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Effect of cobalt doping on antimicrobial, antioxidant and photocatalytic activities of CuO nanoparticles

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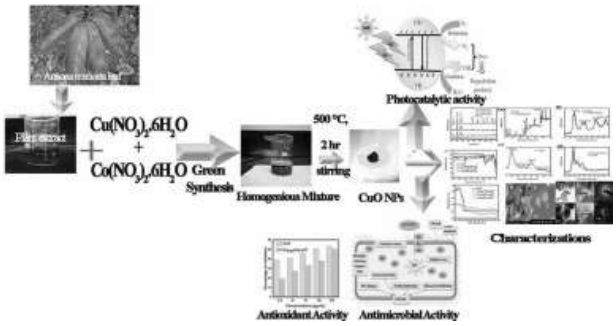
Highlights

- $Cu_{1-x}Co_xO$ (x=0, 0.03, 0.05 & 0.07) nanoparticles was prepared as green route using *Annona Muricata* leaf extract.
- Co doped CuO nanoparticles have monoclinic crystal structure with Cu^{2+} oxidation state and visible light active bandgap.
- Morphology and elemental composition are studied by HR-TEM, SEM and EDX.
- The synthesized nanoparticles possess excellent photocatalytic, antimicrobial and antioxidant activities.

Abstract

Copper oxide nanoparticles doped with 3%, 5%, and 7% cobalt have been prepared via the green method using *Annona muricata* leaf extract to find their antimicrobial, antioxidant and photocatalytic activities. The synthesized nanoparticles was analysed by XRD, FTIR, XPS, EDX, SAED, HRTEM, SEM and UV–Visible techniques. XRD pattern indicate all nanoparticles had single-phase monoclinic structure. Functional groups present in the samples were confirmed by FTIR analysis. The incorporation of Co^{2+} ions into CuO lattice were identified by XPS analysis. Morphological changes of nanoparticles were confirmed by SEM and HRTEM micrograph. Chemical composition of elements were confirmed by EDX spectra. Antimicrobial efficiency of pure and cobalt doped CuO nanoparticles was identified by their zone of inhibition of bacterial and antifungal strains. Moreover, the green synthesized CuO nanoparticles have considerable antioxidant action. Further, the photocatalytic performance of pure and cobalt doped CuO nanoparticles was done by the degradation of methylene blue.

Graphical abstract



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Introduction

Due to the low efficiency of available antibiotics, the rapid emergence of multidrug-resistant microbial strains that cause diseases and infections is now a challenging problem for all living organisms and public health [1]. Presently, antimicrobial resistance is a universal threat due to ineffectiveness of standard treatments, which results in prolonged illness and a greater risk of death [2]. These increases in microbial resistance to drug therapy demands greater attention from researchers in order to discover new antibiotics that are low in cost and high in efficiency [3]. The nanostructured rare earth and semiconductor materials like ZrO [4], ZnO [5], CuO [6], TiO_2 [7] and SnO_2 [8] etc., act as antimicrobial agents due to their high efficiency, high microbial membrane reactivity, low cost, ease of synthesis, remarkable visible light active band gap and large surface to volume ratio [9]. Among these, CuO is an important p-type semiconducting nanomaterial with a narrow band gap of 1.7 eV that is extensively used in a wide range of applications such as superconductors, solar cells, gas sensors, catalytic and biomedical fields [10]. The structural, optical, electrical and magnetic properties of nanoparticles were modified by transition metal doping and are applied in antimicrobial, photocatalytic, magnetoelectronic, nanoelectronics and spintronic devices [11]. Several studies have been reported on the changes associated with the doping of transition metals such as Ni, Fe, Co, Zn and Mn [12]. Among various metal oxides, cobalt is chosen as the best dopant due to similar ionic radii, large surface area and high chemical reactivity to create more active sites for reduction reactions [13]. Doping changes their properties by altering the overall characteristics of the material and causing lattice defects on the surface by controlling interfacial charge transfer via defects sites in CuO nanoparticles doped with cobalt [15]. The impurities interrupt defects centres and contribute electron-hole charge recombination due to their proper p-d orbital interaction, which modifies their electrical, optical and surface properties [16].

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Discrete Applied Mathematics

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In Press, Corrected Proof What's this?

On monophonic position sets in graphs

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Abstract

The general position problem in graph theory asks for the largest set S of vertices of a graph G such that no shortest path of G contains more than two vertices of S. In this paper we consider a variant of the general position problem called the *monophonic position problem*, obtained by replacing 'shortest path' by 'induced path'. We prove some basic properties and bounds for the monophonic position number of a graph and determine the monophonic position number of some graph families, including unicyclic graphs, complements of bipartite graphs and split graphs. We show that the monophonic position number of triangle-free graphs is bounded above by the independence number. We present realisation results for the general position number, monophonic position number and monophonic hull number. Finally we discuss the complexity of the monophonic position problem.

Keywords

General position set; General position number; Monophonic position set; Monophonic position number

1. Introduction

In 1900 Dudeney, famous for his mathematical puzzles, posed the following question[1]: what is the largest number of pawns that can be placed on an $n \times n$ chessboard such that no three pawns are on a straight line? This problem was generalised to the setting of graph theory independently at least three times in[2], [3], [4] as follows: a set of vertices S in a graph G is in *general position* if no shortest path of G contains more than two vertices of S. The problem then consists of finding the largest set of vertices in general position for a given graph G. This has been shown to be an NP-complete problem[4]. The general position problem has been the subject of intensive research; for some recent developments see[5], [6], [7], [8], [9], [10].

Some interesting variants of the general position problem have been considered in the literature. In[11] the authors [illegible] position problem using the *Steiner distance* instead of the normal graph distance. In[12] the authors set a limit on the length of the shortest paths considered. For a fixed integer d, they define a set S of vertices of

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Research Articles

Synthesis, characterization, photocatalytic activity, DNA interaction and antimicrobial studies of some lanthanide(III) complexes with a tridentate Schiff base ligand

B. Shyni, **T. S. Sikha**, J. P. Remiya, Y. M. Thasneem & S. Suhara Beevy

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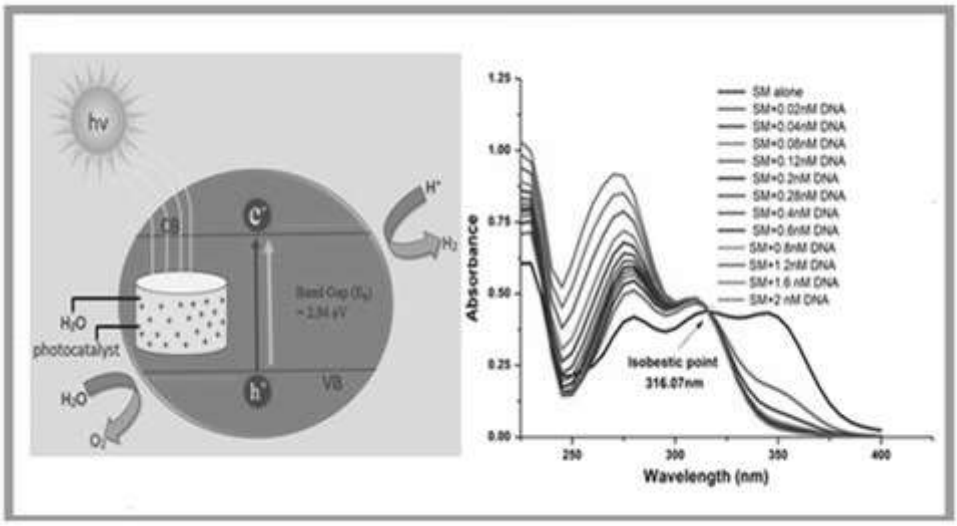
Abstract

Lanthanide complexes of Sm(III), Nd(III), and Dy(III) with a Schiff base ligand, (potassium2-((4-hydroxy-3-methoxybenzylidene)amino)acetate, derived from condensation of 4-hydroxy-3-methoxybenzaldehyde and 2-aminoethanoic acid were synthesized. The compounds were characterized by elemental analysis, IR, UV–Vis, ^{1}H-NMR, ESI-MS, photoluminescence spectra, thermogravimetric analysis, magnetic

susceptibility, and molar conductivity measurements. No well-defined peaks were observed in X-ray diffractograms of the synthesized complexes, indicating an amorphous nature. The Schiff base ligand is tridentate and coordinated with the metal ion through phenolic oxygen, azomethine nitrogen, and carboxylic oxygen. Thermal properties of the metal complexes were studied using thermogravimetric analysis (TG/DTG) and revealed good thermal stability. The photocatalytic efficiencies of the complexes were explored using solar water-splitting. The optical band gaps (E_g) were measured and found to be 2.94, 2.86, and 2.82 eV for Sm(III), Nd(III), and Dy(III) complexes, respectively. These values indicated the semi-conducting nature of the investigated complexes. At room temperature, samarium and dysprosium complexes showed characteristic luminescence of the central metal ions ascribed to the efficient transfer of energy from the Schiff base ligand to the metal center under excitation at 390 nm. The binding properties of these complexes with calf-thymus DNA (CT-DNA) have been investigated using absorption spectrophotometry and fluorescence studies. The physicochemical properties such as hydrodynamic size, zeta potential, and stability of the DNA/complexes were also investigated. DNA cleavage activities of the compounds were assayed using the Agarose gel electrophoresis method. *In-vitro* antimicrobial activities of the compounds were screened against selected pathogenic strains by Agar well diffusion method.



Keywords: Schiff base lanthanide complexes luminescence photocatalytic efficiency DNA interaction

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Journal of Molecular Structure

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Spectral, thermal, structural and DFT studies of new luminescent heterobimetallic MOF of lead and sodium based on diglycolic acid ligand having unusual coordination environment for photodegradation and antibacterial applications

Harisankar A [a], Preethi P C [a], Y Sheena Mary [b], Sreeja T G [a c], Resmi Raghunandan [a]

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Highlights

- Single crystals of a new bimetallic MOF of diglycolic acid ligand with different metals such as sodium and lead have been synthesized via the gel-diffusion method.
- The grown crystals were further characterized by FTIR, PXRD, TG-DTG, BET, and Photoluminescence studies.
- DFT studies of the bimetallic MOF show a high electrophilicity index (5.3148 eV) that reveals high biomolecular binding capacity of the molecule.
- The photocatalytic degradation and biological experiment suggests that the grown crystals are found to be an effective material for the degradation of methylene blue and can be used for antimicrobial applications as well.

