூறுவதாக் காட்டுவர்"[2]

"தமிழண்ணல் இலக்கியத்தைச் சமுதாயத்துடனும் இலக்கிய வகைகளைச் சமுதாயத்தில் இடம்பெறும் குடும்பங்களுடனும் ஒப்பிட்டுக் காட்டுகின்றார்"[3]

"தமிழ் இலக்கியங்களை வகைமை அடிப்படையில் மு.வரதராசனார் இலக்கிய மரபு என்ற நூலில்,

1. பொருள் அடிப்படை,
2. வடிவ அடிப்படை,
3. அடிவரையறை அடிப்படை,
4. எண்ணிக்கை அடிப்படை,

5. சொற்கள் அடிப்படை,
6. உத்தி அடிப்படை,
7. பிற வகை என வகைப்படுத்தியுள்ளார்.[4]

தமிழில் இலக்கிய வகைகள்

தமிழில் இலக்கிய வகை பற்றிய சிந்தனைகள் தொல்காப்பியர் காலந்தொட்டே இருந்து வருகிறது.

> "பாட்டு,உரை,நூலே வாய்மொழி, பிசியே
> அங்கதம்,முதுசொல்லோடு அவ்ஏழ் நிலத்தும்
> வண்புகழ் மூவர் தண் பொழில் வரைப்பின்
> நாற்பெயர் எல்லை அகத்தவர் வழங்கும்
> யாப்பின் வழியது என்மனார் புலவர்"[5]

என்ற நூற்பா மூலம் தொல்காப்பியம் கூறுகின்ற இலக்கிய வகைகள் ஏழு என எண்ணலாம். பாட்டியல் நூலார் ஒவ்வொருவரும் தத்தம் கருத்திற்கேற்ப இலக்கியங்களை வகைப்படுத்தியுள்ளனர். இதனால் "பாட்டியல் நூல்கள் குறிப்பிடும் இலக்கிய வகைகளின் எண்ணிக்கை விரிந்தது. நூல்களைப் பட்டியலிடும் இவற்றில் வகைகளை அறிவியலின்படி அணுகுவதென்பது அரிதாகவுள்ளது."[6] என்று பாட்டியல் நோக்கிலான வகை அருமையை அறிஞர்கள் சுட்டியுள்ளனர்.

காப்பியம்

தமிழ் இலக்கிய வகைகளில் ஒன்றாகிய காப்பியம். "காப்பு+இயம் எனப் பிரித்துக் காப்பு உடையது காப்பியம் ஆயிற்று"[7] என இரா.வ.கமலக்கண்ணனும், "மொழிக்குக் காவலாக, பாதுகாப்பாக அமைவது காப்பியம்"[8] என அ.பாண்டுரங்கனும் கூறுகின்றனர்.

"காப்பியம்' என்ற சொல் ஒரு திரிசொல் என்றும், இது காப்பியம் என்பதன் அடியாகப் பிறந்தது என்றும் கருதுகின்ற எஸ். வையாபுரிபிள்ளை 'காவியம்' என்பது 'கவி' என்ற சொல்லின் அடியாகப் பிறந்தது. கவிஞர்களிடமிருந்து தோன்றியது இதுவே காப்பியம் என்று தமிழில் திரிந்து வரலாயிற்று எனக் குறிப்பிடுகின்றார்".[9]

கவியாற் செய்யப்படுவது காவியம் என்று கி.வா. ஜெகநாதன் காப்பியம் பற்றிய தமது கருத்தினை உரைக்கின்றார். தொல்காப்பியர் மெய்ப்பாட்டியல், உவமையியல், செய்யுளியல் ஆகியவற்றில் கூறும் செய்திகள் காப்பிய இலக்கணத்தைச் சுட்டுவனவாகவே அமைகின்றன. தொல்காப்பியர் சுட்டும் வனப்பின் அடிப்படையில் எழுதப்பட்டவையே காப்பியம் என உரைக்கும் பொ.வே சோமசுந்தரனார் இதனை 'வனப்பியல் நூல்கள்' என்று குறிப்பிடுகின்றார்.[10]

இந்த காப்பிய இலக்கிய வகையில் அடங்கும் கம்பராமாயணத்தில் இடம் பெற்றிருக்கின்ற சிற்சில இலக்கிய வகைக் கூறுகளைக் கீழ்கண்டவாறு பகுத்துணரலாம்.

உலா இலக்கிய வகைக்கூறு

உலா இலக்கியத்தின் அமைப்பு, பாட்டிற்குரிய தலைவனின் வரலாறு, பிறப்பு, பெருமை, சிறப்புக் கூறுதல் தலைவன் உலா வருதல், தலைவி காதல் கொள்ளுதல் என்ற வகையில்

அமைந்து காணப்படுகிறது. உலா என்ற இலக்கிய வகைக்கு அடிப்படை தொல்காப்பியத்தில் "ஊரொடு தோற்றமும் உரித்தென மொழி".[11] என்ற நூற்பாவினால் உணரமுடியும்.

தமிழ்க் காப்பியங்களில் பொதுவாகத் தலைவன் உலா வருதல் இயல்பான ஒன்று. இராமனது குலப்பெருமையைக் கூறும் குலமுறைகிளத்துப் படலம் இடம் பெறுகிறது. கார்காலப் படலம், எழுச்சிப்படலம், சந்திரசயிலப்படலம், வரைக்காட்சிப்படலம், பூக்கொய்படலம், நீர்விளையாட்டுப்படலம், எதிர்கொள்படலம், எனப்பல படலங்கள் அமைத்துப் பின்னர் உலாவியற் படலத்தில் இராமன் மிதிலைப்பட்டணத்து வீதியில் உலா வருகின்ற காட்சியை வர்ணிப்பார். இராமனைக் கண்ட பல பெண்கள் அவன் அழகில் ஈடுபட்டதாக பதினேழு பாடல்களிலும், வியந்து தன் நிலை மாறிய பெண்களின் நிலை இருபத்திரண்டு பாடல்களில் வர்ணிக்கப்பட்டுள்ளது.

"ஆடவர்கள் ரூப சௌந்தர்யத்தைக் கண்ணால் முகந்து மதிப்பீட்டு ரசிக்கக் கூடியவர்கள். இக்காரணங்களில் உலாக் காணுதற்குப் பெண்களே மாளிகைகளிலும், வீதிகளிலும் நெருங்கி நிற்பதாகச் சொல்வது மரபு"[12] என எஸ். வையாபுரிபிள்ளை கூறுவர். கைக்கிளை என்னும் ஒருதலை காமத்தின் அகமரபுப்படி இராமன் மீது காதல்கொண்ட மிதிலை நகரப் பெண்கள் ஒவ்வொருத்தியின் நிலையினையும், காதல் நோயினையும் மையல் கொண்டு மயங்கியதையும் உலாவியற்படலத்தில் கம்பர் பாடியுள்ளார்.

"தோள்கண்டார் தோளேகண்டார் தொடுகழற் கமலம் அன்ன
தாள் கண்டார் தாளே கண்டார் தடக்கை கண்டாரும் அத.ஃதே
வாள் கொண்ட கண்ணார் யாரே வடிவினை முடியக்கண்டார்
ஊழ் கொண்ட சமயத்து அன்னான் உருவு கண்டாரை ஒத்தார்"[13]

உலாவியலுக்குத் தோற்றுவாயாகக் கம்பன் ஏழு பருவப்பெண்டிர் நிலையைக் குறிப்பிடும்போது,

"பேதைமார் முதல்கடைப்பேரிளம் பெண்கள் தாம்
ஏதியார் மாரவேள் ஏவவந்து எய்தினார்
ஆதிவா னவர்பிரான் அணுகலால் அணிகொள்கார்
ஓதியார் வீதிவாய் உற்றவா றுஉரை செய்வோம்"[14]

என்று பேதை முதல் பேரிளம் பெண் வரை சுட்டிக்காட்டியிருப்பது உலா இலக்கிய வகைக்கான அடிப்படைக் கூறு கம்பராமாயணத்தில் சான்றாக அமைந்திருந்தது என்பதை தெளிந்து உணரமுடியும்.

தூது இலக்கிய வகைக் கூறு

ஒருவர் கருத்தை மற்றொருவருக்குத் தெரிவிக்க இடையில் பிறிதொருவரையோ அல்லது பிறிது ஒன்றிளையோ அனுப்புவது தூதாகும். இந்தப் பொருண்மையைக் கொண்டு பாடப்பெறும் இலக்கிய வகையே தூது இலக்கியம் ஆகும். இதனை தொல்காப்பியம் 'ஓதல் பகையே தூதிவை பிரிவே' என்று குறிக்கும், பாட்டியல் நூல்களும் இயம்புகின்ற காலத்து எகின மயில் கிள்ளை என்றும் சுட்டும். புறத்திணை – அகத்திணை என்னும் இரண்டிலும் தூதுப் பொருண்மை இடம் பெறும். கம்பன் காப்பியப் பண்பினை அடியொற்றி அனுமன் செல்லுகின்ற தூதைப் அகத்தூதாகவும், அங்கதன் செல்கின்ற தூதைப் புறத்தூதாகவும் அமைக்கின்றார். கம்பராமாயணத்தில் சுந்தரகாண்டத்தில் உருக்காட்டுப்படலத்தில் அனுமன்

சீதையிடம் சென்று தான் இராமனிடம் கூறுவேன் என்று உரைத்தலை சுட்டுவதிலிருந்து அறிய முடியும்.

"கண்டனன் அனுமனும்: கருத்தும் எண்ணினான்
கொண்டனன் துணுக்கம் மெய்தீண்டக் கூசுவான்
அண்டர் நாயகன் அருள் தூதன் யான் எனாத்
தொண்டை வாய் மயிலினைத் தொழுது தோன்றினான்"[15]

இவ்விடத்தில் தலைமகனுக்காக தலைவியினிடம் ஒருவன் தூது செல்லும் மரபினை ஒட்டிய இலக்கிய நிலையை அறியமுடியும்.

"பூதநாயகன் நீர் சூழ்ந்த
புவிக்கு நாயகன் இப் பூமேல்
சீதை நாயகன் வேறுள்ள
தெய்வ நாயகன் நீ செய்யும்
வேதநாயகன் மேல் நின்ற
விதிக்கு நாயகன் தான்விட்ட
தூதன் யான் பணித்த மாற்றம்
சொல்லிய வந்தேன் என்றான்"[16]

என்பதிலிருந்து தூதாக வந்தமைக்கான பொருண்மையை இராவணனிடம் சொல்வதிலிருந்து அறியலாம்.

பிள்ளைத்தமிழ் கூறுகள்

கோசலநாட்டின் நெய்தல் நிலப்பெண்கள் நிலையைப் பற்றிக் கூறும்போது,

"கற்றிலாத கருங்கண் நுளைச்சியர்
முற்றில் ஆர முகந்துதம் முன்றிலில்
சிற்றில் கோலிச் சிதறிய முத்தமே"[17]

என்று பாக்குகளை எடுத்துக் கொழித்துத் தூய்மைப்படுத்துகின்ற நெய்தல் நிலப்பெண்கள் அவற்றை முற்றத்திற்கு வாரிஎடுத்துச் செல்லும்போது சிதறிய முத்துக்களையே சிற்றிலாக அமைத்து விளையாடுவர் என்ற நிலையில் சிற்றில் பருவம் குறிப்பு இடம்பெறுவதை அறியலாம்.

திருஅவதாரப்படலத்தில் இராமன், இலக்குவன், பரதன், சத்துருக்கனன். என நால்வரின் குழந்தைப் பருவ நிகழ்ச்சிப் பற்றி கூறும் நிலையில் மழலை மொழிப்பேசியும், தளர்நடையிட்டும் இப்பூவுலகில் வளர்ந்தார்கள் என்ற நிலையில்,

"அமிர்து உரு குதலையொடு அணிநடை பயிலாத்
....
குமரர்கள் நிலமகள் குறைவர வளர்நாள்"[18]

இந்திரஜித் இறந்தநிலையில் மண்டோதரி புலம்பும்போது,

"தாளரிச் சதங்கை ஆர்ப்பத்
தவழ்கின்ற பருவம் தண்ணில்".
தளர்நடைப்பருவம் தெளிவுபடும்.[19]

"அம்புலி அம்மாவா என்று
அழைத்தலும் அவிர் வெண்திங்கள்".[20] எனும் நிலையில் அம்புலிப்பருவமும் அமைந்திருப்பதை அறியலாம்.

மூலவதைப்படலத்தில் அரக்கர் தலை மேல் கீழ் வீழ்தல் விசய மங்கை கைகளில் அம்மானை ஆடுதல் போல் இருந்தது என்கிறார். இதனை,

"தெம்மு னைச்செரு மங்கைதன் செங்கையில்
அம்மனைக்குலம் ஆடுவபோன்றவே".[21] என்ற வரிகள் உணர்த்தும்.

பரணி இலக்கியவகைக் கூறு

கும்பகர்கணன் - இலக்குவனுக்கும் நடைபெற்ற போர் பற்றி கூறும் நிலையில் ஆயிரம் யானைகளைக் கொன்று குவிக்கும் வன்மையை இலக்குவன் மூலம் எடுத்து இயம்புகின்றார்.

"ஓர் ஆயிரம் ஆயில் வெங்கணை ஒரு கால் விடுதொடையில்
கார் ஆயரம் விடுனதாரையின் நிமிர்கின்றன கதவுற்று
ஈராயிரம் மதமால்கரி விழுகின்றன இனிமேல்
ஆராய்வதென் அவன் வில் தொழில் அமரசேரும் அறியார்".[22] என்பதிலிருந்து அறியலாம்.

கையறுநிலை இலக்கியவகைக் கூறு

பிரம்மாத்திரப்படலத்தில் இந்திரசித்துவின் பிரம்மாத்திரத்தால் கட்டுண்டு இலக்குவன் மயங்கிய நிலையில் இராமன் மூர்ச்ஜசயற்ற போது சீதை புலம்புவதை.

"மங்கை அழுதாள் வானாட்டு
மயில்கள் அழுதார் மழலிடையோன்
பங்கின் உறையும் குயிலழுதாள்
பதுமத் திருந்த மாது அழுதாள்
கங்கை அழுதாள் நாம மடந்தை
அழுதாள் கமலத்தடம் கண்ணன்
தங்கை அழுதாள் இரங்காத
அரக்கிமாரும் தளர்ந்து அழுதார்".[23] என்பதிலிருந்து அறியமுடியும்.

உழத்திப்பாட்டு கூறு

பாலகாண்டத்தில் சரயுநதி தன்மை, உழவர்களின் செயல் ஆகியவற்றைப்பற்றிக் குறிப்பிடும் நிலையில் உழவர்களை கம்பர் மள்ளர்கள் என்று குறிப்பிடுகின்றார்.

"கதவினை முட்டி மள்ளர்
கையெடுத்து ஆர்ப்ப எய்தி".[24]

சரயுநதி வெள்ளம் மதகுகளின் குறுக்கே வைத்துள்ள கதவுகளை முட்டிச்சென்றது. என்றும்,அதன் கரைகளை வேலைசெய்யும் உழவர்கள் தம் கைகளால் அதனைத் தடுத்து காத்தனர் என்றும் வருணிக்கின்றார். அன்றைய காலந்தொட்டே இத்தகைய இலக்கிய வகைக்கூறுகள் இலக்கியங்களில், பயின்றுவந்துள்ளதைக் கம்பராமாயணம்கொண்டு தெள்ளிதின் உணரமுடியும்.

இதேபோன்று கம்பராமாயணத்தில், பொருண்மை அடிப்படையில் பிள்ளைத்தமிழ், ஆற்றுப்படை, பரணி மற்றும் பாதாதிகேசமும், யாப்பு அடிப்படையில் அந்தாதி, விருத்தம் போன்றனவும், நாட்டுப்புற இலக்கியஅடிப்படையில் ஒப்பாரி, குரவை, பள்ளு போன்ற இலக்கியவகைக் கூறுகளை அறியலாம்.

நிறைவுரை

எந்த இலக்கிய வகையும், தொல்காப்பியத்தில் மூலக்கூறாக, வித்தாகப் பதிவு செய்யப்பட்டுப் பிறகு சங்ககாலத்திலும், அதற்கு அடுத்த காலகட்டங்களிலும் சான்றுப் பாடல்களாக வளர்நிலை அடைந்து, சிற்றிலக்கிய காலத்தில் பேரிலக்கிய வகையாக உருமாறுவதே இலக்கிய வகை எனத் துணியலாம்.

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TAMILAIVU SANGAMAM

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தொடர்பு முகவரி

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தமிழ் இலக்கியங்களில் உணவும் உணர்வும்

முனைவர் க.புவனேஸ்வரி
உதவிப் பேராசிரியர், தமிழாய்வுத்துறை
தேசியக்கல்லூரி (தன்னாட்சி), திருச்சி-1.

தமிழர்களின் பண்பாட்டிலும் பாரம்பரியத்திலும் உணவு இன்றியமையாத இடத்தைப் பெறுகின்றது. விருந்தோம்பல் பண்பானது தமிழர்களின் தலைசான்ற குணம் எனக் கருதப்படுகின்றது.

'அல்லிலாயினும் விருந்துவரின் உவக்கும்
முல்லை சான்ற கற்பின் மெல்லியள்'
- (நற்றிணை. 142)

நள்ளிருள்யாமத்து விருந்தினர் வந்தாலும் அவர்களை வரவேற்று உபசரிப்பதைத் தமிழர்கள் தங்களது கடமையாகக் கருதினர்.

காலந்தோறும் தமிழ் இலக்கியங்களில் பலவிதமான உணவு வகைகளும், உபசரிக்கும் முறைகளும், விருந்தின் தன்மைகளும் இடம் பெற்றுள்ளன. அவற்றில் தமிழ் இலக்கியங்கள் காட்டும் உணவையும் உணர்வையும் பற்றிய சில கருத்துக்களை இங்கே சிந்திப்போம்.

தமிழ் விருந்து:

தமிழ் என்று சொன்னாலே அதைக் கேட்பவரின் செவிகளிலும் மனங்களிலும் தேனும் பாலும் தெவிட்டாது பாயும். அதனால்

'இனிமைத் தமிழ்மொழி எமது எமக்கு
இன்பம் தரும்படி வாய்த்த நல் அமுது'
(பாரதிதாசன் கவிதைகள் ப.77)

என்றும்,

'தமிழுக்கும் அமுதென்று பேர்'
(பாரதிதாசன் கவிதைகள் ப.73)

எனவும் பாவேந்தர் திகட்டாத தெள்ளமுது நம் தமிழ்மொழி என்கின்றார். வேறு ஒரு புலவரோ சாகாதவரம் தரும் அமிழ்தத்தை விடவும் சிறப்பானது தமிழ் எனும் விருந்து என்பதை,

'இமையோர் விருந்து அமிழ்தம் என்றாலும்
வேண்டேன்' (தமிழ்விடு தூது ப.62)

எனக் கூறி இன்பமடைகின்றார்.

இப்படித் தமிழையே தங்கள் உணவாக, உணர்வாக தமிழர்கள் கருதியுள்ளனர். உணவைப் பற்றி

உணவின் மேன்மை:

கொடுமையான பசிப்பிணியை போக்கி உயிர்களை உவகையுடன் வாழ வைத்தலே முதன்மையான அறம் எனக் கருதப்பட்டது.

'பசி வந்திடப் பத்தும் பறந்துபோம்'
(நீதி நூல்கள். ஔவையார் ப.120)

எனப் பசிக்கொடுமையையும், பட்டினிச் சாவுகளையும் பற்றிக் கூறும் கருத்தும் சிந்தனைக்குரியவை.

மனிதன் தனக்குத் தேவையான உணவைப் பெறாதபோது அவனிடமிருந்த அனைத்து நற்குணங்களும் காணாமல் போகும். அத்தகைய அபாயம் மிகுந்தது பசி என்கிறார் தமிழ்ப்பாட்டி.