Abstract

Single crystals of a new bimetallic MOF of diglycolic acid ligand with different metals such as sodium and lead have been synthesized via the gel-diffusion method. The Single crystal X-ray diffraction studies revealed that an unusual

coordination environment arises due to the mutual coordination of both sodium and lead metals. The grown crystals was further characterized by FTIR, PXRD, TG-DTG, BET, and Photoluminescence studies. DFT studies of the bimetallic MOF implies a high electrophilicity index (5.3148 eV) that predicts high biomolecular binding capacity of the molecule. The complex under study has a hardness value of 1.7645 eV, indicating that the material is hard. The simulated PXRD is in good agreement with the experimental PXRD pattern which confirms the structural integrity of crystals within the bulk. The antibacterial activity as well as the degradation property of the material towards methylene blue was also studied in detail. The photocatalytic degradation and biological studies suggest that the grown crystals are found to be an effective material for the degradation of organic pollutant methylene blue and can be used for antimicrobial applications.

Introduction

Methylene blue has a blue color which is commonly used as a therapeutic agent and used as an antimalarial [1], antioxidant [2], and antidepressant drug [3]. Other than all these, methylene blue is used as a vasoconstrictor [4] in patients who are suffering from a medical condition called vasoplegic syndrome which occurs in patients after cardiac surgery. Methylene blue is a thiazonic dye that can exist in different structures by resonating positive charge on nitrogen and sulfur atoms present in its structure. Methylene blue can exist in oxidized as well as in its reduced state. At a reduced state, methylene blue exists as leuco methylene blue (MBH_2^+) which is colourless and stable in an aqueous medium. On the other hand, if it is existing in oxidizing form it has a blue color and will readily be converted into colourless leuco form to attain stability. Methylene blue forms a major component among industrial and hospital effluents due to its high medical as well as therapeutic applicability. Nowadays researchers are using plenty of oxidation processes for the removal of dyes present in aqueous media. Among the degradation methods, researchers are more interested in photodegradation studies due to the reason that photogenerated holes and electrons can easily degrade the toxic ions from an aqueous medium irrespective of their chemical nature.

Metal organic frameworks are three-dimensional coordination polymers formed from inorganic metal nodes with organic counter-ionic parts. Due to the versatility of their isoreticular structure, they find an immense number of applications in catalysis [5], sensing [6], degradation of inorganic as well as organic pollutants [7], non-linear optical activity [8], gas storage [9], sensing of organic and inorganic molecules [10,11], etc. Due to the presence of isoreticular structure, three-dimensional array of ligands, metal nodes, presence of different anionic, and cationic sites and high thermal stability properties, MOF acts as a better candidate for the adsorption of environmental pollutants and also possesses antimicrobial properties.

In this work, we report the synthesis as well as characterization of a heterobimetallic MOF (abbreviated as PDGA) formed from lead and sodium with diglycolic acid ligand having an unusual coordination environment. Diglycolic acid (abbreviated as DGA) is a symmetric, aliphatic, dibasic acid which is colourless and odourless in nature. DGA is an oxygen-bonded acid that is stronger than ethanoic acid but weaker than other aliphatic acids [12]. It is water soluble without any further chemical change. Nowadays diglycolic acid functionalized materials are used for the extraction of rare earths [13], adsorption of heavy metals such as Ce^{3+} and Nd^{3+} from water medium [14], and for the fluorescent detection of heavy metal ions [15]. Metal salts used for the synthesis of MOF contains lead and sodium are water soluble, reactive and have wide range of applications. Lead is a major component in the automobile industry for the manufacture of storage batteries [16] and is used further for the synthesis of cable sheathing [17], ammunition [18], pigments [19], lead crystal glass [20] and in some solders [21]. The sodium finds applications in biological as well as industrial fields. Sodium is an essential metal for the transport of water and nutrients across cell membranes. Sodium–Potassium pumps [22] present in the membranes of cell organelle do this function by maintaining specific concentrations of sodium inside and outside the cells. Other than this, sodium is used as a heat exchanger in nuclear reactors [23]. Sodium vapours used in street lights [24] impart them a yellow color. It is used for the synthesis of sodium salts [25]. In this work, the practical applicability of the grown crystal PDGA as a photocatalyst for the

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Journal of Molecular Structure

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Hydrogen bond mediated turn-on sensor: Ultra-sensitive and label free barium-MOF for probing malathion an organophosphate pesticide

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Highlights

- Single crystals of oxydiacetic acid and Barium metal was grown through gel diffusion.
- SXRD analysis revealed the presence of a three -dimensional structure and crystallizes in orthorhombic system.
- The material showed fluorescence enhancement in the presence of malathion.
- The presence of hydrogen bonding between the uncoordinated functional groups of the ligand present in the crystal and the Malathion results in the fluorescence enhancement.
- A reusable aqueous phase turn-on luminescent sensor for the sensitive detection of malathion with appreciable efficiency.

Abstract

The recent trend in the agricultural field mainly focuses on the production of products with good yield by using potent and highly poisonous pesticides without considering their severe hazardous side effects. These materials are present in the soil, water, and air in trace amounts. Therefore, continuous monitoring of organophosphate (OPs) pesticides is essential from a human health perspective because of their unregulated use. In this study, we describe fluorescence

enhancement sensing for the selective quantification of OPs in aqueous media. For this, single crystals of oxydiacetic acid functionalized barium metal; $[Ba(C_4H_4O_5)(H_2O)]_n$ was developed through gel diffusion technique at room temperature. The crystals grown were found to be an effective turn-on luminescent probe in an aqueous medium for the sensing of malathion; one of the widely used pesticide in the agriculture field. The techniques such as Single Crystal X-ray diffraction, FT-IR, UV-Visible Spectroscopy, TG/DTG, photoluminescent spectroscopy, etc. were used for the characterization of these crystals. The sensing experiments clearly showed that the synthesized material suspended in water can sense malathion in aqueous media with a detection limit of 10.6676 μM/L. From the Benesi-Hildebrand plot, it is clear that there exists a binding interaction between the sensor and the pesticide which is in 1:1 stoichiometry. The PXRD pattern clearly suggests that the material is intact and there is no change in its peak position, as well as no new peaks, has emerged after the sensing experiments. The FT-IR spectra taken after the sensing experiments show peak broadening and peak shift thereby indicating the evidence of hydrogen bonding interactions between electron-withdrawing groups of OPs and electron-rich open metal sites or organic ligand molecules of MOFs. Interestingly, the material retained its sensing ability even after the third cycle of sensing experiments.

Introduction

Nowadays, an increase in the demand for agricultural products has become a challenge for humankind due to the rapid growth of population and economic development [1]. This challenge results in an appreciable change in agricultural productivity by introducing hybrid and genetically modified seeds, advanced agricultural strategies and tools, proper water management systems, utilization of potent pesticides, etc. [2]. Pesticides became an inevitable component in agriculture because approximately 33% of global agricultural production depends on such pesticides. The farmers are forced to use pesticides excessively for attaining good quality agricultural products with high yields. Environmental Protection Agency (EPA) defines pesticides as a group of chemical substances which prevent, reduce or destroy the progression of unwanted plants and pests without destroying the crops [3]. The most commonly used pesticides are organophosphorus compounds (OPs). Besides the various applications in agricultural production, OPs are responsible for several adverse effects on animals. The presence of waste OPs in water, air, soil, and also in fruits, vegetables, crops, etc. was detected in residual quantities, becoming a serious threat to both environment and human life [4]. OPs are highly toxic and their presence in the human body causes cancer, infertility in men, cardiovascular diseases, neurological issues, headache, asthma, immunotoxicity, dizziness, etc. [5]. Several conventional methods such as gas chromatography (GC) [6], mass spectrometry [7], gas chromatography coupled with mass spectrometry (GCMS) [8], high performance liquid chromatography(HPLC) [9], molecular imprinting [10], capillary electrophoresis [11], immunoassays and enzyme-linked immune sorbent assay (ELISA) [12], colorimetric detection [13], fluorescent [14] and chemiluminescence detection [15], etc. are available for identifying the presence of OPs. These methods are found to have some limitations related to the sensitive nature of instruments, time-consuming processes like sample preparation and pretreatments, high analytical costs, etc. [16], [17], [18]. Among the commonly used techniques, fluorescent detection is one of the promising methods for the detection of pesticides like malathion, imidacloprid, chlorpyrifos, parathion, methyl parathion, etc. Recently, malathion is widely used in modern agriculture for pest control and thereby increasing agricultural production. But it is neurotoxic in nature which can suppress the activity of acetylcholinesterase leading to cholinergic syndrome related symptoms. Malathion can easily and effectively adsorb on the lungs, gastrointestinal tract, mucous membranes, and skin. Its excess exposure may cause chest congestion, nausea, unconsciousness, etc. [19,20].

Metal organic frameworks or coordination polymers are an emerging class of compounds consisting of both organic and inorganic counterparts. These are generally formed by the coordination of active sites of the ligand which act as the secondary building units to the metal centers. The extension of the coordination entities results the formation of one-, two- and three-dimensional coordination polymers. Three-dimensional coordination polymers with appreciable porosity are referred as Metal organic frameworks. Recently, metal organic frameworks (MOFs) or porous coordination polymers (CPs) are highly significant due to their variety of properties such as crystalline structure, large surface area,

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DESTINATION IMAGE ON TOURIST SATISFACTION – A BIBLIOMETRIC ANALYSIS

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Abstract:

Purpose: This paper aims to review the body of knowledge on Destination image and its influence on tourist satisfaction. It tries to reveal the significance of studies on destination image which is the basis for tourist decision-making.

Design: The research information for the study was retrieved from the Dimensions database. The data collected are from the time period 2014 to 2022. A total number of 149 papers from different parts of the world were selected for bibliometric evaluation. The research has been done on citation analysis, co-citation analysis, and co-authorship analysis.

Findings: The bibliometric evaluation revealed that China has the largest number of studies done in the field of destination image followed by South Korea. United Kingdom (UK) was placed top for more citations. The year 2021 has the most publications and it has most citations in this field.

Originality/ value: This study figures out the publishing pattern and citation trend of destination image-related studies which is the base for tourist decision-making. As a result, this paper is helpful to upcoming researchers and tourism marketers.

Keywords: Destination image, tourist satisfaction, tourism marketing, bibliometric analysis, VOS viewer, citation analysis.

Introduction:

Bibliometric analysis, which is a scientific method helps in identifying core research works, authors, and their relationship by covering all publications in a particular field. This method aids in analysing the publications in a given area for the purpose of supporting potential researchers. Bibliometric evaluation can be used to track the publication, citation, and co-citation of authors, countries, institutions, etc. Researchers in this field can have an idea about the most cited publications, authors, and countries. This evaluation highlights the strength of publications in any field.

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SMALL BUSINESSES ARE GOING GREEN: HOW MSMES IN INDIA ARE EMBRACING SUSTAINABLE PRACTICES TO MEET THE GROWING DEMAND FOR GREEN CONSUMERISM?

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ABSTRACT
Small businesses play a significant role in India's economy, accounting for over 30% of the country's workforce and contributing significantly to the country's GDP. However, they are also known for their negative impact on the environment due to their lack of resources and knowledge about sustainable practices. With the growing demand for green consumerism, small businesses are now looking towards sustainable practices to reduce their carbon footprint and meet the expectations of eco-conscious consumers. This is a descriptive study that explores how MSMEs in India are embracing sustainable practices to meet the growing demand for green consumerism. It provides a brief account of the importance of sustainable practices for MSMEs, examples of sustainable practices adopted by MSMEs in India, and the challenges and opportunities for MSMEs to embrace sustainable practices.

Keywords: MSMEs, Sustainability, Green consumerism, India, Government initiatives, Sustainable practices

1. INTRODUCTION
India is a country with a rapidly growing economy, and small businesses play a critical role in the country's economic development. According to the Ministry of Micro, Small and Medium Enterprises, At present, the 63 million MSMEs in India account for close to 30 per cent of the gross domestic product (GDP). The sector already contributed to nearly 50 per cent of its exports and in 2022, it has grown by 37 per cent year-on-year (YoY) and employ over 110 million people (MSME Annual Report, 2022). However, small businesses also have a significant impact on the environment due to their consumption of resources, energy, and waste generation. In recent years, there has been a growing demand for green consumerism, and businesses that fail to adopt sustainable practices risk losing out on customers who are willing to pay a premium for eco-friendly products and services. With this in mind, MSMEs in India are now embracing sustainable practices to reduce their carbon footprint and meet the expectations of eco-conscious consumers.

2. THE IMPORTANCE OF SUSTAINABLE PRACTICES FOR MSMES
Small businesses have a significant impact on the environment due to their consumption of resources, energy, and waste generation. As the world is moving towards a sustainable future, small businesses cannot afford to ignore the importance of sustainable practices. In addition to reducing their carbon footprint, sustainable practices can also help small businesses to save money on energy bills, reduce waste disposal costs, and improve their brand image. Moreover, with the rise of green consumerism, businesses that fail to adopt sustainable practices risk losing out on customers who are willing to pay a premium for eco-friendly products and services.

Sustainable practices also offer a range of benefits to MSMEs. Firstly, sustainable practices can help small businesses to reduce their operating costs. For example, adopting energy-efficient practices can significantly reduce energy bills, and using renewable energy can help businesses to

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Phytoplankton Diversity and Physico-Chemical Features of Vamanapuram River, India

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Abstract

This study discusses the analysis of various physical and chemical parameters like water temperature, water pH, light penetration, turbidity, DO, BOD, Primary productivity (Net primary productivity and Gross primary productivity), and nutrient contents (Nitrate, Nitrite, Phosphate, Silicate) along with some of the phytoplankton population collected from different regions (Six stations) of Vamanapuram River were measured from the period of February 2022 to January 2023. The first parameter analyzed was atmospheric temperature, which reported maximum at pre-monsoon. Throughout the year, the study there has prominently the acidic nature of the Vamanapuram River sometimes, except station 6 reported beyond neutrality. While discussing temperature, the pre-monsoon season reported the highest temperature and also less dissolved oxygen content which explained the direct correlation between atmospheric temperature and the dissolution of oxygen in river water. Station 3 has maximum turbidity but yet high GPP because of the low depth of the mentioned river which was also reported in previous studies. The nutrient content was very negligible which explains the oligotrophic situation of the river. This baseline information on the water quality status of the Vamanapuram River will be useful for future ecological assessment and monitoring to conserve this river.

Key words: Nutrient; Chemical parameters; Vamanapuram River; Primary productivity; Gross Primary Productivity.

Introduction

Vamanapuram River which is the longest river in the Trivandrum district having a total length of 88 km and an area of 687.5 km^2, originates from the Chemmungimottai (Elev. = 1717 a.m.s.l) which is situated in the upper slope of the Western Ghats in southern Kerala and finally debouch into the Anjengo lake near Chirayinkeezhu. This river covers 8 panchayats and one municipality having a thick population and all are deadly dependent on the stream. Kalaiparai Ar from Kalakal Mottaigets linked with this river as it traverses a distance of about 7 km. Pennivadi Ar and Ponmudi Ar, two tributaries, join the main river near Kallar. The river flows southwards and a major tributary, Chittar joins the main river near Anapara. The Vamanapuram River flows southwards through Chettachal, Palode, and Choodal and then meanders westwards towards Vamanapuram. The Kilimanoor Ar joins the main river at about 3 km downstream and flows westwards through Ayilam, Attingal, and Chirayinkil and finally, the river drains into the Arabian Sea (Gopal *et al.*, 2013).

Water is the main source of domestic purposes like drinking, bathing, washing, cooking, etc. But eventually because of urban as well as industrial development the usage of water for these activities has increased along with domestic purposes. The quality of water is an important factor for the survival of living organisms and the quality of water is determined by a lot of characteristics including physical, chemical, and microbial factors. But if there is any possibility that there is a correlation

A Study on the Effect of Dietary Fiber on Lipid Metabolism in Rats

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ABSRACT

The effect of dietary fiber in the form of Neutral Detergent Fiber (NDF) from *Coriandrum sativum* (CS NDF) and *Solanum torvum* (STNDF) on lipid metabolism in rats was studied. The rats were fed with synthetic diet containing 10%. NDF. From the study, it was evident that CSNDF and ST NDF significantly reduced the levels of cholesterol, phospholipids and triglycerides in liver, kidney and serum. Lipogenic enzymes including *Glucose 6 phosphate dehydrogenase, HMG CoA reductase* and *malic enzymes* showed significantly decreased activities in the liver of Fibre diet fed rats. Elevated levels of cholic and chenodeoxy cholic acids in the feces in fiber fed rats indicate higher excretion of fecal bile acids. All the results indicate lipid lowering effect of dietary fibers. Among the two fibers, STNDF fed rats exhibited higher lipid lowering effect than CSNDF fed ones.

Key Words :*Coriandrum sativum*, *Solanum torvum,* Dietary fiber, Neutral detergent fiber.

I. INTRODUCTION

Dietary fiber (DF) is principally composed of plant cell walls and other components obtained from the cell walls. Dietary fiber has complex and highly variable composition (Harris, and Ferguson .,1993). Chemically DF is a heterogeneous group of carbohydrate materials (cellulose, hemicellulose, pectin, lignin etc.) with different physicochemical characteristics. Once DF was considered as a physiologically inert component and its contribution to whole body metabolism remained virtually insignificant. But dietary feeding patterns in very diverse societies has suggested an epidemiological link between the consumption of DF and the occurrence or absence of such diseases as colon cancer,

Advances in zooplankton studies- An overview

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Issue

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Section

Review articles

Abstract

Zooplankton are free swimming animals that have a prominent role in the both fresh water and marine ecosystems. They are considered to be bio indicators and since the existence of zooplankton is more important along with their undeniable role in energy transfer through food chains and biogeochemical cycling. To know about different aspects about zooplankton the care should be taken from the level of collection and further in to their preservation, identification, sorting, enumeration and their analysis through different scientific procedures. Studies about zooplankton is still going on all around the world and there have been a lot of advances made at different aspects related to zooplankton study. A nutshell of field as well as laboratory procedures involving different techniques and instrumentation in zooplankton studies and advancements that have been made and currently followed by the researches are included in this review article.

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Environmental Factors Affecting the Distribution of Selected Free Living Isopods in the Southern Coast of Kerala, India

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ABSTRACT

Intertidal isopods are a group of successfully surviving organisms in the littoral region of the sea. The continuous exposure to human activities and other botic and abiotic stresses can influence their distribution and diversity along the seashore. Air and water temperature, salinity, pH, and presence of nutrients such as silicate, nitrate and phosphate are studied for their influence on some of the selected intertidal isopods found in three different beaches of the southern Kerala. Monthly data was collected for the water samples and four different isopod species found in the intertidal region and

Trichodinid ciliates in two economically important fishes,Rastrelliger kanagurta(Perciformes: Scombridae) andOreochromis mossambicus(Perciformes: Cichlidae) from Kerala, India.

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Abstract

Trichodinid ciliophoransare one of the main groups of fish parasitescausing damage to skin and gills,often leading to the death of the infested fish andare still a poorly studied group in India.A study was undertaken to assess the infestation and distributionof trichodinids from the skin and gills of two economically important fishesin India, RastrelligerkanagurtaCuvier, 1816and OreochromismossambicusPeters, 1852.Dried slides were prepared from the smears andimpregnated with silver nitrate (2%) and morphometriccharacteristics were madeusing photomicrographs produced from theslides.O. mossambicus was found positive for two species, viz., TrichodinamagnaVan As and Basson, 1989 and ParatrichodinaafricanaKazubski and El-Tantawy, 1986.R. kanagurta was found to be infested with Paratrichodina sp. Lom, 1963. Seasonal variations in the rate of parasite infestation were observed in T. magnaand P. africana from O. mossambicusand these parasites showed anincrease during post-monsoon while a decrease during monsoon. No seasonal variation was observed in Paratrichodinainfestation in R. kanagurta. The infection induced excessive mucus secretion, paleness in gills, and multifocal whitish areas and lesions that probably permitted entry of opportunistic bacteria. The present study reportsthe first record ofa Paratrichodina sp.onR. kanagurtaand T. magnaon O. mossambicus.