'வயிற்றுக்குச் சோறிடல் வேண்டும் - இங்கு
வாழும் மனிதருக்கெல்லாம்'.
(பாரதியார் கவிதைகள் ப.207)

எல்லாமக்களுக்கும் முதல் தேவை உணவு. அந்த உணவு கிடைக்காவிட்டால்,

'தனியொருவனுக்கு உணவில்லை எனில்
ஜகத்தினை அழித்திடுவோம்'.
(பாரதியார் கவிதைகள் ப.41)

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பசிக் கொடுமையால் புரட்சி உருவாகும். உலகமே அழியக் கூடிய நிலைவரலாம். ஆதலால் அனைவரது பசிப்பிணியையும் போக்கி அறத்ததை வளர்க்க வேண்டும் எனத் தமிழ் இலக்கியங்கள் தெரிவிக்கின்றன.

உபசரிக்கும் முறை:

வீட்டிற்கு வந்த விருந்தினர்களை இன்முகத்துடன் வரவேற்று உபசரித்தலே நம் பண்பாடு.

'கொண்டு வந்து மனைப்புகுந்து

குலாவு பாதம் விளக்கியே
மண்டு காதலின் ஆதனத்திடை வைத்து'
(இளையான்குடிமாற நாயனார் புராணம் - பா.443)

விருந்தினர்களை ஏழடி முன்னே சென்று வரவேற்று, அவர்களை வீட்டிற்குள் அழைத்துச் சென்று, தக்கதொரு ஆசனத்தை அளித்து, அதன்பின்பு உணவிடல் வேண்டும்.

'தண்ணீர் தெளித்துத் தன்கையால் தடவிக்
குமரி வாழையின் குருத்தகம் விரித்து'
(சிலம்பு. ப.283)

வாழை இலையில் தண்ணீர் தெளித்து சுத்தம் செய்து சுவை மிகுந்த உணவைப் பரிமாற வேண்டும். அந்த உணவில் உண்ணல், தின்னல், நக்கல், பருகல் என நான்கு விதமான உணவும், ஆறு விதமான சுவைகளும் இடம் பெறுதல் இன்பம். கணவனும் மனைவியுமாகச் சேர்ந்து வந்த விருந்தினர்களை உபசரிக்க வேண்டும். கணவனைப் பிரிந்து அசோகவனத்தில் சோகத்தின் உருவாகத் திகழும் சீதை தன் துயரை எண்ணி வருந்தாமல், விருந்தினர்களை உபசரிக்க இயலாதே என வருந்துவதாகக் காட்டுகின்றான் கம்பன்.

'அருந்து மெல்லட காரிட அருந்து மென்றழுங்கும்
விருந்து கண்டபோ தென்னுறுமோ என்று விம்மும்'
(கம்பன். சுந்தரகாண்டம் பா.344)

தன் கணவனான இராமனுக்கு யார் உணவளிப்பார்கள்? விருந்தினர்கள் வந்தால் தானின்றி இராமன் எவ்வாறு அவர்களைத் தனியாக நின்று உபசரிப்பான்? என்று எண்ணி சீதை புலம்புவதன் வாயிலாக வந்த விருந்தினர்க்கு உணவளிக்கும் செயலை அறமாகக் கருதிச் செயல்பட்டனர் பண்டைத் தமிழர்கள் எனும் உண்மையை நம் கண் முன்னே காட்சிப்படுத்தியுள்ளான் கம்பன்.

இலக்கியச் சாப்பாடு:

சைவம், அசைவம் என்று அவரவர் வாழும் முறைமைக் கேற்ப தமிழர்களின் உணவுமுறை அமைந்திருந்தது.

கோளிப்பாகல் கொழுங்கனித் திரள்காய்
வாள்வரிக் கொடுங்காய் மாதுளம் பசுங்காய்
மாவின் கனியோடு வாழைத் தீங்கனி' (சிலம்பு ப.283)

கண்ணகி கோவலனுக்குப் பலவிதமான காய்களைக் கொண்டு அறுசுவை உணவு படைத்ததை இளங்கோ இங்கே இவ்விதம் காட்டுகிறார்.

மோழலம் பன்றியோடு முளவுமாக்காதியட்ட
போழ்நிணப் புழுக்கல் தேன்நெய் பொழிந்து
உகப்பெய்து மாந்தி'
(சீவகசிந்தாமணி பா.1233)

பன்றிக்கறியோடு, தேன்நெய் பொழிந்து சமைக்கப்பட்ட புலால் உணவை வேடர்கள் விரும்பி உண்பார்கள் என்று திருத்தக்க தேவர் பாடுகிறார்.

இப்படி அவரவர் வாழும் சூழலுக்கும், வாழ்க்கை முறைக்கும் ஏற்ப உணவுமுறை மாறுபடுகின்றது என்பதை மேற்கண்ட இலக்கிய செய்திகள் நமக்கு நன்கு உணர்த்துகின்றன.

புதுமை விருந்து:

கவிகாளமேகத்தை அவரது நண்பர் ஒருவர் விருந்துக்கு அழைக்கின்றார். அவருக்கு விருப்பமான உணவு என்ன? என்று அந்த நண்பர் கேட்க, காளமேகமும் ஆனைக்கறி, பூனைக்கறி, மன்னர்கறி, அன்னையைக் கொன்றகறி ஆகியவற்றைத் தமது விருப்ப உணவாகக் கூறுகிறார். அந்த நண்பரும் அதன்படியே விருந்து படைத்திட்டார். உண்டு வந்த காளமேகத்திடம் என்ன உண்டாய் எனச் சிலர் கேட்க.

'ஆனை குதிரை தரும்
அன்னை தனைக் கொன்றகறி
சேனை மன்னரைக் கொன்றகறி
துன்னியவரை பூநெய்யுடன்
கூட்டி அமுதிட்டான்'
(தனிப்பாடல் திரட்டு ப.83)

என்று காளமேகம் அவர்களிடம் பதிலளித்தார். அசைவம் சாப்பிடாத நீ எப்படி ஆனைக்கறி, பூனைக்கறி உண்டாய் என வந்தவர்கள் கேட்க,

ஆனை-அத்திக்காய், பூனை- பூவில் ஊறிய தேன்

சேனை-சேனைக்கிழங்கு

மன்னரைக்காய்-நெல்லிக்காய்

அன்னையைக் கொன்றகறி-குலை தள்ளிய வாழைக்காய்.

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இதுவே நான் உண்ட விருந்து என அழகாகப் பதிலளித்தார் காளமேகம்.

உப்புச் சாப்பாடு:

'உப்பில்லாப்பண்டம் குப்பையிலே' என்பது பழமொழி. அதே சமயம் உப்பின் அளவு அதிகரித்தாலும் அற்புதமான உணவை உண்ண முடியாது.

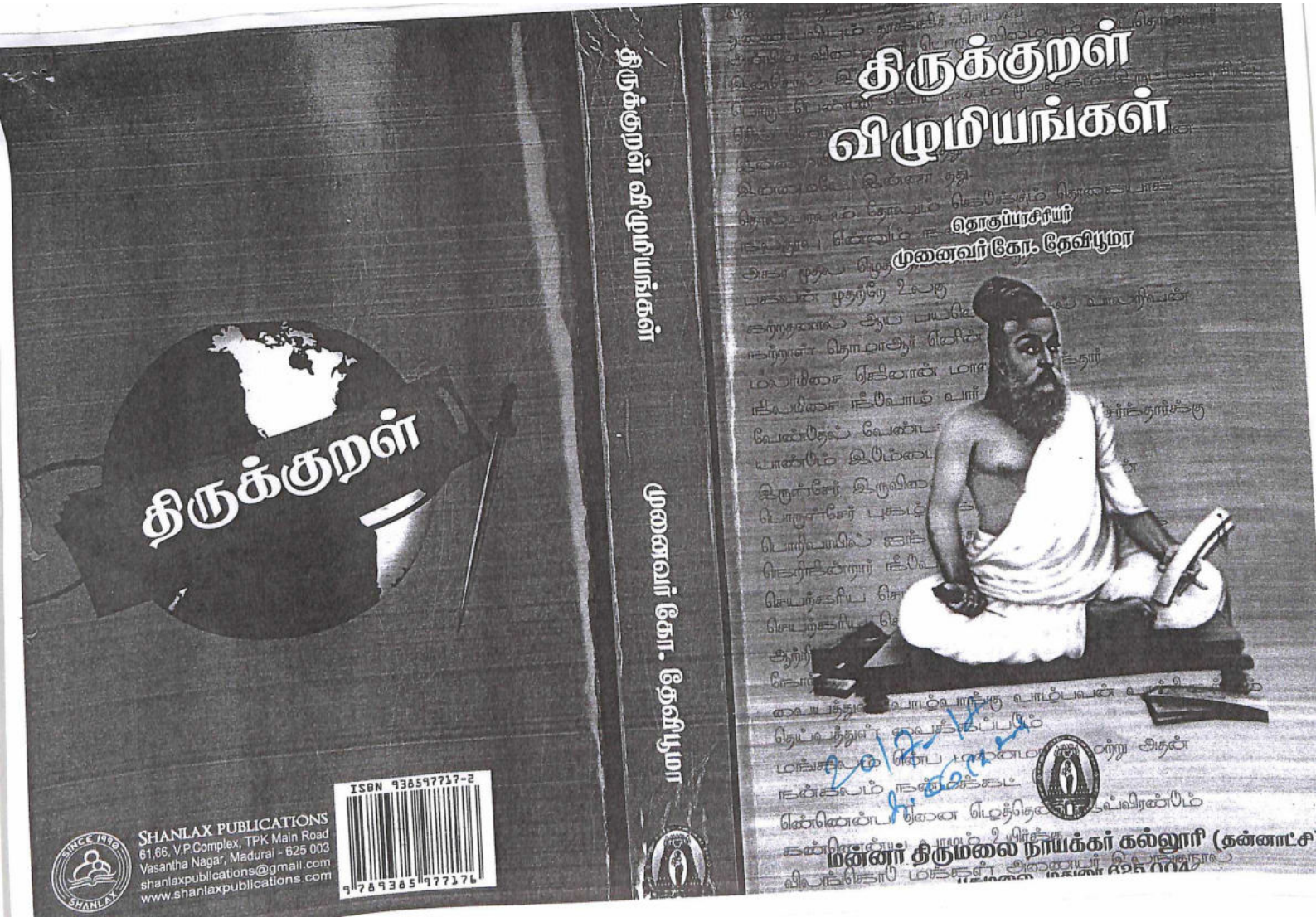
'கரிக்காய் பொரித்தாள்
கன்னிக்காயை தீத்தாள்
பரிக்காயைப் பச்சடியாப் பண்ணினாள்
உருக்கமுள்ள அப்பைக்காய் நெய்து
வட்டலாக்கினாள் அத்தைமகள்
உப்புக்காண் சீச்சீ யுமி'
(தனிப்பாடல் திரட்டு ப.54)

(கரிக்காய்-அத்திக்காய், கன்னிக்காய் - வாழைக்காய்

பரிக்காய் -மாங்காய் : பைக்காய் - கத்தரிக்காய்)

அத்திக்காய் பொரித்து, வாழையை வறுத்து, மாங்காய்ப் பச்சடி வைத்து, கத்தரியை நெய் சேர்த்து கறியாக்கிய அத்தை மகள் அந்த உணவை உண்ண முடியாமல் உப்பை அதிகம் போட்டு உமிழும் படிச் செய்து விட்டாள் என்று கவிகாளமேகம் தன் நண்பருக்கு ஏற்பட்ட அனுபவத்தை அழகிய பாடலாகப் பதிவு செய்துள்ளார்.

இப்படிக் காலந்தோறும் தமிழர்களின் உணவு முறையானது அவர்கள் வாழும் சூழலுக் கேற்பவே அமைந்துள்ளது. தமிழ்மொழியே விருந்தினைப் போல் சுவை மிகுந்தது. அந்த இன்பத்தமிழில் உள்ள இலக்கியங்கள் காட்டும் உணவு வகைகளையும், உபசரிக்கும் முறைமையையும், உணவின் மேன்மையையும் உணர்ந்து கொள்ள இந்த ஆய்வானது உதவி புரியும் எனவும், மேலும் எதிர்காலச் சமுதாயம் தமிழ் மக்களின் பாரம்பரியத்தையும், பண்பாட்டினையும் புரிந்து கொண்டு சரியான முறையில் செயல்படவும் இது பயன்படும் என்றும் நாம் எண்ணமிடலாம்.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முனைவர் கோ. தேவிபூமா
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69. வள்ளுவம் சுட்டும் விழுமியங்கள்

முனைவர் க. முருகேசன்
உதவிப் பேராசிரியர் & தமிழ்த்துறைத்தலைவர் (சுயநிதி) தேசியக் கல்லூரி (தன்னாட்சி), திருச்சிராப்பள்ளி

தமிழிலக்கியத்தில் குறைவான அடிகளைப் பெற்று அறம், பொருள், இன்பம் என்ற பொருளின் பாடப்பட்டவை கீழ்க்கணக்கு நூல்களாகும். இந்நூல்களின் இலக்கணத்தை,

"அடிநிமிர் பில்லாச் செய்யுட் டொகுதி
யறம்பொரு ளின்ப மடுக்கி யவ்வத்
திறம்பட வுரைப்பது கீழ்க்கணக் காகும்"
(பன்னிரு பாட்டியல் மேற்கோள் 133)

என்று பன்னிரு பாட்டியல் குறிப்பிடுகிறது. சங்கம் மருவிய காலத்தில் தோன்றியதாகக் கருதப்படும் கீழ்க்கணக்கு நூல்களில் தமிழ் மாதின் இனிய உயிர் நிலையாகப் போற்றப்படும் நூல் திருக்குறளாகும். புறநானூற்றில்,

"நிலம்புடை பெயர்வ தாயினும் ஒருவன்
செய்தி கொன்றோர்க்கு உய்தி இல்லென -
அறம் பாடிற்றே ஆயிழை கணவ" (புறநானூறு : 34)

'அறம்' என்ற சொல் திருக்குறளைச் சுட்டுவதை உணரலாம். திருக்குறளுக்கு இலக்கணம் பகரும் தொல்காப்பியர்,

நெடுவெண் பாட்டே முந்நூல் அடித்தே
குறுவெண் பாட்டின் அளவுஎழு சீரே (தொல் - 1414)

வெண்பாவிற்குப் பேரெல்லை 12 அடிகள். சிற்றெல்லை ஏழு சீர்கள் ஒன்றே முக்கால் அடியில் உலகை அளக்கும் பொருண்மை கொண்டது திருக்குறள். திருக்குறளில் பாடாத பொருளில்லை எனச் சொல்லுமளவிற்கு பொருள்பொதிந்து கிடக்கும் அறிவுப்பெட்டகமாகத் திகழும் பெருமை சார்ந்தது. இதனை,

"எல்லாப் பொருளும் இதன்பால்உள இதன்பால்
இல்லாத எப்பொருளும் இல்லையால்"
(மதுரைத்தமிழ் நாகனார்)

என்ற கூற்று வழி நிறுவலாம். தாய் தன் குழந்தையை நினைத்தாலே பால் சுரக்கும், வாய் வைத்து உண்டால் பால் சுரந்து கொண்டே இருக்கும். அது போன்றது திருக்குறள். அறிவுடைப் புலவர்க்குப் ஆயுந்தோறும் வெளிப்படும் உண்மைகள் கூறுவார் உத்திரசன்மகண்ணர் இதனை,

"மணல்கிளைக்க நீர்ஊறும்; மைந்தர்வாய் வைத்து
உணச் சுரக்கும் தாய்முலை ஒண்பால் - பிணக்குஇலா
வாய்மொழி வள்ளுவர் முப்பால், மதிப்புல வோர்க்கு
ஆய்தொறும் ஊறும் அறிவு; (உத்திரசன்மகண்ணார்)

என்ற சான்று வழி அறியலாம். மனித இனம் உள்ளவரை பயன்பெறும் நூலான திருக்குறளில் விழுமியங்கள் குறித்த கருத்தாக்கத்தை ஆய்வதே இக்கட்டுரையின் நோக்கமாகம்.

—

விழுமியம்

மனிதர்களின் நம்பிக்கைகள், எண்ணங்கள், கருத்துக்கள் ஆகியவற்றின் அடிப்படையில் அமைவதே விழுமியங்களாகும். மனிதனை மேம்படுத்தற்குப் பயன்கொள்ளும் பண்புகள் அனைத்தும் மனித விழுமியக் கூறுகள் எனலாம்.

பிற உயிர்களிடத்து அன்பு, சேவை செய்தல், நல்லொழுக்கம், நேர்மை, பிறர் நலன் பேணல், உண்மை பேசுதல், சடங்குகளை மதித்தல் முதலியன விழுமியக் காரணிகள் ஆகும். அத்தகைய பண்பினைப் பெற்றிருக்கும் உலகப் புகழ் கொண்ட நூல் திருக்குறளென்றால் அது சாலப் பொருந்தும்.

—

அறமெனப்பட்டதே இல்வாழ்க்கை

அறம் என்பதே இல்வாழ்க்கை தான் என்பாள் தமிழ் மூதாட்டி அறம் என்பதற்கு 'கடமை, நோன்பு, தருமம், கற்பு, இல்லறம், துறவறம், நல்வினை, அறக்கடவுள், தருமதேவன்' கழகத் தமிழ் அகராதி விளக்கம் அளிக்கிறது. (ப.60) அறத்திற்கு விளக்கமளிக்கும் தொல்காப்பியர்,

"காமம் சான்ற கடைகோட் காலை
ஏமம் சான்ற மக்களொடு துவன்றி
அறம்புரி சுற்றமொடு கிழவனும் கிழத்தியும்
சிறந்தது பயிற்றல் இறந்ததன் பயனே"
(தொல். பொருள் கற்பு 1138)

என்னும் நூற்பாவில், இல்லற வாழ்க்கையின் இறுதிக் காலத்தில், பெருமை பொருந்திய மக்களொடு இருந்து, அறம்புரிகின்ற சுற்றத்தோடு கூடியிருந்து தலைவனும், தலைவியும் சிறப்பாக போற்றப்படுகின்ற பண்புகளை இடைவிடாது நினைத்துக் கொண்டிருத்தல் மனையறத்தின் பயனாகும் என்கிறார்.

மற்றவர்களையும் நல்வழிச் செலுத்தித் தானும் நல்வழியில் இல்வாழ்க்கை மேற்கொள்பவன் துறவில் ஈடுபட்டுத் தவம் செய்வோரிலும் மேலான புகழ் பெறுவான். திருவள்ளுவர் இதனை,

"ஆற்றின் ஒழுக்கி அறன்இழுக்கா இல்வாழ்க்கை
நோற்பாரின் நோன்மை உடைத்து" (குறள் : 48)

என்ற குறட்பாவில் நேர்த்தியாகக் கையாள்கிறார்.

தன் சுற்றத்தாருக்கு வருகின்ற துன்பத்தைப் போக்கி அவர்களுக்கு உதவ வேண்டும் என்பதையும் தான் சார்ந்த இனத்தாரும் தம்மைப்போல் வயிறார உண்ணுதல் வேண்டும் என்பதையும் நொதுமலாரும் நம்மோடு உறவினராய்ப் பழகுதல் வேண்டும் என்பதையும்,

"கேள் கேடு ஊன்றவும் கிளைஞர் ஆரவும்
கேள் அல் கேளிர் கெழீஇயதை ஒழுகவும்
ஆள்வினைக்கு எதிரிய ஊக்கமொடு புகல் சிறந்து"
(அகம் 93 : 1-3)

அகநானூற்றுப் பாடல் வழி அறியலாம்.