Language

English

केरलज्योति

केरल हिंदी प्रचार सभा
की मुख पत्रिका
(केंद्रीय हिंदी निदेशालय की
वित्तीय सहायता से प्रकाशित)

पुस्तक 60 अंक 1 अप्रैल 2023

अनुक्रमणिका

पृष्ठचित्र महान अभिनेता इन्नोसेंट

समकालीन हिंदी कहानियों में तृतीय लिंगी मानवों की समस्यायें

डॉ. राजेष कुमार.आर

"Transgender people have a gender identity or gender expression that differs from the sex that they were assigned at birth "

प्रकृति मे पुरुष और स्त्री के अतिरिक्त एक अन्य वर्ग भी है जो न तो पूरी तरह नर होता है और न नारी। जिसे लोग हिजड़ा या फिर ट्रांसजेंडर के नाम से संबोधित करते है। अक्सर लोगो को इस तृतीय लिंग के विषय मे विशेष जिज्ञासा रहती है। किन्नर समुदाय की स्थिति बहुत ही दयनीय है जिससे समाज एकदम अनभिज्ञ और संवेदनहीन है। इतिहास को अगर हम बात करें तो सन्।871। से पहले भारत के तृतीय लिंगी मानवो को ट्रांसजेंडर का अधिकार मिला हुआ था। सन्।871। में अंग्रेजों ने उन्हे क्रिमिनल ट्राइब्स यानी एक जनजाति को श्रेणी में डाल दिया था।

विश्व में उक्त मानव समुदाय को ट्रांसजेंडर के रूप में मान्यता मिली है। भारत में मुख्य चुनाव आयुक्त टी. एन. शेषन ने 1994 में उन्हे मताधिकार दे दिया था। इसके बाद 15 अप्रैल 2014 को सर्वोच्च न्यायालय के एस. राधाकृष्णन और ए. के. सीकरी ने तीसरे जेंडर को मान्यता देते हुए एक ऐतिहासिक फैसला दिया। तृतीय लिंगी समाज की लम्बे समय से चली आ रही मांग को अदालत ने स्वीकार कर लिया।

हिन्दी साहित्य महामंडल के अनगिनत कथाकार अपने कहानियों एवं उपन्यासों के द्वारा उस समुदाय को समाज की मुख्यधारा में लाने की कोशिश की है। यहाँ उनकी समस्याओं पर केंद्रित कुछ कहानियों की चर्चा की गयी है। समकालीन समय में उक्त समुदाय अपनी समस्याओं से जूझते हुए समाज में अपनी पहचान कायम करने के लिए प्रयासरत है।

'बिंदा महाराज' नई कहानी आंदोलन के दौर की, शिव प्रसाद सिंह द्वारा रचित, एक चरित्र प्रधान कहानी है। प्रस्तुत कहानी में तृतीय लिंग के लिए समाज में जो दयनीय स्थिति है, उसका वर्णन किया गया है बिंदा महाराज कहानी का मुख्य पात्र बिंदा हिजड़ा है। उसके अन्दर मानवीय व्यापकता और संवेदनशील हृदय की गहराई है लेकिन स्त्री-पुरुषेतर होने के कारण उसे उपेक्षित जीवन व्यतीत करना पड़ता है। बिंदा महाराज जैसे तमाम स्त्री पुरुषेतर व्यक्ति इस तरह के उपेक्षित जीवन व्यतीत करते है। किन्नर होने की वजह से बिंदा महाराज बिंदिया संबोधन को ज्यादा पसंद करता है। कहानीकार के शब्दों में 'पतला सा शरीर, छरहरी देह, लाल रंग की चुन और बूटेदार छींट की अधबाँहिया... बिंदिया चलती तो गाँव की गलियों में हंसी, ढिठाई और मीठी चुटकियाँ गिराह बाँधकर चलने लगती'। बिन्दा महराज एक ऐसे हिजड़े की कहानी है जिसके जन्म के बाद उसके माता-पिता चल बसते है और जिसके कारण बिन्दा महराज का जीवन अनेक कठिनाइयों से भर जाता है। वे शरीर से भले ही अपूर्ण हो किंतु उनके मन की भावनाएं, संवेदनाएं तथा अपनों के प्रति प्रेम की भावना किसी आम व्यक्ति की ही भाँति विद्यमान रहती है। बिन्दा महराज अपना सम्पूर्ण प्रेम अपने चचेरे भाई के बेटे करीमा पर न्योछावर कर देते हैं। किंतु अंतत उन्हे उनके ममत्व के बदले अपने चचेरे भाई से अपमानित होना पड़ता है और घर से निकलना पड़ता है।

हिजड़ों पर आधारित एक बड़ी ही महत्वपूर्ण कहानी किरण सिंह की *संज्ञा* है। प्रस्तुत कहानी में संज्ञा के इस रूप में जन्म लेने से उसके माता पिता को बहुत पीड़ा सहन करनी पड़ती है। बड़ी हो रही संज्ञा को समाज से बचाकर पालना और आर्थिक स्थिति को संभालना कठिन हो जाता है और उसकी जिज्ञासाओं को शांत करना बड़ा ही कठिन कार्य है। इसी प्रकार बढ़ती उम्र के साथ - साथ उसके विवाह के प्रश्न भी समाज में खड़े होते है इस कहानी में कहानीकार ने बचपन से लेकर अंत तक संज्ञा के पिता और संज्ञा दोनों द्वारा खुद को समाज की नजरों से बचाए रखने की कोशिश दिखाई देती है।

'हिजडा' कहानी जो कि डॉ. कादंबरी मेहरा द्वारा रचित है, उसमें एक स्त्री रोगिनी विपरीत परिस्थितियों की वजह से नकली हिजड़ा बनकर जीवन व्यतीत करती है। इस

करने में उसे अपने जीवन का शारीरिक अत्याचार भी सहन करना पड़ता है। हिजड़ा कहानी में उस समाज के जीवन के पहलुओं को उभारा गया है। हिजड़ा कहानी द्वारा हमारे समाज पर व्यंग्य करते हुए कहानीकार ने कहा है कि समाज की कुरीतियों जैसे विवाह योग्य, अपशिष्टभाग और कष्टपूर्ण जीवन से परेशान होकर भी कुछ लोग और पुरुष किन्नर जीवन अपनाने पर मजबूर हो जाते है। दो पद्मा शर्मा की कहानी इज्जत के नजर से किन्नर जीवन के पहलुओं को उभारा गया है। सोफिया के नेतृत्व में हिजड़ों का समूह एक बलात्कारी गुंडे को नपुंसक बना देते है। क्योंकि बलात्कार की शिकार लड़की का पिता चुप रहने में ही अपनी भलाई समझता है। आज के समय में हिजड़ा वर्ग अपनी समस्याओं में जूझते हुए समाज में अपनी पहचान कायम करने के लिए प्रयासरत है।

मुसीबत किसी व्यक्ति समाज का एक हिस्सा ही नहीं बल्कि संपूर्ण अस्तित्व को प्रभावित करता है। मनोहारी समाज में ये लोग अपनी अस्मिता को पहचान दिए समाज में अपनी पहचान कायम करने के लिए प्रयासरत है।

ये लोग मनोप्रधान की दिशा में कुछ अपने अस्तित्व में लड़ता है, दूसरों से अलग होने की पीड़ा से लड़ता है। निरक्षरता और और साहित्य तथा इस विषय में संवेदित संगोष्ठियों एवं विभिन्न स्वयंसेवी प्रयासों द्वारा इस पर ध्यान दिया जा रहा है और कोशिश की जा रही है कि ये वर्ग उपहास का-पात्र नहीं बल्कि संवेदना का विषय बन सके तथा उन्हें सामाजिक तथा सभी मूलभूत अधिकार सही मायनों में प्राप्त हो।

अमलोद्भव प्राकृत हिंदी विभाग
महात्मा गांधी कॉलेज तिरुवनन्तपुरम

'एक जाति, एक धर्म, एक ईश्वर मानव का'

जाति की पुनर्व्याख्या करते हुए श्रीनारायण गुरु ने कई कविताएँ लिखी, जिनमें शताब्दियों से जाति के नाम में उच्च जातियों द्वारा प्रचारित झूठी धारणाओं का खंडन किया गया। इन कविताओं की कुछ पंक्तियाँ आज और प्रसिद्ध उक्तियों के रूप में आज भी केरल में लोकप्रिय है। सबसे प्रसिद्ध नारा है, 'एक जाति, एक धर्म एक ईश्वर मानव का' का आदर्श।

गुरु ने 1888 में शिव मंदिर की स्थापना के समय लिखी अपनी कविता या वक्तव्य में जाति भेद रंग विद्वेष आदि के बिना भातृभावना में जीनेवाले एक समाज की कल्पना की थी। 1914 में लिखित जाति निर्णय शीर्षक कविता में उन्होंने स्पष्ट किया कि मानव की केवल एक ही जाति है और वह है मानवता या मनुष्यता। उन्होंने वैज्ञानिक आधार पर यह साबित किया कि सभी मानव जाति एक ही जीव वंश या किस्म के स्तन या योनि से निकलता है, इसलिए मानव-मानव के बीच कोई अंतर नहीं है। उन्होंने तार्किक ढंग से यह सिद्ध किया कि मानव द्वारा बनाई गई ब्राह्मण आदि जातियों वास्तव में होती नहीं। उन्होंने इस कविता में यह स्पष्ट किया है कि मानवता या मनुष्यता ही मानव की वास्तविक जाति है, शेष सारी जातियाँ तो इसका ही टूटा भाग है। इन विचारों को समर्थित करने के लिए उन्होंने उपनिषद् और अद्वैत दर्शन का आधार ग्रहण किया और अपनी 'आत्मोपदेश शतकं' शीर्षक कविता में बताया कि इस दुनिया के सारे जीव ब्रह्म या परमसत्य से ही विभक्त हुआ है और चूँकि सभी में एक ही आत्मा विद्यमान है, इसलिए यह भेद करना कि यह ब्राह्मण है या 'यह पुलया है' निरर्थक है।

डॉ. जी. गोपीनाथन द्वारा रचित 'श्रीनारायण गुरु : आध्यात्मिक क्रांति के अग्रदूत' शीर्षक प्रथम से उद्धृत पुस्तक का प्रकाशक है साहित्य अकादमी, दिल्ली - 110 002

केरलज्योति

केरल हिंदी प्रचार सभा
की मुख पत्रिका
(केंद्रीय हिंदी निदेशालय की
वित्तीय सहायता से प्रकाशित)

अनुक्रमणिका

मुद्रणालय : केरल के पूर्व मुख्यमंत्री स्व.उम्मन चांडी

स्वातंत्र्योत्तर हिंदी महिला कहानीकार : एक अंतरंग पहचान

डॉ. राजेष कुमार.आर

सन उन्नीस सौ पचास के आसपास अनेक महिला लेखिकाओं ने कहानी सर्जना के क्षेत्र में अपने हस्ताक्षर छोडे। नई कहानिकारों ने हिन्दी कहानी साहित्य को नया मान प्रदान किया। स्वातंत्र्योत्तर हिन्दी साहित्य में महिला कहानी लेखन उत्तरोत्तर समृद्धि पा रहा था। तब तक भारतीय परिवेश मे भरपूर परिवर्तन आया था। व्यक्तिवाद, अस्तित्ववाद, मार्क्सवाद , फ्रायडवाद और गांधीवाद का प्रचार हो रहा था। स्त्री शिक्षा उन्नति पा रही थी और भारतीय नारियों की जागरूकता बढ रही थी, उसकी प्रतिवाद क्षमता भी। अपनी कमजोरियों और दुर्बलताओं का पता नारियों को मिला, नारी शोषण की व्याप्ति का उसे अवबोध मिला। इस समय अनेक लेखिकाओं ने अपनी सृजनधर्मिता की शुरुआत की। इन्होंने मुख्य रूप से कहानी साहित्य को अपना सृजन केंद्र बना दिया। हिन्दी की लोकप्रिय कहानिकारों की सर्जना इस काल में हुई।मन्नु भंडारी , उषा प्रियंवदा, ममता कालिया, मृदुला गर्ग, चित्रा मुद्गल, मधु कांकरिया, क्षमा शर्मा, गीतांजली श्री, मनीषा कुलश्रेष्ठ, अल्पना मिश्र, नीलाक्षी सिंह, शर्मिला बोहरा, जालान आदि तत्कालीन समय के चर्चित लेखिकाएँ हैं।

समकालीन हिन्दी साहित्य जगत के मूर्धन्य कथाकार मन्नू भंडारी का हिन्दी साहित्य में शीर्ष स्थान है। स्वतंत्रता के बाद उभर आये मध्यवर्गीय जीवन का मन्नू भंडारी की कहानियों में जीवंत अंकन है। स्त्री पुरुष संबंधों के बदलते आयामों का उनकी कहानियों में भावप्रवण चित्रण है। मन्नु भंडारी ने बदलते जीवन संदर्भ को पैनी दृष्टि से आंका है और खुले दिमाग से नारी जीवन की असलियत को देखा परखा है और उन्हें बडी हार्दिकता एवं सादगी के साथ व्यक्त किया है। सजा, क्षय, तीसरा आदमी ,रेत की दीवार, संख्या के पार, यही सच है, एक बार और, त्रिशंकु, एक प्लेट सैलाब आदि आपकी चर्चित एवं लोकप्रिय कहानियाँ है। मन्नू भंडारी की ख्याति का मूलाधार कहानी है सजा। सजा कहानी में मध्यवित्त परिवारों की अन्तर्दशा का सूक्ष्म और मार्मिक चित्रण है। आर्थिक संकट के दौर में परिजनों के व्यवहार की सूक्ष्म पडताल इस कहानी का अभीष्ट है। मनोवैज्ञानिक सूझबूझ से भरी यह कहानी, आरोपी व्यक्ति के व्यवहार शिल्प, उसका अपने बच्चों से संबंध तथा उसके प्रति उसके सगे संबंधियों का अपनत्व तथा दुराव सब इस कहानी में स्थान बनाते हैं।

स्वातंत्र्योत्तर हिन्दी कहानी को श्रीवृद्धि में ममता कालिया का स्मरणीय योगदान है। नारी जीवन के विभिन्न आयामों की गति - विगतियाँ उनकी अनेक कहानियों में अभिव्यक्त हैं। आपकी कहानियों में यह बात विशेष रूप से उभरकर सामने आती है कि आज भी नारी यातना मुक्त नहीं है, आज भी वह पति द्वारा अपमानित है तथा उसके बेमेल स्वभाव और प्रकृति को झेलते हुए नारकीय जीवन व्यतीत करती है। नारी के उत्पीडन तक ममता कालिया की प्रतिभा सीमित नहीं, उन्होंने यह भी सिद्ध किया है कि नारी - मुक्ति के रास्ते में सबसे बडी बाधा नारी के अपने घरवाले ही उपस्थित करते हैं लेकिन इसका तात्पर्य यह नहीं है कि लेखिका केवल नारी विमर्श की लेखिका है। सामाजिक,आर्थिक , राजनैतिक एवं सांस्कृतिक विसंगतियों के अनेक चित्र भी आपकी कहानियों में यथेष्ट मिलते है।

ममता कालिया की बहुचर्चित कहानी है लडकियाँ। ममता कालिया की लड़कियाँ कहानी इस तथ्य को भरपूर जीवंतता से उजागर करती रचना है स्त्री स्वातंत्र्य के रास्ते में सबसे बडी बाधा स्वयं लडकियों का निजी घर है, जिसमें उन्हें भीरु और छुईमुई बने रहने के संस्कार दिये जाते हैं। कोई भी व्यक्ति बचपन से जैसे परिवेश और जैसी अवधारणा में पलता बढता है, उसका व्यक्तित्व उसी के अनुकूल आकार पाता है। प्रस्तुत कहानी में आशा और सुधा दो प्रगतिशील निर्मम तथा महत्वाकांक्षी व्यक्तित्व भरी लड़कियाँ

है, जो कालेज में पढ रही है। एक ओर इन लडकियों का अंतर्संसार है, जो बडा आकाश खोजता है, दूसरी ओर उनके परिवारों की संस्कारगत संकीर्णता है, जिसमें इनकी भी, पिता तथा भाई सब इनके लिए प्रतिबंध ही बनते है।

हिन्दी की सशक्त लेखिका क्षमा शर्मा की लेखनी कहानी के क्षेत्र में उत्तरोत्तर प्रतिष्ठा पानेवाली लेखनी है । क्षमा शर्मा की विविध मुखी कहानियाँ समसामयिक भारतीय जीवन के एक-एक परिच्छेद की कहानियाँ है। इक्कीसवीं सदी का लडका, एक अधूरी प्रेम कहानी, नेम प्लेट, वेलेंटाइन डे, रसोई घर, यही कहीं है स्वर्ग, करवे की लडकी, दादी माँ का बटुआ आदि क्षमा शर्मा की ख्याति प्राप्त कहानियाँ है। रोजमर्रा के जीवन को कहानी का कलेवर देने में क्षमा शर्मा सिद्धहस्त है। कस्बों, नगरों और महानगरों में रहनेवाले मध्यवर्ग की उलझनों, आकांक्षाओं और सपनों को उन्होंने निजी शैली में अभिव्यक्त किया, अपनी कहानियों के माध्यम से। 'इक्कीसवीं सदी का लडका' कहानी आज के समय में एक नयी पीढी की मानसिकता के उदय की तस्वीर पेश करती है। एक मध्य वित्त परिवार में जिसमें एक बच्चे के माता और पिता दोनों ही कामकाजी है, बच्चा किस तरह स्वतंत्र रूप से आत्मनिर्भर होता चलता है और उसका नजरिया कैसे धीरे - धीरे बदलता जाता है, यह कहानी उस विकास यात्रा का एक संवेदना पूर्ण लेखा जोखा है।

स्वातंत्र्योत्तर काल में महिला लेखक गण और गुण की दृष्टि से आगे बढे। कहानी साहित्य के विकास में लेखिकाओं की भूमिका निर्णायक रह गयी। लेखिकाओं की तूलिका से अस्तित्व और अस्मिता के लिए संघर्षरत नारियों के प्रतिरूप निकले। स्वातंत्र्योत्तर काल में नारी लेखन को मान्यता मिली, उनकी लोकप्रियता बढी, हिन्दी साहित्य से नारी लेखन को अलग करना अशक्य रह गया।

असिस्टेंट प्रोफसर, हिंदी विभाग
महात्मा गाँधी कॉलेज
तिरुवनंतपुरम

क्या मैं याद रखूँ?

सुजित.एस

इन सूरतों में क्या मैं याद रखूँ?
पल-पल इन्हें बदलते ही देखा है।

कहा जाता है, रंगीन है ज़िन्दगी
सच्चाई यह है, हमने काला ही देखा है।

नफ़रत के मुखौटे, कभी गिरते ही नहीं,
अपनों को भी, इसे संभालते ही देखा है।
उन सूरतों में इंसानियत नहीं थी,
जिसे गली के कुत्ते में भी देखा है।

अपनों ने ही लूटा है, परायों में क्या दम ?
चीटियों को भी हमेशा, साथ चलते ही देखा है।
सुना था दोस्त हो तो, आईना नहीं चाहिए
पर काँच के टुकड़ों में ही, अपनों को देखा है।

छात्र
आचार्य प्रशिक्षण केंद्र
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THE TRAUMA OF QUEER COMMUNITIES: A STUDY OF GEO-POLITICAL REALITY OF THE NORTH-EAST

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Abstract

The incredible heterogeneity of the Northeast is often ignored by the rest of the country while producing and reproducing preposterous stereotypes about the region. The 'mainland' fails to recognize the diversity within and among the peoples of the North-East which has invariably resulted in the formation of a periphery/mainstream binary, where the North-East forms merely the periphery of Indian culture. A major hindrance in the way of empowerment is the lack of mainstream representation. Mainstream media, through a tactful endorsement of hegemonic ideals, caters exclusively to a heteronormative and racially superior section of the society, thereby pushing the queer Northeastern individual further to the margins of culture. Discrimination and trauma that awaits an average Northeastern queer individual in the metropolitan cities of the country are discussed in this paper. Ethnic and social minorities are often overlooked in the framing of certain influential theories in Trauma studies like that of Cathy Carruth and Kirby Farrell. This study discusses the facets of trauma imposed on Northeastern queer communities through generations of systemic oppression. It is debatable whether Trauma of the Northeastern queer is one single shared experience or if it is an anthology of diverse, personalized traumas. North-East is one of the most heterogeneous regions of the country. Subsequently, the queer experience within the North-East is also not homogeneous. While some tribes and communities within the North-East still nurture vehement homophobia, others have become more tolerant and inclusive. The recent trend, however, is towards progress. Various support groups have taken birth to help encapsulate the internalized trauma of queer communities within the Geo-political reality of the North-East. An analysis of the gay liberation movements in the region is also attempted in the present study.

Keywords: North-East, Queer, Trauma, Mainstream Representation, Support Groups.

Introduction

In addition to systemic ostracism, the North-East of India has also endured variegated persecution including a dearth of mainstream representations. Indians from the Northeastern states of the country have been, since time immemorial, invisible and brutally banished to the margins of culture- their voices fettered and their silences celebrated. Negative and offensive stereotypes about the North Eastern population have given birth to a periphery/ mainstream binary, which is not only preposterous but misleading as well. It robs the people of their very history and even dignity. An average Northeastern individual living in mainland India is a victim of much more than racial othering and cultural subordination. Their body is exploited and excessively sexualised. The unsolicited tag of exoticism and intense eroticism is a perennial curse on the Northeastern body. Even harsher is the plight of queer people hailing from the same geopolitical space.