வள்ளுவரும் இதனை ஒத்த கருத்துடையராக இல்வாழ்வில் நில்லாதவர்க்கும் வறுமையால் இல்லாதவர்க்கும், இறந்து மடிந்தவர்க்கும் குடும்பம் நடத்துபவன் துணையாவான். இல்லார்க்கு ஈதலால், இரப்போரைப் பேணலால் இறந்தோர்க்கு இரங்குதலால், இல்வாழ்வான் இவர்களுக்கு துணையாவான். இதனை,

"துறந்தார்க்கும் துவ்வா தவர்க்கும் இறந்தார்க்கும்
இல்வாழ் வான்என்பான் துணை" (குறள் : 42)

என்கிறார். மேலும்,

"அறன்கடை படாஅ வாழ்க்கையும் என்றும்
பிறன்கடைச் செலாஅச் செல்வமும் இரண்டும்
பொருளின் ஆகும் புனையினை என்றுநம்" (அகம் : 155)

அறவழியில் இல்வாழ்க்கை வாழவும், வறுமையால் இரந்தும் வேறு ஒருவனுடைய வாயிலில் சென்று பணிந்தும், பெறாமல் தன்னுடைய முயற்சியால் பெறும் செல்வமே சிறந்ததாகும். இதே கருத்தை வலியுறுத்தும் வள்ளுவர்,

"பழியஞ்சிப் பாத்தூண் உடைத்தாயின் வாழ்க்கை
வழிஎஞ்சல் எஞ்ஞான்றும் இல்" (குறள் 44)

தீயவழியில் அல்லாமல் நல்வழியில் பொருளைச் சேர்க்க வேண்டும். அப்படிச் சேர்த்த பொருளின் பயனை பகிர்ந்துண்டு வாழ வேண்டும். அத்தகைய வாழ்க்கை அமைவதாயின் அவ்வாழ்க்கையில் ஒரு துன்பமும் இல்லை என்ற கருத்தை எடுத்தாள்கிறார்.

தம்முடன் இருக்கும் சுற்றத்தினரின் துன்பத்தினை நீக்கி அருளும் பண்பு அறிவுடையோர்க்கே உரியதாகும்.

"புணர்ந்தோர் புன்கண் அருளலும் உணர்ந்தோர்க்கு
ஒத்தன்று மன்னால்"(அகம் 108)

தான், சுற்றம், தேடிவரும் விருந்து, தெய்வம், தென்புலம் ஆகிய ஐந்திடத்தும் நல்வினை செய்வது சிறப்புடையதாகும். இதனை,

"தென்புலத்தார் தெய்வம் விருந்தொக்கல் என்றாங்கு
ஐம்புலத்தாறு ஓம்பல் தலை"(குறள் 43)

என்ற குறட்பாவில் அகநானூற்றுப் பாடலில் கருத்தோடு ஒத்த கருத்தாக்கமுடையோராக வள்ளுவர் விளங்குவதை அறிய முடிகிறது.

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விருந்தோம்பல்

இல்லறக் கடமைகளுள் இன்றியமையாதது விருந்தோம்பல் அகநானூறு விருந்தோம்பலை இல்லறக் கடமையாக வலியுறுத்துகிறது. தலைவன் போரிலே வெற்றிப் பெற்று வீடு திரும்பினான். வீட்டை அடைந்ததும் தேரினை விரைவாக-செலுத்திய பாகனைத் தன் தோளுடன் அணைத்துக் கொண்டு வீட்டினுள் சென்றான். தலைவி விருந்து பேணும் வாய்ப்பினைப் பெற்றாள்.

"வரைமருள் மார்பின் அளிப்பனன் முயங்கி
மனைக் கொண்டு புக்கனன் நெடுந்தகை
விருந்தேர் பெற்றனள் திருந்திழை யோளே" (அகம் 384)

தலைவன் தேர்ப்பாகனைத் தன்னுடைய வேலையாள் என்று எண்ணாது விருந்தினராக வீட்டிற்குள் அழைத்துக் செல்கிறான்.

இதே போல் வள்ளுவரும் இன்முகம் காட்டி விருந்தினர்களை உபசரிப்பவன் வீட்டில் மனைமாட்சி, மங்கலம் பொங்க வளரும்; இதனை,

"அகனமர்ந்து செய்யாள் உறையும் முகனமர்ந்து
நல்விருந்து ஓம்புவான் இல்" (குறள் 84)

என்ற குறட்பாவில் வலியுறுத்தக் காண்கிறோம்.

"விருந்தெதிர் பெருகதில் யானே" (புறம் 306)

புறநானூற்றுத் தலைவி நடுகல்லை வணங்கி விருந்தினைப் பெற வேண்டும் என வேண்டுகிறாள். இதேபோல் வள்ளுவரும் வந்த விருந்தினர் போக, வரும் விருந்தினர் வழி பார்த்திருப்பவன் புகழ் உலகுக்கோர் பெருவிருந்தாவான் என்பதை,

"செல்விருந் தோம்பி வருவிருந்து பார்த்திருப்பான்
நல்விருந்து வானத் தவர்க்கு" (குறள் : 86)

என்ற குறள் வழி நிறுவுகிறார்.

சிலப்பதிகாரத்தில் கோவலன், கண்ணகியை விட்டுப்பிரிந்த நிலையில்,

"அறவோர் களித்தலும் அந்தணர் ஓம்பலும்
துறவோர்க்கு எதிர்தலும் தொல்லோர் சிறப்பின்
விருந்தெதிர் கோடலும் இழந்த வென்னை" (சிலம்பு : 16)

என்று தன்னால் விருந்து உபசரிக்க முடியாத நிலையை எண்ணி கண்ணகி வருந்துவதைக் கண்டு தெளியலாம். செல்வமிருந்தும், விருந்து உபசரித்தல் இல்லாத கொடுமை மடையர்களின் தனிப்புரிமையாகும். உண்டிக்கழகு செல்வத்தின் பயன் விருந்தோடுண்ணல் என்கிற கருத்தை,

"உடைமையுள் இன்மை விருந்தோம்பல் ஓம்பா
மடமை மடவார்கண் உண்டு" (குறள் : 89)

வள்ளுவரின் கூற்றால் அறிய முடிகிறது.

பெண்கள் நடு இரவில் விருந்தினர் வந்தாலும் மனம் வருந்தாமல் விருந்து உபசரித்தனர் என்பதை,

"அல்லிலாயினும் விருந்துவரின் உவக்கும்
முல்லை சான்ற கற்பு" (நற் : 142)

என்பதன் மூலம் அறியலாம்.

விருந்தினரை இன்முகத்துடன் வரவேற்க வேண்டும். இலலையெனில் அவர் மனம் மாறுவர் என்பதை,

"மோப்பக் குழையும் அனிச்சம் முகம்திரிந்து
நோக்கக் குழையும் விருந்து" (குறள் : 90)

எனும் நிலையில் விருந்தினரின் மென்மை அனிச்சத்தைக் காட்டிலும் மிகைப்பட்டது என்று திருவள்ளுவரின் கூற்று வழி உணரலாம்.

நிறைவாக

ஒரு தனிமனிதன் பிறரிடம் எத்தகைய பண்பை எதிர்பாக்கிறானோ, அத்தகைய பண்புகளை தானும் பெற்றிருக்க வேண்டும் என்று எண்ணும்போது அந்தப் பண்புகள் யாவும் தன் வாழ்வில்

பின்பற்ற வேண்டிய விழுமியங்கள் ஆகின்றன. அத்தகைய விழுமியங்களின் பெட்டகமாகத் திகழும் நூல் திருக்குறளாகும். ஆதில் இல்வாழ்க்கையின் பயன் குறித்தும் ஒரு நாட்டைக் காவல் செய்யும் சேனையின் வலிமையைக் காவல் செய்வது உணவு என்பார் 'மெக்லெஸ்டர' அத்தகைய உணவின் அங்கமான 'விருந்தோம்பல்' பண்பில் தமிழர்கள் எவ்வாறு சிறந்திருந்தார்கள் என்பதை சான்றுகள் வழி இக்கட்டுரையில் நிறுவப்பட்டுள்ளது.

பார்வை நூல்கள்

1. அகநானூறு, உரையாசிரியர் புலியூர்க் கேசிகன்
2. சிலப்பதிகாரம், புலியூர்க் கேசிகன்
3. தமிழ் இலக்கண நூல்கள், முனைவர் ச.வே. சுப்பிரமணியன்
4. திருக்குறள் உரையாசிரியர், ஞா. மாணிக்கவாசகன்
5. தொல்காப்பியம், பொருளதிகாரம், இளம்பூரணர் உரை
6. புறநானூறு, உரையாசிரியர் புலியூர்க் கேசிகன்

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திருக்குறள் விழுமியங்கள்

முனைவர் கோ. தேவிபூமா

திருக்குறள் விழுமியங்கள்

தொகுப்பாசிரியர்
முனைவர் கோ. தேவிபூமா

மன்னர் திருமலை நாயக்கர் கல்லூரி (தன்னாட்சி)

"கற்புகுத் தன்பு முடித்து நாண் மெய்ப்பூசி
நற்குண நற்செய்கை பண்பாடு – மக்கட்பேறு
ரெண்பதோர் செல்வ முண்டாயின் இல்லன்றே
கொண்டற்குச் செய்தவம் வேறு"

என்றவாறு எடுத்துக் கூறுகிறது.

கொன்றை வேந்தன் மக்கட் செல்வத்தை

"சான்றோ ரென்கை சான்றோர்க் கழகு"

எனவும் எடுத்தியம்புகிறது.

பிறனில் விழைதல்

இல்லற வாழ்வின் ஒட்பற்ற மேன்மையை எடுத்தியம்பிய வள்ளுவப் பெருந்தகை பிறனில் விழைவதால் ஏற்படும் தீமையையும் எடுத்துக் கூறி மக்களுக்கு எச்சரிக்கை விடுக்கிறார். பிறர் மனைவி மற்றும் பிறர்கணவரை விரும்புவது பிறனில் விழைதல் எனப்படும். பிறனில் விழைதல் மிகப்பெரிய குற்றம். பிறனில் விழையாத அறமே இல்வாழ்விற்குத் தேவையான அறம் என வள்ளுவர் வலியுறுத்துகிறார். பிறர்க்குரிய இல்வாழ்க்கை துணையை விரும்புகிறவர்கள் பாவத்தின்கண் நிற்பவர்கள் என்பதை

"அறன்கடை நின்றாருள் எல்லாம் பிறன்கடை
நின்றாரின் பேதையர் இல்"

என வள்ளுவர் கூறுகிறார்.

மனைவி அல்லாத பிற பெண்டிரை விருந்தோம்புவதால் வரும் கேட்டினை நண்டும், சிப்பியும் மூங்கிலும் வாழையும் தாம் அழிவடையும் காலத்தில் கெட்ட கருக்களை ஈனும். அதுபோல் ஞானமும் செல்வமும் வித்தையும் அழியவரும் காலத்தில் மனைவி அல்லாத பிற மகளிரிடத்து மாந்தர் ஆசை வைப்பர் என்று நல்வழிப்பாலும் அறிவுறுத்துகிறது.

"நண்டு சிப்பி வேய்தலி நாதறோப் காலத்தில்
கொண்ட கருவளிக்கும் கொள்கை போல் ஒண்கொடிஇ
போலும் தமை கல்வி போன்றவருங்காலம் அயல்
மாதர் மேல் வைப்பார் மனம்"

இவற்றின் மூலம் பிறனில் விழையா அறமே இல்லற வாழ்விற்கு உகந்தது என்பதை அறிந்து கொள்ள முடிகிறது.

முடிவுரை

அதுகாறும் வள்ளுவர் கூறிய இல்லற மேன்மை இக்கட்டுரையில் உணர்த்தப்பட்டது. வள்ளுவர் காட்டிய வழியில் இல்லறம் நடத்தும் இனியோர்க்கு எந்நாளும் துன்பம் ஏற்படாது.

18. திருக்குறள் வரையறுக்கும் விழுமியங்களில் மனிதநேயம்

சு.கருத்தான்

உதவிப் பேராசிரியர், தமிழாய்வுத்துறை, தேசியக் கல்லூரி (தன்னாட்சி), திருச்சிராப்பள்ளி

நாகரீக வளர்ச்சியில் பின்தங்கிய காலத்தில் மலர்ந்த நேயப்பண்பை விட இக்காலச் சூழலில் மனிதன் மற்ற உயிரிகளையும் தன்னையும் நேசிக்கும் பண்பு தேய்மானத்தை நோக்கியும், தனது வளர்நிலையில் சிக்கலையும் எதிர்நோக்கி உள்ளது. தொய்வடையும் தோழமை உணர்வான நேயப்பண்பை சட்டத்தையும், அதிகாரத்தையும், பணபலத்தையும் கொண்டு வலுப்படுத்த முடியாது. இழந்து கொண்டிருக்கும் ஒழுக்கங்களையும், மனித விழுமியங்களையும் மீட்டுருவாக்கம் செய்தல் வேண்டும். மீட்டுருவாக்கத்தின் அடிப்படை என்பது உயர்ந்த பண்புகளை வலியுறுத்தும் பண்டைய நூல்களைத் திருப்பிப் பார்த்து உள்ளப்புனைத்தலாகும். இந்த அடிப்படையில் வாழ்வியல், இயங்கியல் பொருண்மையைக் கொண்ட வள்ளுவத்தில் பொதிந்துள்ள மனிதநேயச் சிந்தனையைப் பகிர்ந்து கொண்டும், செத்துக் கொண்டிருக்கும் உயிரின் மேன்மைக்குச் செழுமை சேர்க்கும் வண்ணமாக இக்கட்டுரை உதிக்கின்றனது.

மனித நேயம் என்பது உயரப் பிடித்து ஒலிக்க வேண்டிய வார்த்தையாகும். மனமே நேயத்தின் அடிப்படை என்றாலும் அடுத்த அறிவைத் தேடும் மனம் தனது சுயத்தை, முழுமையை மெல்ல மெல்லத் தனக்குத் தெரியாமலேயே இழந்து கொண்டிருக்கின்றது என்பதுதான் உண்மை. நேசிப்பிற்கான கருத்துருவாக்கம் வேறு வேறு பரிமாணங்களையம், பரினாமங்களையும் பெற்று விட்டதே இந்த பின்னடைவிற்கான காரணமாகும்.

- அறிவியலின் அசுர வளர்ச்சியும், அதன் வழியாக நிகழ்ந்து வரும் பண்பாட்டின் வீழ்ச்சியும்.
- நாகரீகம் என்ற பெயரில் மனிதனைப் பழிவாங்கும், உள்ளொன்று வைத்துப் புறமொன்று பேசும் மனநிலை பரவிக் கிடத்தல்.
- நேசம் தன்னிலை திரிந்து பாசம், பற்று என்ற நிலை கடந்து பற்று வெறியாகி வெறியுடன் சுற்றித் திரியும் இந்தக் கலாச்சார

சீரழிவுதான் பண்பாட்டின் உச்சம் என்று கருதும் நிலை, என்ற மேற்கண்ட செயல்நிலைகளைத் தோழமை தொய்வடையக் காரணமாகக் கொள்ளலாம். இந்த எதிர்முரணான நிகழ்வின் மூலாதாரம் வாழ்வியல் உயர்விழுமியங்களை மதிக்கவும், போற்றவும் வளர்க்கவும் தவறிவிட்டோம் என்பதின ஈவு என்று பதிவு செய்யப்பட்டுள்ளது.

எந்தவொரு புறத்தோற்ற பிணைப்புகளும் பொருத்தப்படாமல் அகக்கட்டுமானங்களோடு மனித மனத்தோடு தொடர்புடைய ஒரு மெல்லிய உணர்வின் உச்சம் என்று சொல்லலாம். இந்த நேயத்தின் களனான மனம், காதல், நட்பு, ஜீவகாருண்யம் போன்ற அன்புடன் கலந்த பல பகிர்மானங்களைக் கொண்டுள்ளது எனக்கொண்டோமானால், இதன் முழுமைக்கும், செழுமைக்கம் வள்ளுவத்தில் ஏராளமான இடம் உண்டு.

அன்பு

ஏதோ ஒரு வகையில் உறவு முறையைப் புதுப்பித்தும், புதிதாக உருவாக்கவும் எல்லா வகையான கொள்கலனுக்கும் இடையீடாக இருப்பதுதான் அன்பு. தனிமனிதன், குடும்பம், சமுதாயம் என்ற தொடரமைப்பில் குடும்பமாக இருக்கும் இல்வாழ்க்கையே சில வாழ்க்கைப் பாடங்களைக் கற்றுத் தருகின்றது. இந்த இல்வாழ்வின் பயன் அன்பும் அறனும் உட்கூறுகளாக இருப்பதேயாகும் என்று வள்ளுவம் (குறள்-45) குறிப்பிடுகின்றது. பயத்துடன் மனித நிலைக்குமேல் பார்க்கும் கடவுட் கோட்பாட்டைத் தவிர்த்துப் பாசத்துடன், அன்புடன் வணங்கும் கணவன்மீது கொள்ளும் அன்பே நேயத்தின் முழுமையாகும் என்பதை வள்ளுவம் "தெய்வம் தொழாஅள் கொழுநன் தொழுதெழுவாள்" (குறள்-55) என்று பதிவு செய்துள்ளது. பெறுதற்கரிய இந்த உடலும் உயிரும் இயைந்த மனித வாழ்வு அனைத்து உயிர்களின் மீதும் அன்பு செலுத்துவதற்கேயாகும் (குறள்-73). இல்லோருக்கும் சொந்தப்படுத்துவது அன்பு (குறள்-72) அறம் செய்து வாழும் வாழ்க்கைக்கு அன்பே அடிப்படை (குறள்-6) என்றெல்லாம் அன்பின் உச்சம் பரந்து விரிந்து கிடக்கின்றது. பண்பாட்டு விழுமியங்களுக்கும், அன்பு அடிப்படையானது என்பது குறள் கூறும் செய்தியாகும். இந்த அன்பு தான் நேயத்தின் அடிப்படை. இந்நிலை மாறும்போது அன்பின் பன்முகம் பழுதடைந்தும், நேயம் காய்ந்தும் போகின்றது. "அரம் போலும் கூர்மையரேனும் மரம்போல்வர் மக்கட்

பண்பில்லா தவர்" (குற்ள்-997) என்றும் இங்கு குறிப்பிடும் மக்கட்பண்பு என்பதுவும் தோழமை, நேய உணர்வு என்பது குறிப்பிடத்தக்கது.

நட்பு

வேறு வேறு தளங்களில் சிதறிக் கிடக்கும் மனித சமூகத்தைப் பிணைத்துப் பார்ப்பது நட்பு எனும் நந்தவனமே. புணர்ச்சிப் பழகுதல் வேண்டா உணர்ச்சிதான் நட்பாம் கிழமை தரும்" (குறள்-785) என்று கூறுவதால் உணர்ச்சிதான் நட்பின் வலிமையாகக் கருதப்படுகின்றது. இந்த வலிமையை நட்பின் அடையாளமாகவும் வெளிக் கொணரப் படுகின்றது. இவ்வுலகம் இன்றளவும் தழைத்திருக்கின்றது என்றால் சில கூறுகளில் ஒன்றான நட்பின் பலம் என்றே கருதலாம். மன உணர்வின் மிகப் பெரிய பாலமாக அமைவதே கேண்மை நெறி. இந்த நட்பைப் பகிர்ந்து கொள்ளும்போது வெறுமனே மகிழ்வதற்காக மட்டுமல்லாமல், தவறு நேரும்போது மிகுதிக்கண் மேற்சென்று இடித்தற்பொருட்டு (குறள்-784) என்று நட்பின் விசாலத்தை வள்ளுவம் குறிப்பிடுகின்றது. நட்பின் தன்மையைப் பற்றிக் குறிப்பிடும் போது உடுக்கை இழந்தவன் கைபோல (குறள்-788) என்று குறிப்பிடுகின்றார். உடுக்கப்பட்ட உடை நழுவுமானால் எந்த உத்தரவுமின்றி கை சென்று உடையைப் பற்றிக் கொள்ளும். இது போன்று யாருடைய அனுமதியுமின்றி உதவுதல் என்பது தான் நட்பின் பலம் என்றும், உண்மை என்றும் கொள்ள முடியும். மற்றவரைப் பற்றிச் சிந்தித்தல், மற்றவர்மீது அக்கறை கொள்ளுதல் என்ற தன்மையே மனிதநேயத்தின் மகத்துவமாகும். நட்பின் ஆழத்தையும் அகலத்தையும் குறிப்பிடும் பொழுது விசம் கூட நட்பிற்கு இனிமை தரும் என்கிறார் வள்ளுவர். "பெயக்கண்டு நஞ்சுண்டமைவர் நயத்தக்க நாகரீகம் வேண்டு பவர்" (குறள் 580) இதே கருத்தை நற்றிணை "முந்தை இருந்து நட்டோர் கெடுப்பின் நஞ்சும் உண்பர் நனி நாகரீகர்" (நற் - 355) என வலியுறுத்துகின்றது. உள்ளன்போடு கொண்ட கேண்மையின் வளமை எப்போதும் தோற்றுப் பேரவதில்லை. நல்ல நண்பர்கள் இல்லாத வாழ்க்கை நரகத்தைவிடக் கொடுமையானதாகும்.