A hetero normative society has already assumed the position of the mainstream and has exiled the queer to its periphery. Like the North-East of India, the queer communities of the country are also victimized and are exposed to vicious prejudice. This paper discusses how the homosexual and transgender communities from the Northeastern states are doubly

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Contents

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WORK INTERFERENCE WITH PERSONAL LIFE AMONG EMPLOYEES IN NEWSPAPER INDUSTRY

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Abstract

Both job and personal life are crucial to an employee and he or she must perform the
Most research studies have emphasised the relevance of examining work interference with
life and personal life interference with work in order to find the balance that employees
between their work and non work domains. According to researchers, the direction of interference,
whether work interferes with personal life or personal life interferes with work, is better
domain from where the stronger demand emanates. Apart from the direction of interference,
employed from the direction of work to personal domain, mostly depends upon the nature of
employees in the newspaper sector because the rewards in this industry greatly depend on the
creativity and highly skilled labour. They have a particular work culture which is unpredictable
of organisations, and this study determines whether a marital status based analysis of work interference
with personal life differs among employees in the newspaper sector.

Key words: work interference with personal life, marital status, IT industry, newspaper
industry

Introduction

With the advancement of technology, work is no longer limited to the traditional workplace and
we live in a society where technology is widely used and important to accomplish tasks and
devices are widely available, the workplace and home have become
at all times and places, which might have a negative impact on the personal lives. Work life balance
is both a process and a changing phenomenon. Employees nowadays find it difficult to balance
personal and professional duties since the demands of these positions are contradicted
ways. What happens at work, for some employees, remains at work. Other boundaries
defined, which causes difficulty in combining work and non work life. Technology has
The evolving social, political, and cultural nature of society has influenced and changed
the nature of work and its relationship to life outside of work. Prior studies investigated work
conflict as an inter-role conflict that happens when job responsibilities make it difficult to attend to
non-work commitments (Minnotte et al., 2010). Working extra to reach a deadline may limit the
time a parent spends with his or her spouse or children. According to research, work life
relationships, both work life conflict and life work conflict are negatively connected with life
satisfaction (Hill, 2005; Voydanoff, 2005). Conflict can arise in both directions, i.e., work demands
might clash with non-work demands and vice versa. Work life conflict has been linked to lower
marital satisfaction. According to conflict theory, work and non work spheres are incompatible because
distinct norms and obligations.

Background of the study

When compared to other professions, employees in the newspaper sector have a different work culture
and face different time slots and shift duties. They have to work outside of office hours and report to
duty at odd hours, which can make it difficult to live a normal life, and studies reveal that it depends
highly on their ability to juggle the demands of work and non work activities. Work may interfere with
an employee's capacity to maintain a balanced personal life. Employees' marital status also plays a
vital influence in coping with such situations. Reduced work interference with home life is critical for

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GREEN INVESTMENT INITIATIVES IN INDIA

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ABSTRACT

As part of achieving global sustainable development goals, India is actively contributing efforts towards green finance. The introduction of green investment avenues put forth new horizon in the sustainable development agenda. As per the estimation of International Finance Corporation, India needs an annual investment of 300 billion dollars in climate smart investment. The Covid 19 pandemic scenario nudged more opportunities to the sustainable development funds. Green bonds and Environmental Social and Governance Bonds are the main green investment avenues in India. SEBI sets regulation for the issuance of green bonds. The regulator also issued new sustainability reporting requirements as per the Business Responsibility and Sustainability Report (BRSR) to bring in greater transparency through disclosure of ESG related information and by enabling market participants to access and assess sustainability-related risks and opportunities. This paper intends to focus on the green investment initiatives and trends in India and also the regulation related to the same.

Key words. - Sustainable Development, Green bonds, Sustainability Reporting, BRSR

INTRODUCTION

As per the sustainability development report 2021, India's rank is 120, which revealed the need for more concentrated effort towards inclusive and sustainable development. This circumstance point out the wider the scope of green investment avenues and put forth new perspective in our development agenda. In Green investment, the investment activities should be aligned with environment friendly business activities and the conservation of natural resources. The green infrastructure projects offer promising investment opportunities.

Indian capital market witnessed a sharp change in the investment behaviour of people. There is a sharp increase in the number of retail investors and also increase in the demand or sustainable finance. SEBI is one of the pioneer regulator introduced guidelines for the issue of Green Bonds and Environment Social and Governance (ESG) Funds. In 2012 itself, as part of disclosure SEBI adopted Business Responsibility Reporting (BRR) norms for listed companies as per the ESG principle. Later in 2021, the introduction of new sustainability related reporting requirements called Business Responsibility and Sustainability Report (BRSR) ensures more transparency in the green investment initiatives in India.

GREEN BONDS

Green bonds are debt instruments, the proceeds of the same are use to fund projects which generate environmental benefits. International Capital Market Association comes up with the voluntary guidelines for the issue of green bonds known as Green Bond Principles. The core components are as follows

- Use of proceeds
- The process adopted for the project evaluation and selection
- Transparency n the management of proceeds
- Reporting of information relating to the use of proceeds.

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CONTENTS

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EAK FORM EFFICIENCY OF GODREJ CONSUMER PRODUCTS LIMITED - A STUDY ON *EFFICIENT MARKET HYPOTHESIS*

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Abstract

According to efficient market theory, the market can be broken down into three [illegible] is [illegible] efficiency, semi-strong efficiency, and strong efficiency. This division reflects [illegible] idea [illegible] the 'market' is constantly changing due to the flow of information. Despite being a cornerstone [illegible] modern financial theory, the EMH is very contentious and is constantly challenged. It is useless, [illegible] to believers, to look for inexpensive companies or try to predict market movement, using [illegible] technical analysis. The objective of this work is to evaluate the Random Walk Theory [illegible] variant of effective market theory on Godrej Consumer Products Limited under weekly basis [illegible] 2-2020 to 14-11-2022. This study aims to test Random Walk Theory, a common weak [illegible] efficient market theory. Serial Correlation Test was undertaken to examine the weak [illegible] of efficient market theory. It is concluding that Godrej Consumer Products Ltd based on the [illegible] difference on NSE does not follow a random walk and market is not efficient in weak form

[illegible] words Efficient Market Theory, Random Walk Theory, Serial Correlation, Modern Financial Theory

Introduction

[illegible] Efficient Market Hypothesis holds that it is challenging to "beat the market" because stock [illegible] performance enables all pertinent information to be both assimilated and represented in [illegible] share prices. The EMH contends that stocks on stock exchanges continue to trade at their fair [illegible] making it challenging for investors to purchase discounted securities or to sell securities for [illegible] and inflated prices. As a result, it should be challenging to outperform the overall market [illegible] the selection of expert stocks or market timing, and the only way an investor can possibly [illegible] higher returns is through purchasing riskier investments. This theory, which implies the [illegible] idea that the "market" is always changing based on information, divides the market into [illegible] explanations for comparison.

[illegible] Efficiency is the first. The company is so unbreakable that nothing can really surpass [illegible] technological developments in the knowledge sharing process, no one can always [illegible] guarantees a profit margin. The following category demonstrates what we refer to as [illegible] This emphasises the claim that despite the [illegible] fundamental Semi-Strong Efficiency [illegible] market, the rand[illegible] [illegible] Share Prices [illegible] public, preventing [illegible] is known as Strong efficiency [illegible] of the market [illegible]

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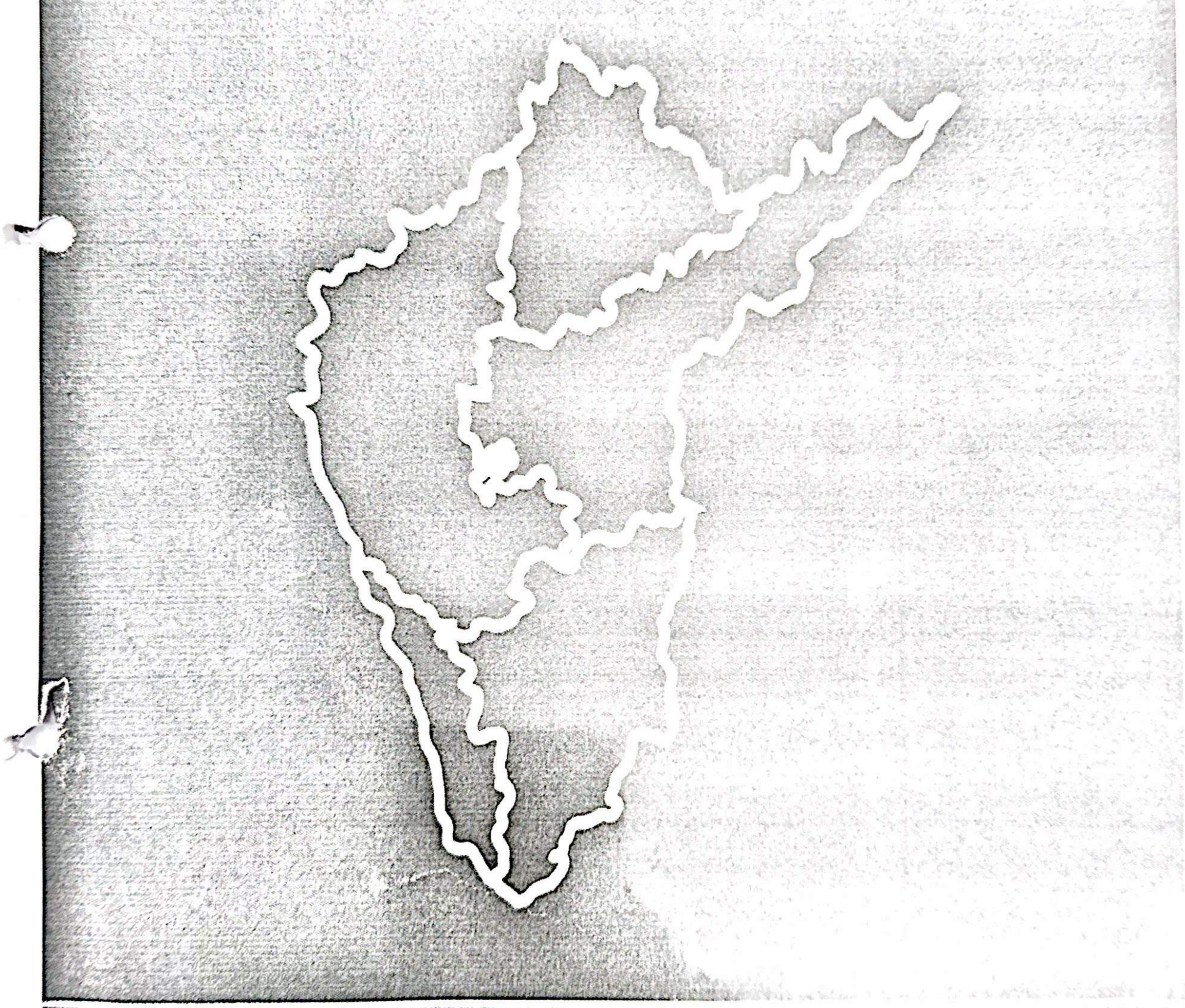

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CONTENTS

SOUTH INDIA JOURNAL OF SOCIAL SCIENCES
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SEMI STRONG FORM EFFICIENCY OF ITC LIMITED – RESIDUAL ANALYSIS

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Abstract

Semi-strong form efficiency describes a market where share prices accurately and equitably reflect all information that is now available to the public as well as all information in the past. If news and price changes are unpredictable, then a diversified portfolio held by a rookie investor and an expert investor would produce similar returns independent of their level of experience. The closing day security prices of ITC Limited under weekly basis from 16-11-2020 to 18-11-2022 were taken. *Data source* was from the Stock market quotations and the *Techniques of analysis* Residual Analysis. The study concluding that with regard to the ITC Limited's stock returns the semi-strong form of efficiency is partially supported. .

Key words: Semi-strong form efficiency, Diversified portfolio, Residual Analysis, Stock return.

Introduction

The Efficient Market Hypothesis (EMH) has a component known as semi-strong form efficiency, which holds that stock prices will react quickly to the disclosure of any new public information. Semi-strong form efficiency describes a market where share prices accurately and equitably reflect all information that is now available to the public as well as all information in the past. Semi-strong form efficiency argues that market information is reflected in price adjustments to new equilibrium levels and that security prices have taken this information into account. Although it is thought to be the most useful EMH hypothesis, it is unable to explain the context for significant non-public information (MNPI). It indicates that neither technical nor fundamental analysis can be used to obtain higher gains, and it suggests that only MNPI would be advantageous to investors looking to make abnormal rate of return.

Theoretical framework of the study

EMH claims that asset prices accurately reflect all available information at any one time and in a liquid market. US economist Eugene Fama's PhD dissertation from the 1960s served as the foundation for this hypothesis. The EMH assesses the impact of MNPI on market pricing and comes in three varieties: weak, semi-strong, and strong. According to EMH, attempts to outperform the market are susceptible to chance rather than talent because markets are efficient and current prices reflect all available information. This reasoning is based on the Random Walk Theory, according to which all price movements represent a chance deviation from earlier prices. Share prices quickly reflect all available information; therefore tomorrow's prices will only represent tomorrow's news because they are independent of today's prices.

If news and price changes are unpredictable, then a diversified portfolio held by a rookie investor and an expert investor would produce similar returns independent of their level of experience. The strong version of EMH also implies that all publicly available and private information is reflected in the stock prices at the moment. It asserts that market and non-market information are both taken into account when determining the price of a security and that no one has monopolistic access to pertinent information. It draws the conclusion that excess returns cannot be regularly attained under the premise of a perfect market.

Testing the Semi Strong form of Efficiency

The Single-Index Model can be expressed by the following equation: $R_i = \alpha_i + \beta_i R_m + \varepsilon$, where R_i = Total return of a stock or portfolio i ; β_i = Investment beta; R_m = Market portfolio return ; α_i = Time regression investment's alpha ; ε_i = Time regression residuals

The analysis is known as Residual analysis. The excess return earned on the security is represented by the positive difference between the actual return and the predicted return. If the

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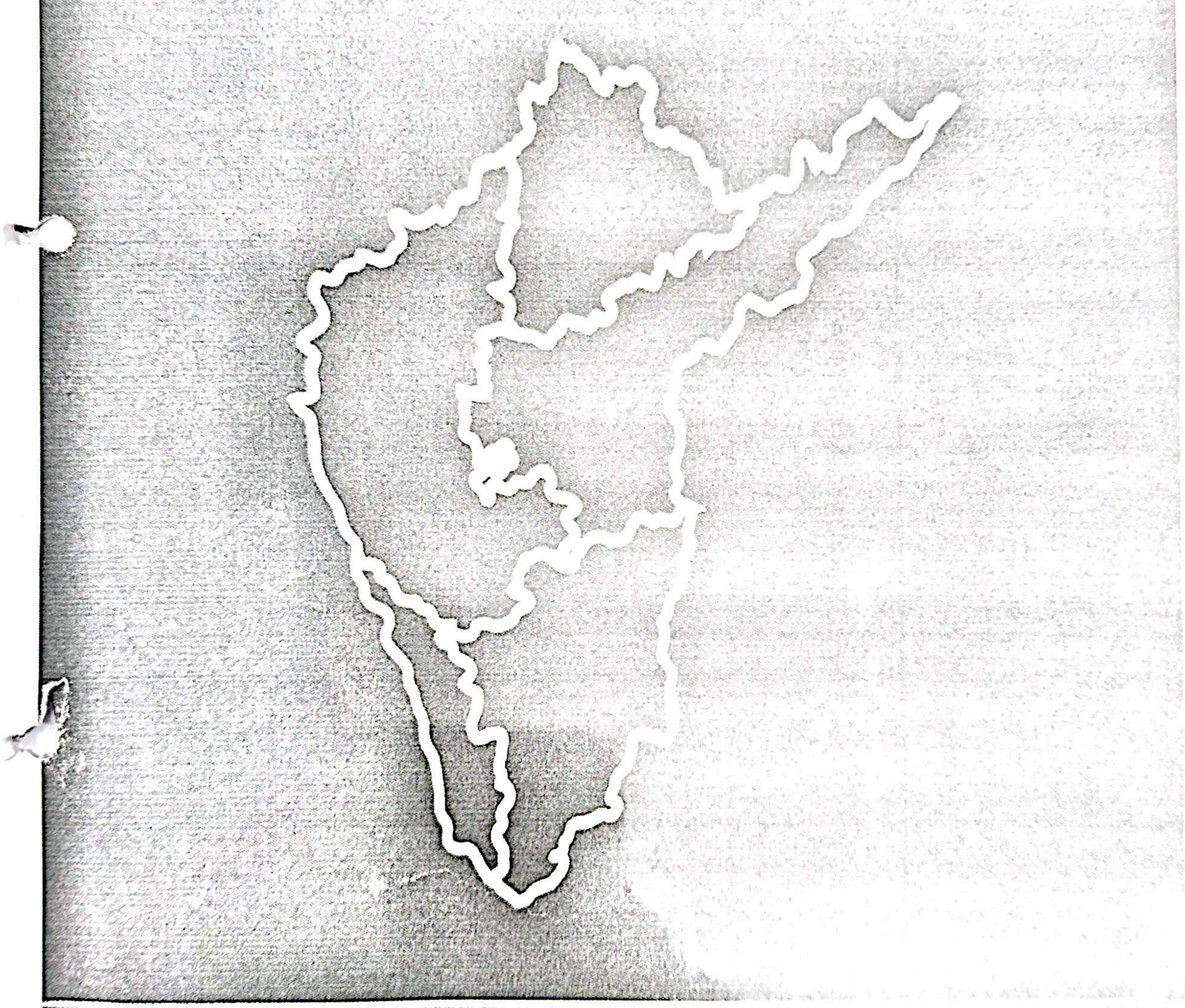

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CONTENTS

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SIGNALING THE SHARE PRICE MOVEMENT-PREDICTION USING MACD OSCILLATOR

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Abstract

MACD is one of the most widely utilised in technical analysis. MACD can assist in determin whether an asset is overbought or oversold. The present study is an analytical in nature based on t secondary data collected from 14-12-2020 to 14-11-2022 on weekly basis closing day security pric of Godrej Consumer Products Limited, ITC Limited and Vedanta Limited were used in the pres study. Currently as per the MACD graph for Godrej Consumer Products Limited, a selli opportunity, but a chance for bullish trend is possible. The MACD graph of ITC Limited is alm similar to the MACD graph for Godrej Consumer Products Limited, except the current period, whe a bullish trend is visible. Investors can purchase the security of ITC Limited. MACD graph Vedanta Limited graph seemed to be a buying opportunity, but it cannot be fixed at this lev Therefore, the investors are asked to be very cautious on their investment and the chance of risk high.

Keywords: Moving Average Convergence Divergence (MACD), Oscillator, Exponential Movi Average.

Introduction

The momentum indicator known as moving average convergence divergence, or MACD, is one of t most widely utilised in technical analysis. Gerald Appel created this at the end of the 1970s. B computing the difference between two time periods, which are a collection of historical time serie this indicator is utilised to comprehend the momentum and its directional strength. 'Moving averag of two different time intervals are utilised in MACD (often on historical closing prices of securities), and a momentum oscillator line is generated by subtracting the two moving averages, al known as 'divergence,' from one another. One moving average should be shorter in time than t other, according to a straightforward formula for taking two moving averages. Generally, Exponen Moving Averages (EMA) is considered for this purpose.

Importance of MACD

When the MACD line crosses over the signal line (to purchase) or drops below it, technical sign are generated (to sell). By alerting traders to the strength of a directional advance and signalling t possibility of a price reversal, MACD can assist in determining whether an asset is overbought oversold. Simple trading regulations apply. When the oscillator crosses over the oscillator's slow exponential moving average, investors can buy. Investors can sell, however, if the oscillator cross from above to below the oscillator's exponential moving average. Finally, the MACD has t potential to diverge. The ideal signal would exhibit divergence, clearly deviate from a dominant tre line, and show the MACD lines crossing.

The MACD and signal line move above and below the zero axis or centreline to signal a trend such overbought and oversold conditions. When the EMA points are close to each other, that is call convergence, and when they are apart, it is called divergence. The shorter the moving average, t more the reaction of the MACD line. There are three ways to interpret the MACD.