காதல்

காதல் என்ற புனிதம் இல்லையென்றால் மனித மனம் என்றோ மீண்டும் விலங்கின் தன்மையை ஏற்றிருக்கும். காதல் என்கின்ற சொல் குறுகிய வட்டத்திற்குள் சிக்கிக் கொள்ளும் போதுதான் தவறானதாகவும்,

இழிவானதாகவும், கருத்தில் கொள்ளப்படுகின்றது. சமூகத்தால் மிக உயர்வாகக் கருதப்படுவதும் உயர்த்திப் பேசப்படுவதும் மனிதர்களிடையே உட்பிணைப்பை ஏற்படுத்துவதும், நேயத்தை மேன்மையுறச் செய்வதும் காதல் என்கின்ற நேசிக்கும் பண்பு தான். இந்தக் காதலை வள்ளுவரை விட மென்மையாகவும், அதே சமயம் ஆழமாகவும் வேறு எவரும் குறிப்பிடவில்லை என்றே கருதலாம். காதலின் வளர்நிலையில் காலையில் அரும்பிப் பகலெல்லாம் போதாகி மாலையில் மலரும் இந்நோய் (குறள்-1227) என்று. மலர் மலர்வதைப் போல மெல்மையாகவும் உடலில் ஏற்படும் நோய் போன்று மனதிற்கு ஏற்படுமாறு மிளிர்வதாக, வள்ளுவர் குறிப்பிடுகின்றார். காதலின் மென்மையைப் பற்றிக் குறிப்பிடும்போது மலரினும் மெல்லியது (குறள்-1289) என்று பதிவு செய்கின்றார். இந்த மென்மையான உணர்வின் அடிப்படையிலேயே, அதிர்வுகளிலேயே நேசிப்பும், காதலின் உயிர்ப்பும் அடங்கியிருக்கின்றது.. காதலின் வலிமையைப் பற்றிக் கூறும்போது உடம்பிற்குக் கள் குடிப்பதினால் மயக்கம் வரும், ஆனால் காதலியின் நினைவோடு கலப்பதினாலும், கண்களால் காண்பதினாலுமே கள் போன்ற மயக்கம் தரும் வலிமை கொண்டது காதல் உணர்வு (குறள்-1281) "அணங்கு கொல் ஆய்மயில" (குறள்-1081) "யான் நோக்குங்காலை நிலன் நோக்கும் நோக்காக்கால் தான் நோக்கி மெல்ல நகும்" (குறள்-1094) என்ற மன நேசிப்பிற்குப் பெரும் பங்காற்றுவது காதல். சாதி, மதம், இனம், மொழி என்ற குறுகிய எல்லை கடந்து மனித நேயத்தை வளர்க்கும் மாபெரும் சக்தி காதல். எனவே தான் பாரதி காதல் செய்வீர் உலகத்தீரே எனக் காதலின் வழியாக நேயத்தை வலுப்படுத்துகின்றார். வாலிப நெஞ்சங்களைப் பிணைப்பதோடு, மகன் - தயார் மகன் - தந்தை. விலங்கு - மனிதன் மனிதன் - தாவரங்கள், மனிதன் - பறவை என உயிரினத் தளங்களுக்கு நீண்டு செல்லும்போது தான் காதலின் பலம் பெருகி நேசிப்பு விரிகின்றது.

ஜீவகாருண்யம்

அன்பு என்னும் தாயும் அருள் என்னும் சேயும் இருந்தால் மட்டுமே ஜீவகாருண்யத்தைப் போற்ற முடியும் (குறள்-757) அனைத்து உயிர்கள் மீதும் அன்பைச் செலுத்தும் நிலை, அது ஈகையாக, கருணையாக, பரிவாக, பல்வேறு பரிமாணங்களைப் பெற்றுத்திகழும். அன்பையும், அருளையும் கொடுத்து நேசிக்கும் பண்பைக் கொண்டவனே மனிதன். மற்ற உயிர்களின் மீதும் அன்பு செலுத்தும் மனப்பக்குவம்தான்

இன்னும் மனிதனைத் தன் நிலையிலிருந்து தாளாமல் மனிதனாகவே அடையாளப்படுத்துகின்றது. தம் பெற்றோர்களையே முதியோர் இல்லத்தில் சேர்க்கும் இந்தத் தலைமுறையினருக்கு வள்ளுவத்தை முழுப்பொருளாழத்துடன் கற்றுக்கொடுப்பது சமூகத்தேவையாகும். வகுப்பறை மட்டுமல்லாமல் வெளிப்புறச் சூழலிலும் வள்ளுவம் ஒலிக்கும் வகைசெய்யும் கட்டாயச் சூழலை உருவாக்குவதே மனிதநேயத்தை மலரச் செய்வதற்கான முதற்படியாகும்.

நேய மறுமலர்ச்சிக்கான வழியைசல் சொன்ன வள்ளுவர், வெறுமனே போற்றும்படியான ஒழுக்க நிலைகளைக் கடைபிடிப்பதோ தவறுகளைத் சுட்டிக்கேட்கும் மற்றொரு நிலையும் நேயப் பாதுகாப்பாகக் கொள்ள முடியும். தோழமை உணர்வு, நேயப்பண்பு சாயும் போது தாங்கிப் பிடித்துக் கொள்வதினால் அவ்வப்போது நேசிப்பு காப்பாற்றப்படுகின்றது. நேயம் தழைக்கின்றதா? செழிக்கின்றதா? என்றால் இல்லையென்று தான் சொல்ல முடியும். நமக்கென்ன என்று ஒதுங்கிச் செல்லும் சுயநலமும் கொடுமைகளைக் கண்டு பொறுத்துக்கொள்ளும், கோழைத்தனங்களுமே நேசத்தளவின் செழுமை இன்மைக்கு ஏதுவாகக் கருதலாம். இதுபோன்று தவறு நடக்கும்போது தட்டிக் கேட்டு தோழமையை வளர்த்துக் கொள்ள வள்ளுவத்தில் வழிமுறைகள் காணப்படுகின்றன. மற்ற மனிதர்களின் சுகதுக்கங்களையும் உள்வாங்கிக் கொள்வது மட்டுமல்லாமல் அதனைத் தனதாக்கிக் கொண்டு உணர்தல் வேண்டும். இதுவே தன்னையும் மற்ற உயிர்களையும் பேணிப் பாதுகாக்கும் பண்பாகக் கொள்ளப்படுகின்றது. ஒத்ததறிவான் உயிர்வாழவான் (214) என்று குறிப்பிடுவது இதற்காகவேயாகும் அஞ்சுவதற்கு அஞ்சல் வேண்டும் என்று வள்ளுவர் குறிப்பிடுவது (குறள்-428) அஞ்சக் கூடாததற்கு அஞ்ச வேண்டாம் என்பதை வலியுறுத்தவே, இந்த பொருளாழத்தை முன் வைக்கின்றார்.

மிகுதிக்கண் மேற்சென்று இடிக்கும் துணிச்சல் (குறள்-784) அனைவருக்கும் இயல்பாக மிளிர வேண்டுமென்பதே மனித நேய மிளிர்வின் அடையாளமாக இருக்கும். பிறர்பழி எப்பொழுது தன்பழியாக மதிக்கப்படுகின்றதோ அப்பொழுது காயமாகும் நேயம் கூட செழிப்புறும். இதில் மேலோர் கீழோர் என்பவர்கள் இல்லை. உயர்வு தாழ்வு கிடையாது. எந்தப்புற அளவுகோலும் மனிதத்திற்கான முழுமையைத் தீர்மானிப்பதில்லை. எனவே தான் பிறப்பொக்கும் எல்லா உயிர்க்கம் (972) என்று வள்ளுவம் அழுத்தமாகக் குறிப்பிடுகின்றது. இதுபோன்று தோழமை உணர்வு, நேய உணர்வு தொடர்ந்து மிளிர்வதற்கு அடிப்படைப்

பண்புகளை மக்கள் யாருடைய திணிப்புமின்றி இயல்பாக உள்வாங்கிக் கொண்டு செயலாக்கத்தில் ஈடுபட வேண்டும் என்பதை வள்ளுவம் பதிவு செய்துள்ளது. மனித நேயத்திற்கான முழுமையான கருத்தாழத்தை, செறிவாகப் பதிவு செய்ததோடு பல ஒழுக்கநெறிகள் எப்போதும் உயரிய மதிப்புகளைக் காத்து நிற்க வேண்டுமென்பதற்காக மேற்கண்ட பல உயர்பண்புகளையும் வள்ளுவம் பதிவு செய்துள்ளது. இருண்ட காலத்தில் வெளிவந்த வள்ளுவத்தில் நேசிப்பு செழுமையடைந்ததற்குச் சில அடிப்படைகளைக் கூறமுடியும்.

- சங்க காலத்திலும் அதற்கு முந்தைய காலத்திலும் மனித உயிர்கள் மலிவாக எடுக்கப்பட்டதன் விளைவயாக மனிதன் நேசிக்கவும், உயர்பண்புகளை நிலைநிறுத்தவும், உயர் விழுமியங்களை மேன்மையடையச் செய்ய வேண்டிய கட்டாயம் ஏற்பட்டிருக்க வேண்டும்.
- இயற்கையோடு வாழ்ந்து, நேசித்த மனிதன் தன்னையும், தன்னைப் போன்ற பிற உயிர்களையும் நேசித்ததாலேயே நேயப் பண்பு வலுப்பெற்றிருக்க வேண்டும். என்பதைப் புரிந்து கொள்ளலாம். இவ்வாறு கருத்தாழமும் மனிதப் பண்பின் பன்முகங்களையும் நேசத்தின் ஊற்றுக்களையும் தன்னுள் அடக்கி உயர் விழுமியங்களை உள்கட்டுமானமாக்கி, இயங்கியல் பொருண்மையோடு, ஜீவ ஒளியையும் கொடுத்த வள்ளுவத்தின் காலம் இருண்ட காலம் என்பதை விட பொற்காலம் என்று சொல்வது சாலப் பொருத்தமாக அமையும்.

ஒருமணி நேரம் மகிழ்ச்சியாக இருக்க வேண்டுமா? நன்றாகத் உறங்குங்கள், ஒருநாள் முழுவதும் மகிழ்ச்சியாக இருக்க வேண்டுமா? கற்றுலா செல்லுங்கள். ஒரு மாதம் முழுவதும் மகிழ்ச்சியாக இருக்க வேண்டுமா? திருமணம் செய்து கொள்ளுங்கள். ஒரு வருடம் முழுவதும் மகிழ்ச்சியாக இருக்க வேண்டுமா? நிறைய செல்வங்களைச் சேர்த்து வைத்துக் கொள்ளுங்கள். வாழ்நாள் முழுவதும் மகிழ்ச்சியாக இருக்க வேண்டுமா? உங்களை நீங்கள் நேசிக்கக் கற்றுக் கொள்ளுங்கள். என்பது ஒரு சிந்தனையாளர் கூற்று. தங்களை நல்ல முறையில் நேசிப்பவர்களால் நிச்சயமாக மற்றவர்களையும் நல்ல முறையில் நேசிக்க முடியும். அவ்வாறு அமைந்தால் நம் சமூகம் சொர்க்கமாகும். அதற்கான விதை விழுமியமாக வள்ளுவததில் பொதிந்திருக்கிறது.

19. திருக்குறள் காட்டும் வாழ்வியல் விழுமியங்கள்

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திருச்சிராப்பள்ளி.

முன்னுரை

காலத்தை வென்று வாழ்வன நல்ல இலக்கியங்கள். அந்த வகையில் உலகம் முழுமைக்கும் உரிய ஒப்பயவர்வற்ற நூல் திருக்குறள்.இந்த நூல் எம்மனிதனும் தன் வாழ்க்கையில் கடைப்பிடிக்க வேண்டிய நெறிகளை சாதி, சமயம், மொழி, இனவேறுபாடு அற்ற நிலையில் எடுத்தியம்புகின்றது. உலகில் தோன்றிய அனைத்து மனிதர்க்கும் அறம் பொதுவானது. சில கடமைகள் பொதுவானவை என்பதை இந்நூல் தெளிவுப்படுத்துகின்றது. இத்தகு உயர்வுபெற்ற திருக்குறள். எழுதப்பட்ட சூழலில் சமுதாயச் சிந்தனை எத்தகைய சூழலில் இருந்தது என்பதை ஆயும் போக்கில் இக்கட்டுரை அமைந்துள்ளது. திருக்குறளின் வழியில் தமிழ்ச் சமூகத்தின் கல்வி,இல்லறம்,,சமத்துவம்,ஈகை, இனியவைகூறல், அடக்கமுடைமை, இவை எவ்வாறு சிறப்புற விளங்கின என்று காண்பதே இக்கட்டுரையின் நோக்கம் ஆகும்.

கல்வி

திருவள்ளுவர் கல்வி, கல்லாமை, கேள்வி, அதிகாரத்தில் சமுதாயவியல் பற்றிப் பேசுகின்ற பொருட்பாலில் குறிப்பாக அரசியலில் அமைந்துள்ளார். கல்வி தருவதற்கு அரசே பொறுப்பு என்பது மறைநிலை உண்மை. அனைவரும் கல்வி கற்க வேண்டிய இன்றியமையாமையை கல்லாமை அதிகாரத்திலும், மற்ற குறட்பாக்களிலும் எதிர்மறை வாய்பாட்டால் இடித்துரைக்கின்றார்.

ஆய்த எழுத்து
தமிழியல் ஆய்வு இதழ்

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சான்றிதழ்

திரு/திருமதி/செல்வி முனைவர் ப.சுமதி என்பவர்/என்பவர்களால் எழுதப்பட்ட தமிழ் இலக்கியங்களில் அறம் என்ற ஆய்வுக் கட்டுரையானது ஆய்த எழுத்து – பன்னாட்டு தமிழியல் ஆய்வு இதழில் (ISSN 2278-7550) (மார்ச்-2018 – மலர்-6, இதழ்-3) பிரசுரிக்கப்பட்டுள்ளது என்பது சான்றளிக்கப்படுகிறது.

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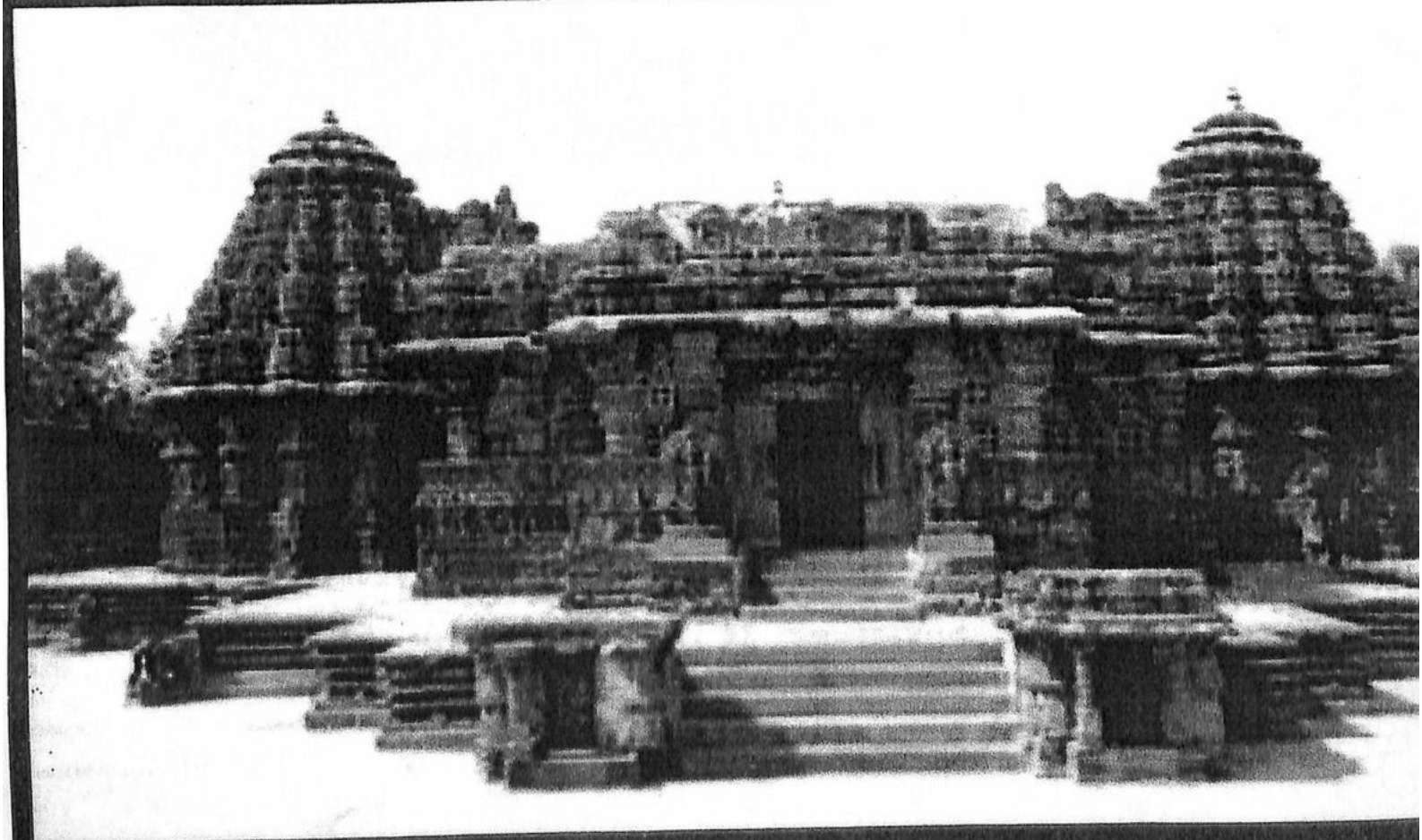

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பொருளடக்கம்

தமிழ் இலக்கியங்களில் அறம்

*முனைவர் ப.சுமதி, *உதவிப் பேராசிரியர், தமிழ்த்துறை, தேசியக்கல்லூரி (தன்னாட்சி), திருச்சி -1, தமிழ்நாடு (இந்தியா).*

முன்னுரை

அறம் அன்பினை முதலாகவும் இறுதியாகவும் கொண்டு ஈட்டப்படுதலும் நுகரப் பெறுதலும், செய்யப்பெறுதலும் வேண்டும். உண்மையன்பு இன்றி ஏதாவது ஒரு பயன் கருதி ஆற்றும் அறம் நன்மை பயவாமை நன்கு அறியப்படும். இங்ஙனம் பயன் கருதி அறம் செய்வார் தமது கைப்பொருளாலன்றிப் பிறரது பொருளாற் செய்தற்கும் துணிவர். இன்று நாம் பல துறைகளில் பணிபுரிந்து கொண்டு இருக்கிறோம். எல்லா உயிர்களிடத்தும், எல்லா மக்களிடத்தும் நெகிழ்ந்த அன்பு கொண்டு, எவ்வுயிர்க்கும் எவர்க்கும் தீங்கு நேராத முறையில், பெயர் புகழை வேண்டாது அறம் செய்வோர்க்கும் பிறருக்கும் உண்மையில் பயன்படும் வகையில் செய்ய வேண்டும். இம்மை இன்பம் விழைந்து தாம் அன்பு பாராட்டி மனைவி மக்களோடு ஒருங்கிருந்து நடத்திய அன்பு வாழ்க்கையும், மறுமை இன்பம் பெற வேண்டியதன் பயனையும் இலக்கியங்கள் வழி கூறியுள்ளதை இக்கட்டுரையில் காணலாம்.

அறமாண்பு

"அறம், பொருள், இன்பம் வீடு அடைதல் நூற்பயனே"

என்பது நன்னூல் விதி வழி வழியாக தமிழர்கள் மரபாக வழங்கி வந்த அறக்கருத்து இலக்கணத்தில் காணப்பெறுகின்றது. வடமொழியாளர்கள் இக்கருத்தை தர்மம், அர்த்தம், காமம், மோட்சம் என்று கூறுவர்! தமிழர்களிடம் அறம், பொருள், இன்பம், வீடு என்ற நான்கு பொருள்களுள் இன்பம் என்ற 'அறமானது' தனிப்பெருமையும் சிறப்பையும் பெருகிறது. இவ்விடத்தில் மணிவாசகப் பெருமான் அவர்கள் திருவாசகத்தில்

"புல்லாகிப் பூவாகிப் புழுவாகிப் மரமாகிப்
பல்விருக மாகிப் பறவையாய்ப் பாம்பாகிக்
கல்லாய் மனிதராய்ப் பேயாய்க் கணங்களாய்
வல்லசுர ராகி முனிவராய்த் தேவராய்ச்
செல்லாஅ நின்றஇத் தாவர சங்கமத்துள்
எல்லாப் பிறப்பும் பிறந்திளைத்தேன் எப்பெருமானே"

என்று கூறும்பொழுது மக்கள் வாழ்க்கையில் அறத்தோடு வாழ்வதற்கு சிறப்புடையவர்கள். இவ்வாறு மக்கள் வாழும் வாழ்க்கை சிறப்புடன் அமைவதற்கு 'மனம்' என்னும் சிறந்த கருவி

அமையப் பெற்று அதை அவன் பண்படுத்தவும் பயன்படுத்தவும் வல்லவனாக விளங்குதல் வேண்டும்.

'அறம்' என்ற சொல் விரிந்த பொருள் - உடையது. மனிதன் புரியும் நற்செயல்கள் அனைத்தையும் இதில் அடக்கிக் கூறலாம். தமிழர் வாழ்க்கையில் அக வாழ்க்கையிலும் புறவாழ்க்கையிலும் அறம் கடைபிடிக்கப்பட்டு வருதலைத் தமிழ் இலக்கியங்களில் குறிப்பாகவும் தெளிவாகவும் புலப்படுத்தியிருப்பதைக் கண்டு மகிழலாம். திருமுருகாற்றுப் படையில்

"அறு – நான் கிரட்டி இளமை நல்லியாண் (டு)

ஆறனிற் கழிப்பிய அறனில் கொள்கை" (அடிகள் 188-189)

என்ற அடிகள் 'அறனில் கொள்கை' நன்மை தருவதாக எண்ணி செயல்பட வேண்டும்.

மக்களாட்சி நடைபெறும் இக்காலத்தில் தேர்தலில் வெற்றி பெறுவது பணபலத்தால் மட்டுமன்று, தேர்தலுக்கு நிற்பவர் தம்முடைய நற்செயலாலும், உயர்ந்தபண்பாலும் மக்கள் மனதைக் கவர்ந்திருக்கும் மாண்பினாலும் ஆகும். சங்க இலக்கியங்களில் காணும் சில அரசர்கள் அரச முனிவர்களாகக் திகழ்கின்றனர்; பெரும்பாலான புலவர்கள் அந்தண அறவோராகக் காணப்படுகின்றனர். சில வேளிர்கள் தந்நலம் காணா வள்ளல்களாகத் திகழ்கின்றனர். பிறர்க்கென வாழும் பெற்றியர்களாப் பிறங்குகின்றனர். வீரர்களும் புலவர்களும் [illegible] மறவாச் செம்மல்களாக விளங்குகின்றனர். மாதர்கள் நடுநிலைப் பிறழாதவர்களாகத் திகழ்கின்றனர். எனினும் பொதுமக்கள் மனத்தூய்மையின் அடிப்படையில் வாழவேண்டும் திருவள்ளுவர் திருக்குறளில்

மனத்துக்கண் மாசிலன் ஆதல் அனைத்தறன்

ஆகுல நீர பிற (கு.எ.34)

என்ற குறட்பாவில் மனத்தூய்மையினை விளக்குவார். மனத்தூய்மை காதலியோடு வாழும் போது தெரிவதில்லை. பொது வாழ்வில் கடமையை ஏற்றுச் செய்யும்போது அது புலப்படுவதில்லை. மனிதன் தன்மை இன்னது என அறிந்து அறநெறியில் நிற்றலே இன்ப வாழ்க்கைக்கு வழி வகுப்பதாகும். அறநெறியைப் போற்றி வாழ்வதால் இந்த உலக வாழ்வுக்கு இடையூறு என்றாலும் அந்த இடையூற்றினை ஏற்றுக்கொள்வதே நல்லது என்று அறமாண்பின் அவசியத்தை இலக்கியங்கள் கூறுகின்றன.

அகப்பொருளில் அறவாழ்வு

இன்பத்தை நுவலும் அகப்பொருள் முழுவதிலும் அறம் இழையோடுவதைக் காணலாம். பருவம் நிரம்பிய ஆண்மையும் பெண்மையும் பார்த்தும் உள்ளம் ஒன்றி காணப்படுவர். அறத்தொடு நிற்கும் முறையும் ஒருவித ஒழுங்கிலேயே நடைபெறுவதாக அகத்துறை இலக்கணமும், அகத்துறைப் பாடல்களும் உணர்த்துகின்றன. தலைமகளால் தோழிக்கும், தோழியால் செவிலிக்கும் செவிலியால் நற்றாய்க்கும், நற்றாயால் செவிலிக்கும், தந்தை தன்னையர்க்கும் களவொழுக்கச் செய்தி குறிப்பிடுவதாக இலக்கண ஆசிரியர்கள் குறிப்பிடுவர் நம்பி அகப்பொருளில்

'தலைவி பாங்கிக் கறத்தொடு நிற்கும்

பாங்கி செவிலிக் கறத்தொடு நிற்கும்

செவிலி நற்றாய்க் கறத்தொடு நிற்கும்

நற்றாய் தந்தை தன்னையர்க் கறத்தொடு

நிற்கும் என்ப நெறியறிந் தோரே"

என்று நாற்கவிராச நம்பியார் களவொழுக்கத்தை யார் யாருக்கு வெளிப்படுத்தலாம் என்ற அறநிலைப்பண்பினைக் கூறுவார்.

அறத்தொடு நிற்றலின் நன்னோக்கம் சங்ககாலச் சான்றோர்கள் நெஞ்சைப் பிணித்துப் பல பாடல்களை உருவாக்கியுள்ளனர். இலக்கியத்தில் அறத்தொடு நிற்றல் என்னும் நேர்வழியைத் தலைவியும், தோழியும் மேற்கொள்வர். நாணை விட்டேனும் கற்பைத் தலையாகப் போற்றிக் காக்க வேண்டும் என்பது பண்டைத் தமிழர் கண்ட வாழ்க்கை நெறி இவற்றினை தொல்காப்பியர்

'உயிரினும் சிறந்தன்று நாணே; நாணினும்

செயிர்தீர்க் காட்சிக் கற்புச் சிறந்தன்று"

என்பது தொல்காப்பியத்தில் நாணத்தைக் காக்க உயிர்விடுக; கற்பைக் காக்க நாணத்தை விடுக என்று கூறுவார்.

மணிவாசகப் பெருமானின் திருக்கோவையாரில் தலைவியின் நோயைத் தவறாகப் புரிந்து கொண்டு செவிலி எடுக்கும் வெறியாட்டம் நிகழாவண்ணம் தடுக்க நினைத்து வேலனை நோக்கிக் கூறுவதாக பாடலில்

"விதியுடை யார் உண்க வேரி

விலக்கலம் அம்பலத்துப்

பதியுடை யான்பரங்குன்றினில்

பாய்புனல் யாம்ஒழுகக்

கதியுடை யான்கதிர்த் தோள்நிற்க

வேறு கருதுநின்னின்

மதியுடை யார்தெய்வ மே இல்லை

கொல் இனி வையகத்தே"

என்று கூறுகிறார். தோழி வேலனை நோக்கி "அடக்கடவுளே! நின் செயல் அழகியது - எம்பெருமாட்டியின் நோய்க்குக் காரணம் அன்றொரு நாள் அவள் புனலில் மூழ்கிய போது அப்புனலினின்றும் அவளைக் கரையேற்றி அவளுக்கு உயிர் தந்து உதவினாளே ஒரு வள்ளற்பெருமான், அவனுடைய ஒளிமிக்க தோள்களாகும். அங்ஙனமிருக்க நீ வெறியாடுதலால் யாது பயன்? வெறியாடலால் நீங்கள் கள்ளுண்ணலாம். கள் உண்பாரை யான் தடுக்கிலேன் வேண்டும் அளவு உண்க. காரணம் காணாமல் நோய் தீர்க்க முயலும் உன் புத்தியே புத்தி. உன்னையன்றி என் அன்னைக்கு அறிஞர் பிறர் யாரும் இடைத்திலர் போலும்" என்று எள்ளி உரைப்பதுடன் தலைவியின் அறச்செயலை உணர்த்துவதாக அமைந்துள்ளன.

இலக்கியப் பாடல்களை நுணுகி ஆராயின் களவின் வந்த பழைய காதலர்க்கும், களவின் வழிவராத காதலர்க்கும், இன்ப நிலையிலும் அன்பு நிலையிலும் அற நிலையிலும் யாதொரு வேறுபாடும் இல்லை என்பதை அறியலாம். இரண்டு நெறிகளையும் எண்ணி ஆராய்ந்தால், இலக்கியத்தின் வழி அகப்பொருளில் தமிழ்ச் சமுதாயத்திற்கு அறவழிப்பாட்டக் கருத்துக்களை முழு வடிவமாக உணர்த்தப்படுகின்றன.

புறப்பொருளில் அறவாழ்வு

புறப்பொருளில் 'அறம்' செயல்படுவதை இலக்கியப் புலவர்கள் தமது இலக்கியங்களின் வாயிலாக உணர்த்தியுள்ளனர். மனத்தாய்மை அறத்திற்கு அடிப்படை என்று வள்ளுவர் பெருமான் கூறியுள்ளார். அவர் கூறும் அடிப்படையில் 'அறமே வாழ்க்கைக்கு வேண்டிய

சிறப்பைத்தரும், செல்வத்தை தரும், ஆகையால் அறத்தை விட உயிருக்கு ஆக்கமானது வேறு எது என்ற வினாவின் அடிப்படையில்

சிறப்பீனும், செல்வமும் ஈனும், அறத்தினூ உங்கு

ஆக்கம் எவனோ உயிர்க்கு (கு.எண்.31)

என்பது அவர்தம் வாய்மொழி ஆகும்.

அறநெறி வாழ்க்கையில் நடுநிலை தவறாமல் நீதியைப் போற்றுதல் வேண்டும். நடுநிலையைக் கடந்த செயலால் நற்பயன் விளைவதில்லை. ஒருகால் நன்மை உண்டாவதாக இருந்தாலும், நடுநிலை தவறி உண்டான ஆக்கம் உடனே அதனைக் கைவிடுதல் வேண்டும். தன் நன்மை தீமையை மறந்து அறத்தைப் போற்றுவது நெறியாகும். இதனைத்தன் திருக்குறளில்

"நன்றே தரினும் நடுஇகந்தாம் ஆக்கத்தை

அன்றே ஒழிய விடல் (கு.எண்.113)

என்பது வள்ளுவரின் கருத்தாகும்.

நடுநிலைமையைச் சிறந்த அறமாகக் கொண்டு போற்றுவோர் கடைபிடிக்க வேண்டிய பேருண்மை ஒன்று உண்டு வாழ்வு என்பது எப்போதும் உயர்வும் தாழ்வும் உள்ள ஓர் அமைப்பு ஆகும். உள்ளத்தில் கோணுதல் இல்லாத தன்மையே முன்னர் உறுதியான சொல்லில் கோணல் பிறக்காது. நடுநிலைமையானது சிறப்பாக வணிகர்களுக்கு இன்றியமையாதது. வணிகர் பலர் 'சமன் செய்து சீர்தூக்கும் கோல்' போன்ற நல்ல வணிகரை கொண்டிருப்பவர் என்பதை

"கொடுமேழி நசையுழவர்

நெடுநுகத்துப் பகல்போல

நடுவுநின்ற நன்னெஞ்சினோர்"

என பட்டினப்பாலை வணிகப்பெருமகனின் அறச்செயலைப் பேசுகின்றது.

இச்செயல் அறத்தின் நிலைப்பாட்டினை உணர்த்துகிறது இதனைத் தாயுமானவரும்

"தம்முயிர்போல் எவ்வுயிரும்

தான் என்று தண்ணருள் கூர்

செம்மையருக்கு ஏவல் என்று

செய்வேன் பராபரமே"

என்று பராபர அடிகள் தம்முயிர் போல் எந்த உயிரையும் துன்புறுத்தாது நேசிக்க வேண்டும் என்று அன்பின் அறச்சிறப்பினைக் கூறுகிறார்.

போரில் அறம்

பகையும் போரும் இவ்வுலகில் எக்காலத்தும் இருந்து வரும். ஆயினும் பண்டைக் காலம் போர் முறையில் அறம் கடைப்பிடிக்கப்பட்டது. அக்காலத்தில் ஓர் அரசன் மாற்றரசனுக்குரிய நாட்டின் மீது படை எடுக்கும் அந்நாட்டில் வாழும் உயிர்களை எல்லாம் நாசமாக்குவதில்லை; பசுக்களையும், பார்ப்பார்களையும், பெண்டிரையும், பிணியாளரையும் இவர் போன்ற பிறரையும் போர் நிகழும் நிலத்தை விட்டுப் புறத்தே போய்விடும்படி எச்சரித்து அவர்களை அகற்றுவான். இத்தகைய அறப்போர் பாண்டியன் பல்யாகசாலை முதுகுடுமிப் பெருவழுதியிடம் அமைந்திருந்ததாக நெட்டிமையார் என்ற புலவர் பாராட்டுவார். இக்கருத்தினை புறநானூற்றிவரிகள்

"ஆவும் ஆனியற் பார்ப்பன மாக்களும்
பெண்டிரும் பிணியுடை யீரும் பேணித்
தென்புலம் வாழ்நர்க் (கு) அருங்கடன் இறுக்கும்
பொன்போற் புதல்வர் பெறா அ தீரும்
'எம்அம்பு கடிவிடுதும் நுன்அரண் சேர்மின் எதை
அறத்தாறு நுவலும் பூட்கை மறத்தின்
கொல்களிறு மீமிசைக் கொடிவிசும்பு நிழற்றும்
எங்கோ வாழிய குடுமி" (புறநானூறு-9)

என்று அறப்போர் புரிந்த பாண்டியனைப் புலவர் புகழ்ந்து வாழ்த்துவதைக் காணலாம்.

"அறத்திற்கு மட்டுமே அன்பு துணையாக நிற்கும் என்று சொல்லுவது அறியாமை; மறத்திற்கும் அதுவே துணையாகும். ஆறிய கற்புடைக் கண்ணகி பாண்டியன் சபையில் வழக்குரைத்து, அரண்மனையை விட்டு வெளிவரும் போது

"மட்டார் குழலார் பிறந்த பதிப்பிறந்தேன்
பட்டா கியானுமோர் பத்தினியே யாமாகில்
ஒட்டேன் அரசோடு ஒழிப்பேன் மதுரையும்"

என்று சீறும் போது, ஆவேசத்தின் கொடுமுடியில் நின்ற காலத்தும் அறவுணர்வு பிறழாது செயல்பட்டதை சிலப்பதிகாரம் பேசுகின்றது. அறம் வழுவாமல் அறத்தொடு நிற்பது குற்றமில்லாத இன்ப உலகிற்கு அழைத்துச் செல்லும் பேற்றினை அடையப் பெறும். உலகில் எந்தமொழி இலங்கியங்களிலும் காணப்படாத உயர்ந்த தத்துவம் தமிழ் இலக்கியங்களில் காண முடிகிறது.

முடிவுரை

அறவுணர்வு வாழ்க்கையில் எல்லா நிலைகளிலும் நிற்க வேண்டும் வள்ளுவர் வகுத்த நெறியிலும் பண்டைய சான்றோர்கள் சுட்டிய வழிகளிலும் வாழ வேண்டும் நம் வாழ்க்கையைக் கூர்ந்து நோக்கினால் எல்லா நிலைகளிலும் அறவுணர்வு குன்றி வருவதையும் காணமல் இல்லை, நல்லுணர்வுள்ள நாம் எல்லோரும் அறவுணர்வு குன்றாதிருக்க பண்டைய இலக்கியங்கள் காட்டிய வழியில் வாழவேண்டும். அறத்தை காத்து புகழுடன் வாழ்வதால் எக்காலத்திலும் அருள்பெறுகின்றன தன்மை கிடைக்கும் என்பதை இலக்கியங்களின் வழி உணர்த்தப்பட்டுள்ளன.

துணை நின்ற நூல்கள்

1. இளங்கோ அடிகள் : சிலப்பதிகாரம் (ந.மு.வேங்கடசாமி நாட்டார் உரை-கழக வெளியீடு)
2. சங்கப் புலவர்கள் : புறநானூறு பழைய உரையுடன் (உ.வே.சாமிநாதய்யர் பதிப்பு)
3. தாயுமான அடிகள் : தாயுமானவர் பாடல்கள் (தருமபுரப்பதிப்பு)
4. திருவள்ளுவர் : திருக்குறள் - பரிமேலழகர் உரை (கழக வெளியீடு)
5. தொல்காப்பியர் : தொல் - பொருளதிகாரம் (இளம்பூரணர் - கழக வெளியீடு)
6. நாற்கவிராசநம்பி : அகப்பொருள் விளக்கம் (கழக வெளியீடு)
7. பவணந்தி முனிவர் : நன்னூல் காண்டிகை உரை
8. மாணிக்கவாசகர் : திருக்கோவையார் உரையுடன்.

Research Article

Evaluation of antiovulatory activity of *Thespesia populnea* (L.) bark in albino rat model

Priya Ganesan, Saravanan Kaliyaperumal*

ABSTRACT

Background and Aim: Several synthetic contraceptive piles and mechanical contraceptive devices are available today but these methods possess several side effects. Herbal medicinal plants have been used as safe alternatives of these contraceptive methods. **Methods:** In the present study, the effect of oral administration (6.6 mg/kg/bwt/day for 15 days) of *Thespesia populnea* bark extracts (ethanol, ethyl acetate, and aqueous) on the ovulation of female albino rats was investigated. Changes in the duration of different stages of estrous cycle, number of egg production, and reproductive hormonal levels were assessed after the continuous treatment *T. populnea* extracts. **Results:** Treatment with ethanol, ethyl acetate, and aqueous extracts caused extend in the duration of estrus, diestrus, and proestrus stages. They also reduced the number of egg in oviduct especially ethyl acetate extract drastically reduced the egg production. Significant reduction in the follicle-stimulating hormone, luteinizing hormone, progesterone, and estradiol levels and an increase in the prolactin level in the extract treated rats. From the results, it is concluded that all extracts of *T. populnea* bark exhibited female antiovulation activity. It was found that aqueous extract and ethyl acetate extract of *T. populnea* bark was more effective than the ethanol extract.

KEY WORDS: Antiovulatory activity, Estrous cycle, Hormonal level, Ovary, *Thespesia populnea*

INTRODUCTION

Ancient literature mentions the use of a number of plants/preparations for fertility regulation. Some plant-based contraceptive agents have also been described in various traditional texts including Ayurveda.[1] In the modern system of medicine, about 25% of prescriptions contain active principle derived from plants. Plant kingdom, therefore, holds a great promise for the discovery of new and effective antifertility agents.[2] In recent years, there has been a considerable interest in plant with possible antifertility effect.[3] Several animal studies have revealed antizygotic, blastocytotoxic, anti-implantation, and abortifacient properties of many commonly used medicinal plants.[4]

Thespesia populnea is a small evergreen tree; the bark is corrugated with scaly twigs. It inhibits the female reproduction regulating herbs widely used in south Asian countries.[5] However, no scientific study is available. Thus, the present study was aimed at evaluating the antiovulation activity of bark extracts of *T. populnea* (L.) in female albino rats.

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MATERIALS AND METHODS

Extraction of Plant Material

T. populnea bark was cut out from an old tree in and around villages of Puthanampatti. Bark pieces were dried under room temperature and powdered with the help of mechanical grinder.

Animal Model

The healthy female albino rats *Rattus norvegicus* (150–200 g body weight) with normal estrous cycle were used for the study. The rats were obtained from Tamil Nadu Veterinary and Animal Science University, Chennai, and brought to the laboratory and maintained under controlled environment. The rats were maintained as per animal care (Ethical Committee's Approval No.BDU/IAEC/2014/NE/32/dt.18.03.2014) were followed throughout the experimental period. All animals were fed with standard pellet feed (Sai Durga Feeds and Foods, Bangalore).

Experimental Design

Rats were divided into four groups. In each group consisted of four rats.

Group I: Control;

Group II: Ethanol extract of *T. populnea* bark treated rats (6.6 mg/kg/bwt/day);

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Group III: Ethyl acetate extract of *T. populnea* bark treated rats (6.6 mg/kg/bwt/day); and
Group IV: Aqueous extract of *T. populnea* bark treated rats (6.6 mg/kg/bwt/day).

Extract Administration

Experimental rats (Group II, III, and IV) were treated with ethanol, ethyl acetate, and aqueous of *T. populnea* extracts (6.6 mg/kg/bwt) by oral administration. Extract administration was started before commence of estrous cycle. The extracts treatment was done for 15 days to cover three regular estrous cycles.

Effect of *T. populnea* Treatment in the Duration of Estrous Cycle and Ovulation

Determination of estrous cycle stages

Effect of *T. populnea* extracts on the estrous cycle was determined by measuring the duration of each stage of estrous cycle. The stage of estrous cycle was confirmed by vaginal smear analysis.[6] Vaginal smear samples were collected by the aspiration technique. Vaginal secretion was collected with a plastic pipette filled with 10 µl of normal saline by inserting the tip into the rat vagina but not deeply. Vaginal fluid was placed on glass slides. A different glass slide was used for each animal and observed under microscope and noted the stage of estrous cycle based on the cell types (cornified cells, epithelial cells, and leukocytes). The presence and absence of these cell types and the relative proportion of each cell type, stages of the estrous cycle were determined. The duration of the estrous cycle in rats is normally 4–5 days. Vaginal smear from the experimental rats was observed on each morning between 8.00 am and 9.00 am; and evening between 5.00 pm and 6.00 pm to know the stage of estrous cycle. The estrous cycle was studied by stained preparation of vaginal smear of the animals. The stages of estrous cycle and its duration were determined as described by Desta.[7]

Effect of T. populnea on ovulation

Production of ova by the albino rats after treatment with *T. populnea* extracts was determined by counting the ovum present in the oviduct. After 24 h of last dose (i.e. 16th day), the rats from each group were anesthetized and sacrificed. Then, the oviduct was dissected out, suspended in normal saline and placed on slide, observed under microscope, and count number of ova found in the oviduct.

Collection of Blood

Blood was collected by heart punching method and prepared serum for hormonal analysis.

Hormonal Analysis

The quantitative determination of hormones, namely, follicle-stimulating hormone (FSH), luteinizing hormone (LH), progesterone, prolactin, and estradiol was done by enzyme immunoassay method using the ADVIA Centaur(R) system.

Statistical Analysis

Values were represented as mean ± standard deviation. Analysis of variance (one-way ANOVA) and *post hoc* multiple comparisons test (Student-Newman-Keuls test) was performed at necessary places. All the statistical analyses were made using Windows-based SPSS software.[8]

RESULTS AND DISCUSSION

Antiovulation activity of *T. populnea* was evaluated by studying changes in estrous cycle, number of egg production, and reproductive hormonal levels.

Changes in Duration of Estrous Cycle

Cyclic changes in the vaginal smear observed in the estrous cycle gives a reasonable index of the ovarian activity and its hormonal synthesis of estrogen and progesterone. In the present study, treatment with extracts of *T. populnea* bark caused a significant decrease ($P < 0.005$) in the estrus and metestrus with concomitant increase ($P < 0.005$) in the duration of diestrus and proestrus phases [Figure 1 and Table 1]. Among the extracts, ethanol and ethyl acetate extracts highly altered the duration of different stages of estrous cycle compared to aqueous extract of *T. populnea* [Figure 1 and Table 1]. The prolongation of diestrus phase may explain the remote chance of the rats to get pregnant.[9] The prolongation of the proestrus phase indicates that maturation of the follicles in the preovulatory phase was delayed leading to nonmaturation of Graafian follicles.

Changes in Ovulation in the *T. populnea* Extracts Treated Rats

Ovulation in rat is known to be correlated with the appearance of estrus phase, manifested by the presence of almost 100% cornified cells in the vaginal smear in every 4–5 days.[10] In the present evaluation, the *T. populnea* bark extracts treatment caused severe reduction in egg production. Ethyl acetate and ethanol extracts treatment significantly ($P < 0.005$) reduced the production of eggs compared to control rats (15.8 ± 1.71). Average production of eggs (per cycle) by the ethanol, ethyl acetate, and aqueous extracts of *T. populnea* treated rats was 3.0 ± 0.82, 1.8 ± 0.96, and 9.0 ± 1.83, respectively [Table 2 and Figure 2]. It might be due to the prolongation of the proestrus phase which might be the maturation of the follicles in the preovulatory phase was delayed leading to nonmaturation of Graafian follicles.

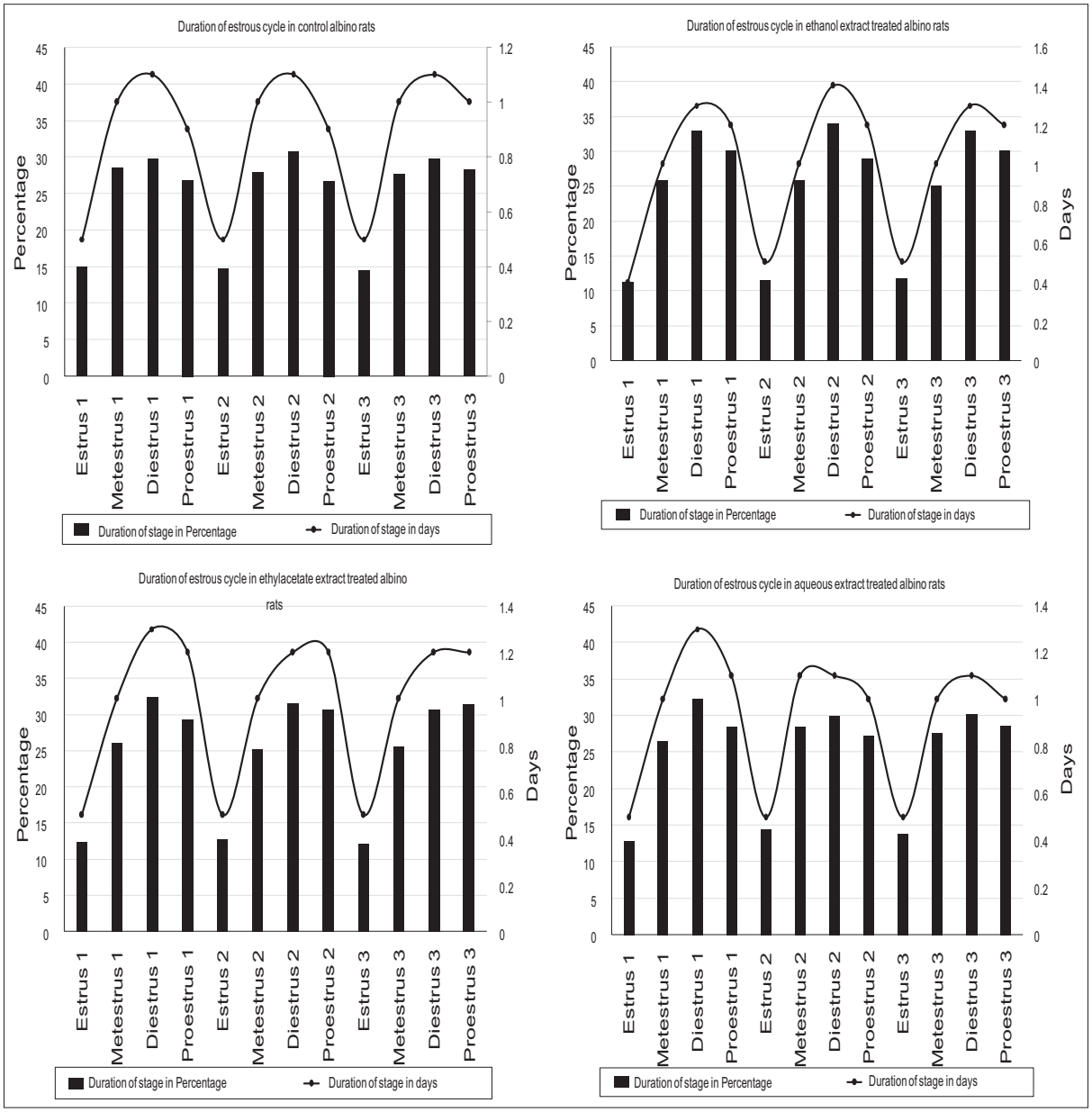

Figure 1: Changes in duration of estrous cycle in the *Thespesia populnea* extracts treated female albino rats. Group I: Control. Group II: Ethanol extract of *T. populnea* treated rats (6.6 mg/kg/bwt/day). Group III: Ethyl acetate extract of *T. populnea* treated rats (6.6 mg/kg/bwt/day). Group IV: Aqueous extract of *T. populnea* treated rats (6.6 mg/kg/bwt/day)

Changes in Reproductive Hormonal Levels

Ovarian hormones are produced by different cell types of the ovary like granulosa cells of the mature follicles and the corpus luteum.[11] Present results exhibited that treatment with *T. populnea* extracts caused significant reduction in the LH, progesterone, and estradiol levels, and produced a significant increase in the prolactin hormone. Imbalance in these hormones leads to irregularity in the ovarian functions and duration of the estrus cycle.[12-14] Reduction in the estrus and metestrus phases indicates nonavailability of the matured Graafian follicles or nonmaturation of secondary follicles. Therefore, ovulation was inhibited. Present results showed a significant reduction in the FSH level in *T. populnea* extracts treated rats. Ethanol and ethyl acetate extracts caused severe reduction in FSH level compared to aqueous extract. FSH is the central hormone of mammalian reproduction, essential for gonadal development, and maturation at puberty as well as gamete production during the fertile phase of life. It stimulates the growth and maturation of ovarian follicles by acting directly on the receptors located on the granulosa cells. The reduction in the level of FSH by the extracts may hamper folliculogenesis and delay maturation of the follicle in the preovulatory phase. It is possible that the extracts might have exerted its effect on the anterior pituitary or the hypothalamus since the secretion of stimulating hormone is regulated by the gonadotrophic-releasing hormone secreted by the hypothalamus. Evans *et al.*[15] have shown that the

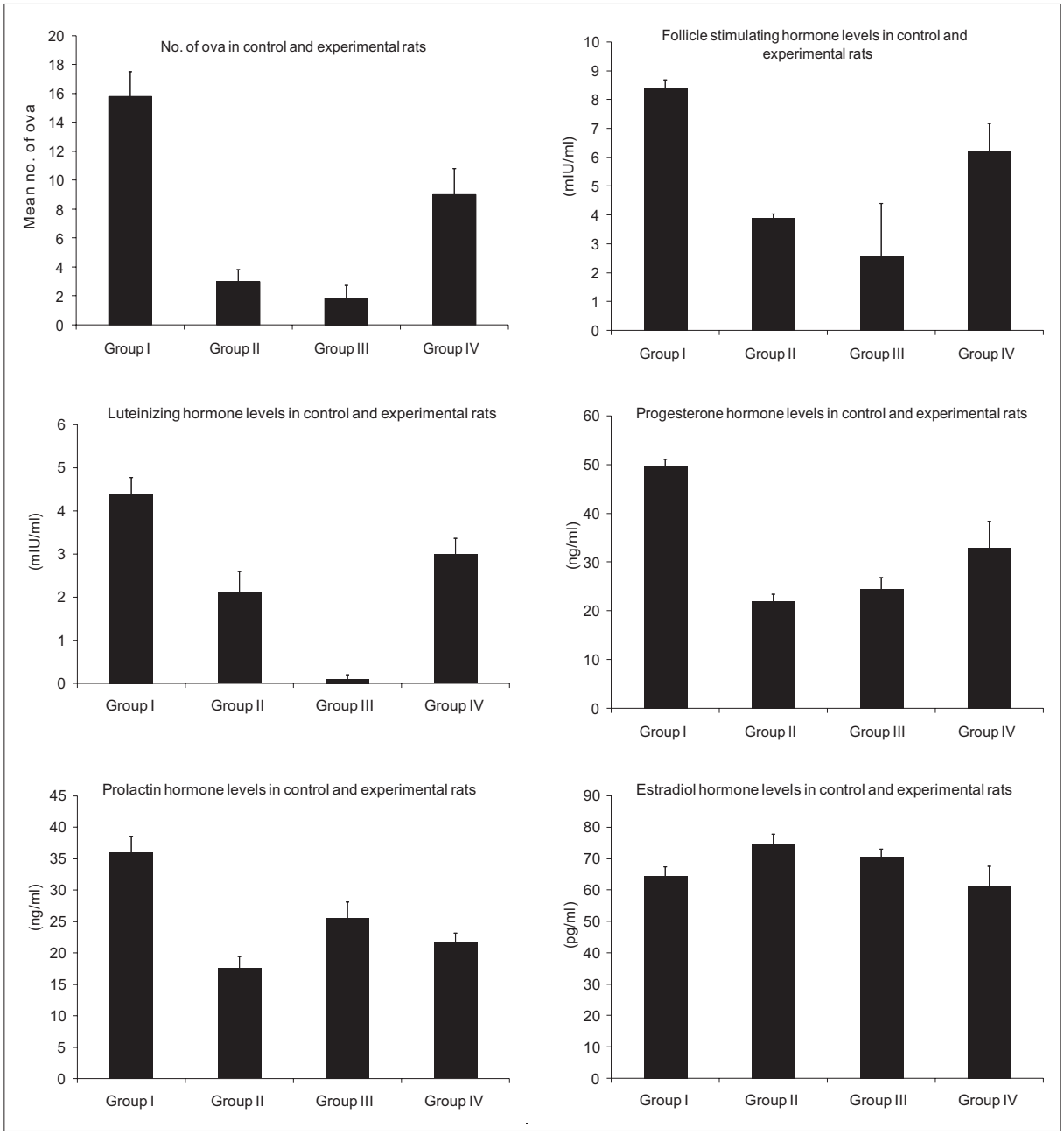

Figure 2: Changes in number of ova in the oviduct and levels of reproductive hormones in the *Thespesia populnea* extracts treated rats at the end of antiovulation study

ovarian androgen and inhibin secretion by follicles may play an important part in the regulation of FSH secretion and follicular dynamics. The integral role in the control of ovarian function is played by the hypothalamopituitary unit. Functioning in a coordinated manner with appropriate signals provided by ovary through pituitary gland is responsible for the synthesis and storage of gonadotrophins (LH and FSH).

Administration of *T. populnea* extracts (except aqueous extract) significantly increased the prolactin hormone. Prolactin helps to stimulate lactogenesis by inducing lobuloalveolar growth of the mammary gland. High prolactin level tends to suppress the ovulatory cycle by inhibiting the secretion of both FSH and gonadotropic-releasing hormone which are necessary for ovulation. Such increase in prolactin may inhibit ovulation and promote the loss of estrus cycles which will hinder conception.[16] Enhanced prolactin secretion was suppressed LH secretion due to prolongation of estrous cycle.[17] However, administration of the *T. populnea* bark extracts to the female rats showed a remarkable decrease in the level of estradiol hormones. Estradiol is the most potent naturally occurring ovarian and placental estrogen in mammals. It prepares the uterus for implantation of the fertilized ovum and promotes the maturation and

Table 1: SNK *post hoc* test shows the effect of *T. populnea* extracts on the duration of estrous cycle of female *R. norvegicus*

Parameters	Subset for alpha = 0.05 Group			
Estrus (duration in %) (one-way ANOVA; $f_{3,44}$=29.77; P<0.05)	11 (0.11) (Group II)	12 (0.12) (Group III)	13 (0.14) (Group IV)	15 (0.15) (Group I)
Metestrus (duration in %) (one-way ANOVA; $f_{3,44}$=9.21; P<0.05)	26 (0.26) (Group III)	26 (0.26) (Group II)	27 (0.28) (Group IV)	29 (0.28) (Group I)
Diestrus (duration in %) (one-way ANOVA; $f_{3,44}$=9.06; P<0.05)	30 (0.31) (Group I)	32 (0.31) (Group IV)	32 (0.32) (Group III)	33 (0.34) (Group II)
Proestrus (duration in %) (one-way ANOVA; $f_{3,44}$=11.9; P<0.05)	27 (0.28) (Group I)	28 (0.28) (Group IV)	29 (0.30) (Group II)	30 (0.31) (Group III)

Mean values are arranged in ascending order (values in the parentheses are arcsine value of respective mean). Horizontal lines connect similar means. SNK: Student-Newman-Keuls, *T. populnea: Thespesia populnea, R. norvegicus: Rattus norvegicus*, ANOVA: Analysis of variance

Table 2: SNK *post hoc* test to know the effect of *T. populnea* extracts on ovulation and reproductive hormones level of female *R. norvegicus*

Parameter	Subset for alpha=0.05 Groups			
Number of ova (one-way ANOVA; $f_{3,12}$=84.13; P<0.05)	1.8 (Group III)	3.0 (Group II)	9.0 (Group IV)	15.8 (Group I)
FSH (mIU/ml) (one-way ANOVA; $f_{3,12}$=24.89; P<0.05)	2.6 (Group III)	3.9 (Group II)	6.2 (Group IV)	8.4 (Group I)
LH (mIU/ml) (one-way ANOVA; $f_{3,12}$=95.16; P<0.05)	0.1 (Group III)	2.1 (Group II)	3.0 (Group IV)	4.4 (Group I)
Progesterone (ng/ml) (one-way ANOVA; $f_{3,12}$=62.62; P<0.05)	22.0 (Group II)	24.5 (Group III)	32.8 (Group IV)	49.8 (Group I)
Estradiol (pg/ml) (one-way ANOVA; $f_{3,12}$=51.69; P<0.05)	17.5 (Group II)	21.7 (Group IV)	25.5 (Group III)	36.0 (Group I)
Prolactin (ng/ml) (one-way ANOVA; $f_{3,12}$=9.11; P<0.05)	61.5 (Group IV)	64.6 (Group I)	70.8 (Group III)	74.5 (Group II)

Mean values are arranged in ascending order. Horizontal lines connect similar means. SNK: Student-Newman-Keuls, *T. populnea: Thespesia populnea, R. norvegicus: Rattus norvegicus,* ANOVA: Analysis of variance, FSH: Follicle-stimulating hormone, LH: Luteinizing hormone

maintenance of the female accessory reproductive organs and secondary sexual characters. Plants with estrogenic property can directly influence pituitary action by peripheral modulation of LH and FSH, decreasing secretion of these hormones, and blocking ovulation.[18] Thus, the reduction in the serum concentration of estradiol observed in the low-dose group may be attributed to a decreased aromatase activity or substrate supplementation during estrogen synthesis.[19] Consequently, such decreased in estradiol levels may hamper ovulation, preparation of the reproductive tract for zygote implantation, and the subsequent maintenance of pregnancy state.[19]

CONCLUSION

Treatment of *T. populnea* extracts remarkably reduced the duration of estrus and metestrus stages, especially in ethanol extract treated rats. However, the extract treatment extremely increased the duration of diestrus and proestrus stages. They were extraordinarily prolonged in ethanol extract treated rats. Further, they decreased the FSH and LH levels and increased prolactin level and led to the stoppage of ovulation. The present study agreed that synergy effect of all reproductive hormones, the ovulation was stopped. The synergy effect may be due to the presence of bioactive compounds such as flavonoids, alkaloids, saponin, and tannin in the *T. populnea* bark extracts.

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Comparative Study on the antibacterial activity in the coelomic fluid of Eudrilus eugeniae (Kinberg, 1867) and Polypheretima elongata (Perrier, 1872)

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ABSTRACT

In the present investigation an attempt was made to test the antibacterial activity in the coelomic fluid of the epigeic species of earthworm, *Eudrilus eugeniae* and the anecic species of earthworm, *Polypheretima elongata*. The Eudrilus eugeniae was collected from Selvam Vermicomposting farm, Udumalpet, Tamil Nadu, India. Likewise, the *Polypheretima elongata* was also collected from the soil of National college campus, Tiruchirappalli, Tamil Nadu, India. Both worms were identified by following standard taxonomical key characters. After identification, both worms were cultured under favorable laboratory condition for 30 days providing the food material consisting of 50% predeomposed organic waste and 50% predecomposed cow dung in separate cement tanks. At the end of 30 days a pool of 20 healthy worms was selected from both cultures for the extraction of coelomic fluid. Later on, the fluid was extracted by electric shock method employing 9 volt electrode. The extracted coelomic fluid (100%) was used to test the antibacterial activity against two gram positive bacteria namely *Staphylococcus aureus* and *Pseudomonas aeruginosa* and one gram negative bacterium namely *E.coli*. Among the selected bacterial strains, the coelomic fluid of *Eudrlus eugeniae* and *Polypheretima elongata* showed the maximum inhibition zones 7.01 ± 0.28mm and 2.43 ± 0.38 mm against *Staphylococcus aureus* respectively when compared to inhibition zones 2.35 ± 0.31 mm and 2.28 ± 0.29 mm; 2.66 ± 0.31 mm and 1.35 ± 0.17 mm produced by *Eudrilus eugeniae* and *Polypheretima elongata* against *Pseudomonas aeruginosa* and *E.coli* respectively. Besides that the coelomic fluid of *Eudrilus eugeniae* exhibited more inhibition activity than the zone (3.70 ± 0.13mm) produced by the positive control (standard antibiotic, penicillin) against *Staphylococcus aureus*. But at the same time there is no remarkable difference between the inhibition zone of the coelomic fluid of *Polypheretima elongata* and the positive control experiment against all the bacterial strains tested. However, the control experiment showed more inhibition zone (3.97 ± 0.24 mm) than the inhibition zone produced by the coelomic fluid of Polypheretima elongata against *Pseudomonas aeruginosa*. As for the present study the bacterium *Staphylococcus aureus* activity is highly inhibited by the coelomic fluid of both species of earthworms than the other bacterial strains tested even though there is remarkable difference in the size of zone of inhibition. The data were statistically analyzed at 5.0% level employing ANOVA.

Introduction

Earthworms are macro invertebrates which constitute the most important group of the soil invertebrates biodiversity in terms of their influence on soil formation and maintenance of soil fertility in agro-ecosystems (Edward *et al.*, 1995), and also form more than 80% of the invertebrate biomass in world ecosystems (Senepati, 1992). Earthworms are physically aerators, crushers and mixers; chemically decomposers; and biologically stimulators, in the decomposer systems. They effectively harness the beneficial microflora, destroy the soil pathogens and convert the organic wastes into vitamins, enzymes, antibiotics, growth hormones and protein rich casts (Prabha *et al.*, 2007). Of late, these organisms have drawn the attention of scientists because of their involvement in organic waste degradation to produce a marketable bio-fertilizer, vermicompost (Edwards and Bohlen, 1996). It is a good substitute for commercial fertilizers and has high level of N, P and K than the normal heap manure (Srivastava and Beohar, 2004). Besides, these organisms are a source of animal protein in the diet of animals such as poultry birds and fish (Harwood,1976; Mekada *et al.*,1979; Sabine,1978; Guerrero,1983; Xu *et al.*,1984;Stafford and Tacon,1988) and indigenous people (Edwards and Lofty,1972;Macdonald,1983). Apart from this, recently earthworms play an important role in the pharmacological studies.

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Earthworms have been used in medicine for various remedies since 1340 AD (Stephenson, 1930). Earthworm has been recognized in oriental medicine as anti-inflammatory, analgesic and anti-pyretic agent (Noda *et al.*, 1992). It shows anti-cancer effect by preventing excess glucose uptake (Nagasawa *et al.*, 1992). Microorganisms are known to play a major role in soil characteristics; invertebrates are believed to act as regulators of antimicrobial activity. Earthworm surface excreta were found to have potent antimicrobial activity (Oleynik and Byzov, 2008).

It is also having anti-coagulatory and fibrinolytic activity which results in the facilitation of blood circulation (Wang *et al.*, 1989). The earthworm has been suspected to contain proteases which dissolve the fibrin clots are anticoagulant which selectively interfere with the intrinsic pathway of blood coagulation cascade (Mannet *et al.*, 1990 Davie *et al.*, 1991, Leipner *et al.*, 1993 Kim *et al.*, 1995 and Woo *et al.*, 1996). Medicinal properties of earthworm have also been described by authors like Bristow (1932), Ogata and Mori (1938), Ogata *et al* (1939), Carr (1951) and Yegnanarayan *et al* (1987).

Besides that earthworms have largely been used internally and externally as powerful aphrodisiacs (Vohora and khan, 1978). The anti-inflammatory and anti-pyretic activities of biologically isolated extract from whole earthworm, Lampito mauritti was determined (Balamurugan *et al*, 2008). Antimicrobial potency of Eudrilus eugeniae extracts on certain plant pathogens was studied (Shobha and Kale, 2007). Several isolated bacteria strains exhibited at a high pathogenic effect when injected into Eisenia coelomic cavity (Lassbgues *et al.*, 1981). Anti-tumor activities of earthworm fibrinolyic enzyme on human hepatoma cells were studied (Hong, 2007). In 1983 it was also reported that very strong and novel fibrinolytic enzymes could be extracted from the earthworm, Lumbricus rubellus. These enzymes were fractionated and purified as six novel fibrinolytic enzymes and named collectively as Lumbrokinase (Mihra *et al.*, 1996; Tang *et al*,.2000; Li *et al*,.2008). It was also found that earth worm powder contains two kinds of inhibitory substance for the platelet aggregation induced by collagen and ADP. This novel substance also displays a relaxation effect for the canine saphenous vein induced by prostaglandin F in vitro and an inhibitory effect on the active partial Thromboplastin time (APTT) (Mihara *et al.*, 1996). Earthworm powder can be given orally; thus for this reason, earthworm powder has potential application as a thrombolytic and also exerts an inhibitory effect on platelet aggregation, an anticoagulant effect and a relaxation effect for the vascular systems, which are all effective for thrombotic therapy (Kim *et al.*, 1998). Earthworm powder represents a very promising agent for the treatment of thrombosis (Mihara *et al.*, 1996). Its tonic properties also make it beneficial support for the live and other organ system.

In china, Korea, Vietnam and most of Southeast Asia, Lumbricus has been used for their therapeutic benefits for thousands of years and referred to as earth dragons. It has been found that coelomic fluid of the earthworm contain more than 40 proteins and exhibits several biological activities as follows; cytolytic, proteolytic, antimicrobial, hemolytic, hemagglutinating, tumorolytic, mitogenic activities (Cotuk and Dales 1984; Lange *et al.* 1997; Lange *et al.* 1999; Cooper and Roach 2003; Lassegues *et al*, 1981) found that this hemolytic factor also inhibited the growth of different bacterial species which were isolated from nature. The coelmic fluid of Eisennia fortida Andrei was demonstrated to possess an antimicrobial activity against Aeromonas hydrophila and Bacillus megaterium which are known as earthworm pathogens (Valembois *et al.* 1982 and Pan *et al.* 2003). Afterwards, Milocha *et al.* (1997) obtained two proteins, named Fetidins from dialyzed coelomic fluid of earthworms and confirmed that this antibacterial activity was due to fetidins. Cho *et al.* (1998) found that Lumbricus rubellus also has two antibacterial agents named Lumbricin 1 and Lumbricin 2. Of late, Kathireshwari et.al. (2014) have reported that the antimicrobial activity of the two species of earthworms namely Lampito mauritii and Megascolex konkanesis have revealed the maximum inhibition activity against the bacterial strains such as Aeromonas hydrophilla, Bacillus subtillus and Vibrio para haemolyticus and they also stated that the coelomic fluid of the earthworms namely Darwida impertusa and Darwida lennora showed less inhibition activity against these bacterial strains.

Recently, two types of antibacterial factors which include lysozyme-like molecules with hemolytic activity as well as a pattern recognition protein named coelomic cytolytic factor (CCF) have been identified in Eisenia foetida earthworm (Kohlerova *et al.* 2004). Bruhn *et al.* (2006) started that lysenin which was a different protein of Eisenia foetida and lysenin-like proteins had several cytolytic activities which exerted hemolytic, antibacterial and membrane-permeabilizing properties. Many proteins are involved in immunodefense of earthworms, such as lysozyme, lysenin, fetidins and CCF-1 (Cooper *et al.*2002). However, it is not known whether antimicrobial peptides contribute to the innate defense of earthworms. To date only one antimicrobial peptide, lumbricin I, has been isolated from the earthworm Lumbricus rubellus. Lumbricin I, which belongs to proline- rich antimicrobial peptides group, kills both bacteria and fungi without hemolytic activity in vitro (Cho *et al.* 1998). Despite their immense economic importance, the investigation on the antibacterial activity of earthworms is limited to three to four species. Hence, in the present investigation an attempt was made to bring out new antimicrobial agent or components from the coelomic fluid of earthworms, Eudrilus eugeniae and Polypheretima elongata. In addition to that the present study will definitely lead to formulation of new natural antimicrobial agent and this may be found useful in future prospectus for mankind.

Materials and methods

Collection and identification of earthworms

The earthworms were collected with the help of shovel by digging and hand sorting method from the soil of National College Campus Area. The soil was dug up to a depth of 0-100 cm and the worms were hand collected cautiously without any damage and they were washed in clean surface water. Among the collected worms some of them were segregated to study the taxonomical characters. They were allowed in enamel tray half filled with water. They were narcotized by gradually adding ethanol to water. The narcotized worms were fixed in 5%-10% formalin solution depending on the size of the worms for 24 hrs in straightened position. The fixed worms were examined morphologically and anatomically to study the taxonomical characters (Julka and Paliwal, 1993).

Both external and internal characters are considered important in earthworm taxonomy. It is therefore, necessary to dissect the earthworms for their internal observations.

Earthworms were examined in various growth stages. This is indicated in the material examined as 2-4-7, denoting 2 juveniles, 4 aclitellate and 7 clitellate worms (Julka, 1988). Lengths of uniformly contracted worms were measured with a linear scale, and their diameter was measured on segments just anterior to clitellum. The worms were dissected longitudinally slightly left or right side of the mid-dorsal line by using a sharp tissue culture blade. Morphology, location and presence or absences of internal organs were recorded.

A Distance between setae of a worm was measured by an ocular micrometer. Measurement of pineal or copulatory setae was also taken by an ocular micrometer under high magnification. Slides were prepared for studying spermathecae and different kinds of setae. All illustrations were drawn with the help of a camera lucida.

Culturing of earthworms

Among the collected earthworms some of them were segregated to culture under favoural laboratory condition. They were cultured in suitable cement tanks (1m length ×1 meter breadth×50cm height) by providing the feeding material consisting of 25% decomposed organic waste and 25% predecomposed cow dung and 50% garden soil. A pool of 20 healthy matured worms was selected to extract the coelomic fluid for the study of antibacterial activity.

Cleaning and removing of gut content of earthworms

Fully matured earthworms were washed in running tap water in order to remove the sand particles from the surface of earthworms. Then the washed earthworms were soaked in N-saline solution and the solution was exchanged every time after wash till the gut of earthworms was thoroughly cleaned (Abhishek mathur *et al.*, 2010).

Extraction of coelomic fluid

Coelomic fluid was extracted by applying a potential difference across a pool of worms, causing them to extrude coelomic fluid. A pool of twenty worms were placed in a large petridish in an electrolyte solution (0.1%Nacl) that was also served to collect the extruded coelomic fluid (ECF), and a potential difference of 9 V was applied across the worms for 20^30 s. The coelomic fluid was collected with the help of micropipette. The collected coelomic fluid was centrifuged for 5 minutes at 350 rpm and the filtrate was used. The fluid was used at the concentration of 100% to study the antibacterial activity (Bundy *et al.*, 2001).

Antibacterial assay

Disk method was used to assay the antibacterial activity of coelomic fluid of Eudrilus eugeniae. Bacterial cells were grown overnight in LB medium and inoculated into 5ml of molten 0.6 g/l agar with a final concentration of 106 colony forming units per ml, which was overlaid onto a 90mm petridish containing 10ml of 2g/l LB solidified agar. After the top agar hardened, sterilized blotting paper (about 6.0 mm in diameter), free from antibacterial activity, were impregnated with $20\mu L$ of coelomic fluid to be tested and placed on agar dishes inoculated with one bacterial strain. The dishes were incubated over night at 37.0℃ . Control tests were performed with penicilin.

Bacterial strains used for determining antibacterial activity included Escherichia coli, *Staphylococcus aureus* and *Pseudomonas aeruginosa* which were obtained from Clab cultural laboratory, Trichirappalli, Tamilnadu, India. Antibacterial activity was determined by determining the Relative Magnitude of Inhibition (RMI). The data were statistically analyzed at 5.0% level employing ANOVA.

$$RMI = \frac{[Area\ defined\ by\ zone\ of\ inhibition\ (including\ disc)]}{Area\ defined\ by\ the\ disc}$$

Results and Discussion

Table 1 shows the antibacterial activity of the coelomic fluid of the epigeic species of earthworm *Eudrilus eugeniae* and the anecic species of earthworm *Polypheretima elongata* against two strains of gram positive bacteria namely *Staphylococcus aureus* and *Pseudomonas aeruginosa* and one strain of gram negative bacterium namely *E. coli*. Among the selected bacterial strains the maximum inhibition zone of coelomic fluid of *Eudrilus eugeniae* (7.01 ± 0.28mm) and *Polypheretima elongata* (2.43 ± 0.80mm) was noticed against the same species of bacterium *Staphylococcus aureus* when compared with the inhibition zones produced by other bacterial strains tested in the present study. The maximum antibacterial activity in the coelomic fluid may be due to the presence of the range of humoral defence factor including agglutinins (e.g. lectin), lysosomal enzymes (e.g. acid phosphatase) and bactericidins (Cooper, 2005). But at the same time the coelomic fluid of *Polypheretima elongata* exhibited the minimum inhibition zones (2.43 ± 0.80mm, 1.35 ± 0.19mm and 2.28 ± 0.29mm) against all the bacterial strains tested than the inhibition zone produced by the coelomc fluid of *Eudrilus eugeniae* against these strains (Plate 1, 2,3,4,5 and 6).

Besides, the antibacterial activity in the coelomic fluid of both species of earthworms against *Pseudomonas aeruginosa* did not make much difference in the size of zone of inhibition. As for *E.coli Eudrilus eugeniae*'s coelomic fluid showed higher inhibition zone against this bacterium than the zone produced by the ceolomic fluid of *Polypheretima elongata*. According to control experiment the maximum and minimum inhibition zones were noticed against *Pseudomonas aeruginosa* and *Escherichia coli* respectively. However, the coelomic fluid of *Eudrilus eugeniae* showed high inhibition zone against *Staphylococcus aureus* and *Escherichia coli* than the control experiment whereas the control test revealed high inhibition activity against *Pseudomonas aeruginosa* than the coelomic fluid of *Eudrilus eugeniae*. But at the same time the control experiment revealed high inhibition zone against all the bacterial strains than inhibition zone of coelomic fluid of *Polypheretima elongata*. Dhanam *et al.* (2016) also suggested that the antimicrobial function of earthworm skin extraction to *S. marcescens* exposure was highest and the diameter of the growth of inhibition was 3mm whereas *S. aureus, K. pneumonia, B. aryabhattai, B. megaterium, P. putida* did not have the activity. Moreover, in the present investigation it has been proved that on the whole *Staphylococcus aureus*'s activity is highly inhibited by the coelomic fluid of both species of earthworms than the other bacterial strains tested.

The earthworm is a first terrestrial invaded organism and it is living in the soil with millions of microorganisms. During the microbial infection the immune system in the earthworms has evolved to protect them from pathogens, microbes, viruses and infected cell. Popovic *et. al.* (1996) have reported that the antibacterial activity in the coelomic fluid of earthworm may be duc to the presence of innate immune mechanism and detect the microorganisms by recognizing conserved molecular pattern. The present study corroborate with those of Ramasamy *et al.*(2008) and Zasloff (2002), who stated that anti-microbial peptides constitute a

very important component of the innate immune system of *Eudrlus eugeniae* and *E.foetida* respectively.

Invertebrates in general and earthworm in particular apparently lack lymphoid organs, lymphocytes and immunoglobulins but they have very efficient host defence system, because the body fluids contain a range of humoral defence factors including agglutinins (e.g. lectin), lysosomal enzymes (e.g. acid phosphatase) and bactericidins (Cooper, 2005). Earthworms have primitive non-specific recognition systems, and they are mediating through innate immune responses. Earthworms have extremely effective physiochemical barriers and are acting as first line of defence against pathogens. During infection, group of leucocytes, free within blood vessels, or occupying fluid filled body cavities known as coelom, are ejected out through dorsal pores, bind to microbes, engulf and then kill them. The coelomocytes of earthworm otherwise known as leucocytes (monocytes, macrophages polymorphonuclear and neutrophils) are responsible for innate immune functions such as phagocytosis and encapsulation against pathogens and parasites. With this effect the worms are able to survey the danger exposures necessitated by their more sluggish habit (Renganathan.2006).

Earthworms kill microorganism by recognizing conserved molecular patterns (lipopolysaccharides (LPS) or peptidoglycans from bacterial cell walls, β-1, 3-glucan of fungal cell walls, and double stranded RNA of viruses) on pathogen's body surface. Recognition of molecules for foreign material has been named as pattern-recognition proteins (PRPs) (Medzhitov and Janeway, 1997) because the host's primitive effecter cells would recognize molecular patterns rather than particular structures of the invading microorganisms. When bacteria invade into the coelomic cavity of earthworm, the coelomocytes starts to connect with each other by their adhesive structures around the bacteria and form "brown bodies" (Valembios, *et al.*, 1982). At the same time the coelomocytes intensively synthesize and secrete proteins that adhere to the bacteria, forming aggregations and may inhibit their further proliferation. These proteins attach to the lectin like monosaccharide of the cellular membrane of the bacteria. Different proteins and peptides of different species of earthworms have been extensively studied and different mechanisms of actions have been proposed (Marta *et al.*, 2010). Hence, it is very difficult to define which molecule and mechanism of coelomic fluid or extract of earthworms is responsible for its antibacterial activity.

Milochau *et.al* (1997) revealed the anti-bacterial activity of dialyzed coelomic fluid of *Lumbricid, Eisenia foetida Anderi.* The antibacterial l activity of coelomic fluid of *Esienia foetida* was proposed by Valem *et al (1982). Liu et.al., (2004)* identified and purified a novel antibacterial peptide namely OE3121 which is responsible for the efficient immune response of earthworm. It has been reported that the coelomic cytofactor I isolated from the coelomic fluid is involved in the activation at prophenoloxidase carcade via recognition at gram negative bacterial cell wall molecules, such as glucan and lipopolysaccharide (Hrzenjak *et al.* 1992). The present investigation states that it is difficult to define which molecules of coelomic fluid are responsible for its antibacterial activity. Hence, the further detail study is needed for screening out the exact molecules which are responsible for its antibacterial activity.

Plate 1. Inhibition zone of coelomic fluid of earthworm, Eudrilus eugeniae against Staphylococcus aureus

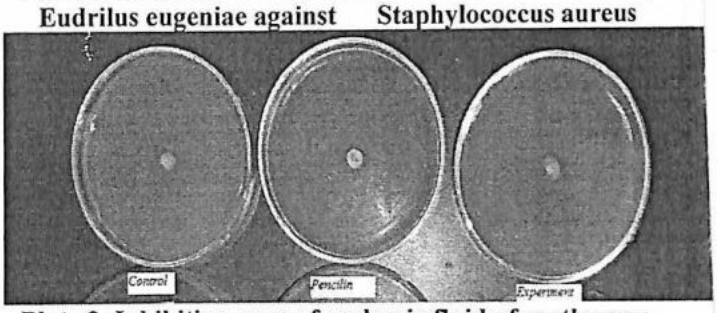

Plate 2. Inhibition zone of coelomic fluid of earthworm, Eudrilus eugeniae against Pseudomonas aeruginosa

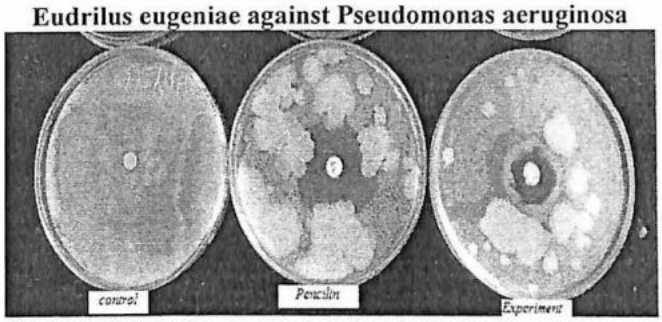

Plate 3. Inhibition zone of coelomic fluid of earthworm, Eudrilus eugeniae against E.coli.

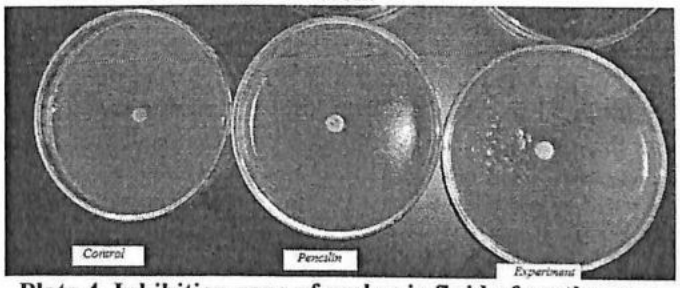

Plate 4. Inhibition zone of coelomic fluid of earthworm, Polypheretima elongata against Staphylococcus aureus

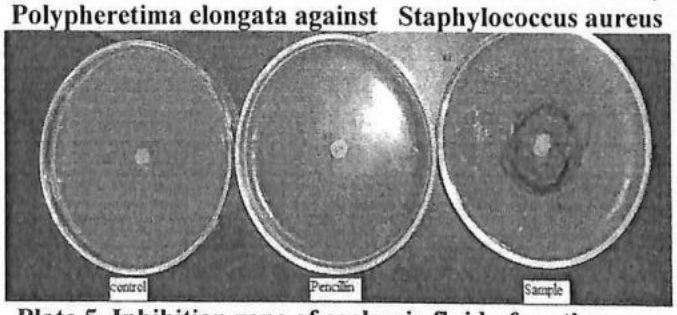

Plate 5. Inhibition zone of coelomic fluid of earthworm, Polypheretima elongata against Pseudomonas aeruginosa

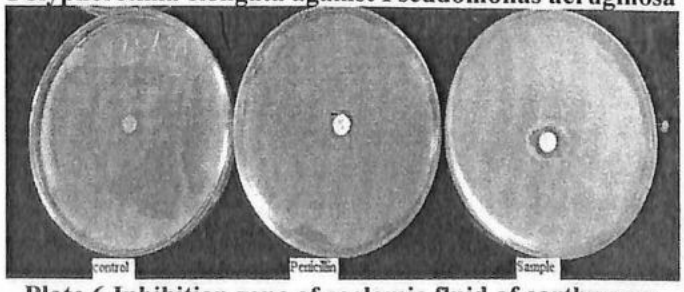

Plate 6.Inhibition zone of coelomic fluid of earthworm, Polypheretima elongata against E.coli.

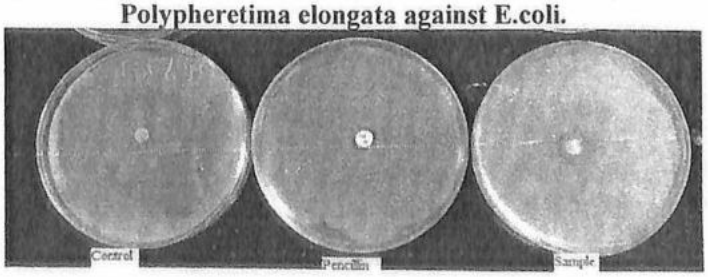

Table 1. Comparative study on antibacterial activity in the coelomic fluid of *Eudrilus eugeniae* and Polypheretima elongata against different species of bacteria. Size (mm) of the zone of inhibition produced by 6mm disc on bacterial lawn.

Species of bacteria	Inhibition zone (mm) of coelomic fluid of *Eudrilus eugeniae*			Inhibition zone (mm) of coelomic fluid of Polypheretima elongata		
	A1	A2	A1/A2=RMI	A1	A2	A1/A2=RMI
Control	0	0	0	0	0	0
I Gram- positive -*Staphylococcus aureus* -*Pseudomonas aureus*	42.60 14.10	6.0 6.0	7.01 2.35	14.60 13.60	6.0 6.0	2.43 2.28
II Gram-negative - E.coli	16.0	6.0	2.66	8.10	6.0	1.35
III Antibiotic (Penicillin) -*Staphylococcus aureus* -*Pseudomonas aureus* - *E.coli*	Zone of inhibition(mm) of antibiotic(Penicillin)					
	A1		A2	A1/A2 = RMI		
	21.0 21.4 6.6		6.0 6.0 6.0	3.70 3.97 1.77		

A1- Area defined by zone of inhibition (including disc) A2- Area defined by the disc RMI- Relative magnitude of inhibition

Statistical analysis for table 1

S.No	Species of bacteria	Zone of inhibition(mm) of coelomic fluid of *Eudrilus eugeniae*	Zone of inhibition(mm) of coelomic fluid of *Polypheretima elongata*
1.	I- Gram positive - *Staphylococcus aureus* - *Pseudomonas aureus*	7.01 ± 0.28 2.35 ± 0.31	2.43 ± 0.38 2.28 ± 0.29
2.	II- Gram negative - E.coli	3.66 ± 0.31	1.35 ± 0.19
3.	III- Antibiotic (Penicillin) -*Staphylococcus aureus* -*Pseudomonas aureus* - *E.coli*	3.70 ± 0.13 3.97 ± 0.24 1.77 ± 0.44	

Values are explained by mean ± SD of six samples - significant at 5% level

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Effect of chlorpyrifos on biochemical changes in freshwater mussel *Lamellidens marginalis*

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Abstract
The freshwater mussel *Lamellidens marginalis* was exposed to sub-lethal concentration (5ppm) of an organophosphorus insecticide, chlorpyrifos for 30 days and allowed to recover for seven days. Alanine aminotransferase (ALAT), aspartate aminotransferase (AAT), and acetylcholinesterase (AChE), were assayed in plasma and different tissues at regular intervals of day and after recovery period of seven days. The ALAT and AAT activities were increased in plasma and muscle, where as hepatopancreas and gill showed decrease. AChE activity was observed in gill, muscle and hepatopancreas, and reduction of 73% was observed in hepatopancreas. There was a significant recovery in all the above biochemical parameters studied in plasma and different tissues, after seven days recovery period. These results revealed that chlorpyrifos affects the intermediary metabolism of *Lamellidens marginalis* and that the assayed enzymes can work as good biomarkers of organophosphorus contamination.

Keywords: Chlorpyrifos, *Lamellidens marginalis*, Marker enzymes, AChE

1. Introduction
Responses to OP insecticides by aquatic organisms are broad ranged depending on the compound, exposure time, water quality and the species [5, 9]. Acetylcholinesterase (AChE, E.C: 3.1.1.7) enzyme is widely used for rapid detection to predict early warning of pesticide toxicity [4]. The enzyme acetylcholinesterase (AchE) is responsible for hydrolyzing the neurotransmitters acetylcholine into choline and acetic acid [10]. The enzyme control ionic currents in excitable membrance and plays an essential role in nerve conduction processes at the neuromuscular junction. The inhibition on the AchE is liked directly with the mechanism of toxic action of organophosphate pesticides. Viz., irreversible or reversible binding to the catalytic site of enzyme and potentiation of cholinergic effect as an indicator of exposure to these compounds acetylcholinesterase and non-specific cholinesterase activities in blood and tissues emerged as a diagnostic tool in the biomedical area. The quantification of this enzyme has been applied to laboratory and field studies with both vertebrates and invertebrates to assess exposure to organophosphorus and carbamate insecticides.
The inhibitory effects of OP insecticides are dependent on their binding capacity to the enzyme active site and by their rate of phosphorylation in relation to the behavior and age [12]. The alanine aminotransferase (ALAT) and aspartate aminotransferase (AAT) are liver specific enzymes and they are more sensitive measure of hepatotoxicity and histophathalogic changes and can be assessed within a shorter time [2]. The increase in ALAT and AAT indicate the tissue damages in liver, kidney and gill [8, 11]. In toxicological studies of sub acute exposure, the alterations in the enzymatic activities directly reflect the metabolic disturbances and cell damage in specific organs [3]. Hence, the present study is designed to study the sub-lethal effects of chlorpyrifos on biochemical parameters of plasma, gill, hepatopancreaes and muscle tissues of freshwater mussel, *Lamellidens marginalis*.

2. Materials and methods
2.1. Animal maintenance
All the reagents used in the present study were of analytical grade and were used without further purification. The freshwater mussel, *Lamellidens marginalis* were collected from Cauvery River (Tamilnadu), which is relatively free from pollutants, and were brought to the laboratory in a large aerated drum.

Later, they were acclimatized for 30 days in a cement tank (800mm length, 300mm width, and 400mm height) were set up each containing 50 mussels. The mussels were fed with dried green algae (Spirulina), weighing 10 g were transferred to a glass aquarium (60 X 30 X 30 cm) of 40-l water capacity for a further period of seven days and were fed with dried green algae for conditioning. The water in the aquarium was renewed daily and was aerated mechanically. The natural photoperiod of 13:11 L: D hours was maintained. The average values for water quality data holding in exposure tanks was temperature 26 ± 2 ºC, pH 7.10 ± 0.05, dissolved oxygen 8.15 ± 0.064 mg l^{-1}, total hardness 634.69 ±0.88 mg l^{-1} asCaCO3, alkalinity 298.75 ± 2.06 mg l^{-1} (as CaCO3), and chlorides 276.785 ±0.92 mg l^{-1}[1].

2.2. Sub-lethal studies

During sub-acute studies a total of 45 mussels (15 mussels per aquarium) were exposed to 5ppm (1/10 of the LC_{50}) for a period of 30 days. The required concentration was maintained by adding the toxicant directly in 40 l of water and renewed daily with out aeration. The control experiments were also performed without toxicant. The biochemical changes in the freshwater mussel, plasma, gill, hepatopancreas and muscle were studied at regular intervals i.e., on day, 5, 15, 30 and the recovery levels of various enzymes were studied after the day 7, of the post exposure period.

2.3. Biochemical studies

AAT (E.C. 2.6.1.1) and ALAT (E.C. 2.6.1.2) activity in plasma, gill, hepatopancreas and muscle were estimated according to the standard procedure of [13]. The enzyme activity was expressed as µmol of pyruvate formed/mg protein/h. AchE (E.C. 3.1.1.7) activity (µmol /mg protein/min) was determined by the method of [14].

2.4. Statistical analysis

The experiments were repeated on three different occasions in triplicate and that data were analyzed by Student's t-test. Statistical comparisons were done between control and exposure data from the same species. Significant differences from control values $P < 0.05$, $P < 0.01$ and $P < 0.001$ were accepted as levels of statistical significance.

3. Results and discussion

In the present study significant changes of AAT, ALAT and AChE was observed and were time dependant and are presented in Table 1 & 2. Mussel exhibited higher AAT and ALAT activities in plasma and muscle and significant reduction was observed in gill and hepatopancreas tissues. Plasma activity concentrations of AAT and ALAT are the most commonly used biochemical markers of hepatocellular necrosis [6, 7]. The AChE activity in the gill, muscle and hepatopancreas showed a continuous decrease as the exposure progressed. The maximum reduction in AChE activity of the gill, muscle and hepatopancreas of exposed mussels were 65%, 66% and 73% respectively by the end of exposure. At the end of recovery period hepatopancreas AChE value was still 13% below controls whereas the gill and muscle AChE were 9% and 32% below control.

4. Conclusions

The present biochemical alterations in the freshwater mussel, *Lamellidens marginalis*, sub-lethal intoxicated with chlorpyrifos suggests that the treated mussels faced a serious metabolic crisis. The results revealed that chlorpyrifos affects the intermediary metabolism of *Lamellidens marginalis* and that the assayed enzymes can work as good biomarkers of organophosphorus contamination. Fortunately, most of the metabolic disorders did not persist when the freshwater mussels were allowed to recover in clean water for less than a week.

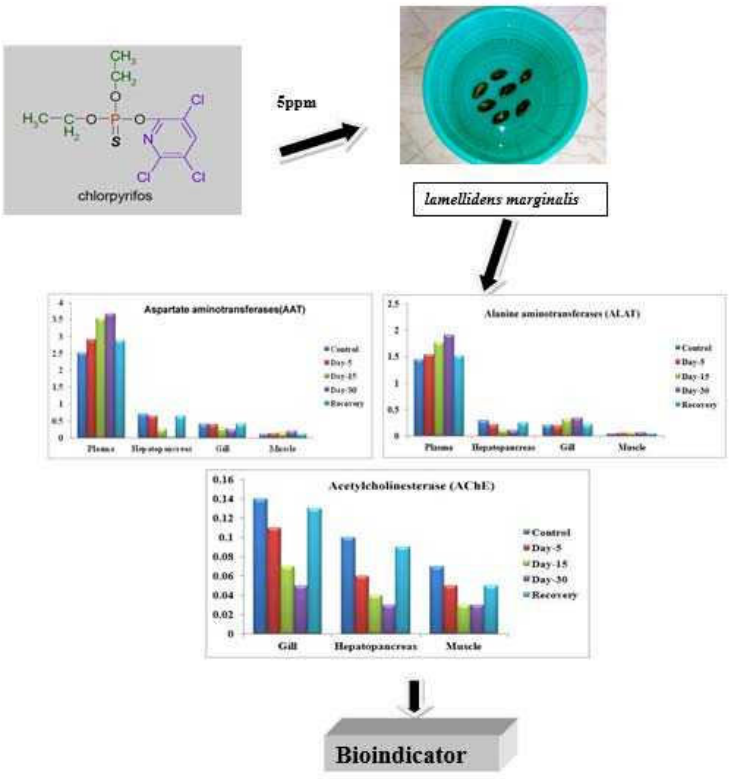

Table 1: Changes in AAT[A] and ALAT[A] levels in different organs of *Lamellidens marginalis* after treatment with Chorpyrifos

Days	Plasma	Hepatopancreas	Gill	Muscle
Aspartate aminotransferases (AAT)				
Control	2.51 ± 0.06	0.697 ± 0.031	0.402 ± 0.003	0.101 ± 0.005
Day-5	2.91 ± 0.03[c] (16)	0.637 ± 0.054 (–8)	0.381 ± 0.004[b] (–5)	0.122 ± 0.003[b] (21)
Day-15	3.54 ± 0.08[c] (41)	0.253 ± 0.052[c] (–64)	0.289 ± 0.003[c] (–28)	0.164 ± 0.006[c] (62)
Day-30	3.66 ± 0.07[c] (46)	0.015 ± 0.006[c] (–77)	0.241 ± 0.002[c] (–40)	0.185 ± 0.004[c] (83)
Recovery	2.88 ± 0.05[b] (15)	0.644 ± 0.047 (–8)	0.397 ± 0.003 (–1)	0.109 ± 0.003 (8)
Alanine aminotransferases (ALAT)				
Control	1.45 ± 0.03	0.292 ± 0.002	0.209 ± 0.004	0.038 ± 0.002
Day-5	1.53 ± 0.03[a] (6)	0.211 ± 0.004[c] (–28)	0.193 ± 0.003 (–8)	0.047 ± 0.003[a] (24)
Day-15	1.77 ± 0.02[c] (22)	0.127 ± 0.002[c] (–57)	0.320 ± 0.005[a] (53)	0.061 ± 0.001[c] (61)
Day-30	1.91 ± 0.03[c] (32)	0.101 ± 0.002[c] (–65)	0.345 ± 0.004[a] (65)	0.065 ± 0.001[c] (71)
Recovery	1.51 ± 0.04 (4)	0.258 ± 0.003[c] (–12)	0.213 ± 0.002 (1)	0.042 ± 0.002 (11)

Significant differences from control values [a](P < 0.05), [b](P < 0.01) and [c](P < 0.001).
Values in the parenthesis indicated as percent induction or percent reduction (indicated as negative).
[A] µmol pyruvate formed/mg protein/h. Each value is the mean ± SE of three individual observations.

Table 2: Effect of chlorpyrifos on acetylcholinesterase (AChE)[A] activity in different tissues of *Lamellidens marginalis*

Days	Gill	Hepatopancreas	Muscle
Control	0.14 ± 0.002	0.10 ± 0.002	0.07 ± 0.003
Day-3	0.11 ± 0.003[c]	(24) 0.06 ± 0.001[b] (45)	0.05 ± 0.002[c] (27)
Day-15	0.07 ± 0.001[c] (59)	0.04 ± 0.003 (63)	0.03 ± 0.003[c] (65)
Day-30	0.05 ± 0.001[c] (65)	0.03 ± 0.003[a] (73)	0.03 ± 0.002[c] (66)
Recovery	0.13 ± 0.003[a] (13)	0.09 ± 0.004 (9)	0.05 ± 0.003[c] (32)

Significant differences from control values [a](P < 0.05), [b](P < 0.01) and [c](P < 0.001).
Values in the parenthesis indicate percent reduction.
[A] lmol acetylcholine hydrolysed/min/mg protein. Each value is the mean ± SE of three individual observations.

Highlights

- Effect of chlorpyrifos on biochemical changes in freshwater mussel *lamellidens marginalis.*
- Sublethal concentration creates alteration, but not physiology or lethality.
- Self regulating mechanisms might have prevented from Lethality.
- Biochemical altered with increasing dose levels of chlorpyrifos

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