(6)

HEALTH CARE DISPARITIES AMONG TRANSGENDERS: NEED FOR RECONCEPTUALISING MEDICAL FACILITIES

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ABSTRACT

In the pscho-medical literature, gender diverse groups have been pathologized through classification of mental illness by the American Psychiatric Association's Diagnostic and Statistical Manual of Mental Disorders and International Classification of Disease until WHO-approved ICD-11which removed trans-relateddiagnostic codes were removed from the category of 'Mental and Behavioral Disorders' and gender incongruence was added as a sexual health condition. However, problems still exist as in many countries they are required to accept mental diagnoses to access gender-affirming health care. These groups are still subjected to transphobic institutional as well as social prejudice and violence thathinder them from accessing necessary health care. This study attempts to outline thediscrimination faced by transgender people in healthcare settings, analyses the gaps in the existing medical curriculum in protecting their health, and the need for specific educational interventions to enhance the knowledge, awareness, and skills related to gender-affirming health care among medical professionals.

INRODUCTION

The word transgender is often used to describe individuals who transcend socially defined gender boundaries. These individuals experience continuous discomfort and a feeling of inpropriety about the given sex. Owing to their apparent gender non-conformity, these individuals are stigmatized and discriminated against, marginalized, and excluded in almost all communities which hinders their access to necessities like appropriate quality health care, social assistance, education,and work. Globally, transgender and gender-variant persons face considerable health inequalities and access barriers to proper health treatments. In India, despite the passing of "The Transgender Persons (Protection of Rights) Act, 2019" Act, they are predominantly striving for their right to health where trans people have consistently identified this right as one among their key priorities. When compared to the general population, transgender people have higher rates of posttraumatic stressdisorder, anxiety, depression, and substance misuse. Numerous studiesreported high rates of suicidal ideation and attempts among these people. Each of these variables puts transgender people at risk and raises their likelihood of experiencing adverse health consequences.

Everyone has the right to the best possible quality of health, which involves access to appropriate and accessible health care facilities for all persons without regard to their gender identity and sexual orientation. International, regional, and national human rights standards and the expanding body of health standards that respect and safeguard human rights offer unambiguous benchmarks for the respect, protection, and fulfillment of the health and human rights of transgenders and other gender-variant groups. It includes freedom from non-consensual medical treatment, experimentation, and torture, as well as the right to self-determination.

Population studies estimates transgender persons as between 0.5 percent to 1.3percent of adults are transgender and that there are around a 25million transgender people globally.Numerous studies have revealed that transgender people are medically underserved and face stigma, financial difficulties, and discrimination, resulting in a variety of poor health outcomes and high disease burden rates. Compared to the general population, these people were more likely to have lower incomes, chronic mental and physical health issues, and greater health care use.

A safe and protective environment in healthcare settings is crucial for transgenders and other gender-variant groups. Being unable to live as per their self-identified gender greatly affects their overall health and wellbeing and alsoexacerbates other forms of ill health. Transgender people often face multiple health threats and are always put in a vulnerable position because of the discrimination faced by them in obtaining the proper health care they need. Financial barriers, appropriate medical care, lack of experts in transgender medicine, health system, and barriers like inappropriate health

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JUDICIAL TRENDS ON TRANSGENDER RIGHTS IN INDIA

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ABSTRACT

Gender is a tool of control that is exposed as socially constructed even though it initially appears biologically imperative. Prior to the NALSA decision, a gender diverse person seeking justice has to prove before the court that their identity has to be protected even though their identities conflict with the prevailing normative norms of gender. According to Indian law, the sex-gender duality seems to have a significant role and the judiciary finds to defy those who differ from their binary biological sex while confronting the issues of transgender litigants. Hence the development of transgender rights has not been linear and is often filled with contradictions.This article discusses the progress made by the Indian court in advancing the rights of transgender people by scrutinizing the case laws that came before and after the landmark NALSA judgment in protecting transgender rights and their identities which shaped the normative conceptions of gender.

INTRODUCTION

As early as pre-colonialization, the law has had a significant impact on those who identify as gender diverse. The Criminal Tribes Act, 1871 of British criminalized Hijras by referring to them as habitual sodomites and 'unnatural'. As part of postcolonial development, the Habitual Offenders Act, Immoral Traffic (Prevention) Act, the prohibition of begging in many states- all corroborates that there was no discernible transition in such groups legal or social standing. 'Controlling the unwanted actions of eunuchs' and keeping a registry of 'all eunuchs' living in the region were incorporated in the Act after the Karnataka government substituted the word 'eunuchs' with 'persons' in the Police Act in 2011. The visible shift of the Indian judiciary towards the transgender community is evident in the NALSA judgment where the Supreme Court has taken a proactive step in protecting their rights.

JUDICIAL DECISIONS PRIOR NALSA JUDGEMENT

In *Queen Empress v. Khairati*[1], a case was registered under Section 377 IPC and the police arrested a crossdresser who was found singing with a group of people. The accused was later acquitted as he was identified to be a "habitual sodomite" on medical tests.

In *Illyas and Others v. Badshah alias Kamla*[2], the Madhya Pradesh High Court had already made a ruling before the decision of Supreme Court in NALSA, recognizing Hijras and their customs. Hijras guru chela inheritance system was affirmed by the court in its ruling based on the reasoning that Hijras are community identities with historical, legal recognizable tradition and hence their customs and beliefs should be respected.

Later on, in "*Kamala Alias Kamala Jaan Alias Hijrah v. Sadiq Ali & others*"[3], the Court ruled that a Hijra who presented herself as female couldn't contest inthe election as mayor for the position allocated for females, using the stringent biological definition of the word "women"; thus held the election of hijra candidate as void. The court ruled that hijras do not have the physical ability to give birth. They couldn't take the mayoral election since they weren't women.

THE RUPEE-DOLLAR RATIO FLUCTUATIONS: CHALLENGES AND IMPACT ON THE ECONOMY

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ABSTRACT

Indian witnessed its record lowest ever currency fall in a matter of few days. The Rupee loss meant that it's a gain for the US Dollar. There have been numerous reasons which paved way to the diminishing value of Indian rupee. Within a timeframe of just 75 years a sharp rise to 79INR/1USD could be witnessed in the year 2022. The value of Rupees has diminished by about seventeen times during this time frame. There has been numerous reasons for the fall inthe vale of Rupee such as the Russia-Ukraine war, inflation rate, crude oil price change etc. the fall in Rupee value has put the Indian economy in great stress and challenge creating an impact on the economy. This paper attempts to make a Rupee-Dollar comparison since 2016 to 2022 using data collected from reliable sources and using SPSS software to evaluate the results obtained.

Keywords: Depreciation, Rupee value, Rupee-Dollar ratio, currency fluctuation.

INTRODUCTION

Indian witnessed its record lowest ever currency fall in a matter of few days. The Rupee loss meant that it's a gain for the US Dollar, as Dollar rates continue to become stronger against theIndian rupee, it is believed that the Dollar-Rupee ratio will soon become 80INR/1USD withina very short span of time and the rising Dollar is surely not favourable for the Indian rupee. When India gained Independence in the year 1947, 1USD was worth 1.46INR only. However,within a time frame of just 75 years a sharp rise to 79INR/1USD could be witnessed in the year2022. The value of Rupees has diminished by about seventeen times during this time frame.

There have been numerous reasons which paved way to the diminishing value of Indian rupee:In the year 1957, it was decided to divide 1Rupee by 100 paise which contributed to the depreciation of Rupee value. The 1960s also witnessed major crisis during the Indo-Pak and Indo-China war which shook the economy to a great extent. Following this was India's majorfinancial crisis of 1966, 1991 and 2008 which further contributed to the devaluation of Rupees. The Government of India also initiated Demonetization of 500 and 1000 rupees notes and released new 500 and 2000 rupees notes in the year 2016 which led to a significantly long-termimpact on the Rupee value. The Foreign Direct Investment also affected the value of India

OUTH INDIA JOURNAL OF SOCIAL SCIENCES
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REDRESSING THE RISK OF COMPETITION: MODERATING EFFECT OF DIGITAL MARKETING AND SERVICE QUALITY

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bstract

very firm must act effectively to address the risk of competition in order to exist in the market. gital marketing can be exploited to extend the reach of marketing efforts. But it cannot be nsidered as a unique solution to overcome the intensity of competition. In our current age of formation overload and the digital world, the benefits of digital marketing can be exploited to tend the reach of marketing efforts. But it can also be copied by competitors so this cannot be nsidered a unique solution.Businesses need to engage customers in a long-term relationship with em, this is possible only through the quality of service provided. This study aims to examine and plain the moderating effect of digital marketing and service quality in mitigating the risk of ensity of competition. *However, because service quality is a core component, it is difficult for mpetitors to adapt. To mitigate the risk of competition, the interaction effect of digital marketing d service quality serves the purpose.*

Key words: Digital Marketing, Service Quality, Risk of intensity of Competition, Moderating effect, Adaptability

roduction

markets expand in scope and become more globalised, several critical risks emerge. According Poter's five forces study, the biggest concerns are competitive rivalries that are getting reasingly sensitive, as well as threats from existing and new entrants. Many large firms face alry from both small and large firms since large firms are in the purview of the business and can ntify the risk, whereas new entrants cannot be predicted or are undervalued by large firms. en it comes to controlling competitive risk, many organisations find that a strong defensive roach is essential. Countering new market entrants and responding to competitors should be top orities for anyone running a business.

combat the risk of competition, many organisations use a variety of tactics such as product dification, technological improvement, cost-cutting measures, and so on. When a company mpts to reduce the level of competition, the gains are only temporary. In the long term, petitors can embrace any change, and they are arriving with sophisticated features. This could due to intense competition and information overload. Because the market is efficient, everyone access to every new piece of information, and by digesting the knowledge correctly, they can kly become superior.

ry firm must act effectively to address the risk of competition in order to exist in the market. It asible with considerable marketing. In our current age of information overload and the digital ld, the benefits of digital marketing can be exploited to extend the reach of marketing efforts. it can also be copied by competitors so this cannot be considered as a unique solution to come the intensity of competition. Through digital marketing the information disseminating ess can be done effectively but there must be some effort from the part of business to engage omers and made a long term relationship with them, it is possible only through the quality of ice provided, otherwise the customers will no longer exists with the firm only because of the al marketing strategy. In this study aims to examine and explain the moderating effect of digital eting and service quality in mitigating the risk of intensity of competition.

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"ASSESSING THE ROLE AND IMPACT OF DIGITAL MARKETING ON TOURISM IN KERALA"

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ABSTRACT

Over the last few years, several innovative marketing strategies have been emerged in India. Among them the most famous and effective strategy which was implemented to increase the awareness about tourism destinations is called as Digital marketing. It is a marketing technique which uses internet for marketing the tourism products and services. It use computer, tablets, smart phones, cell phones and other devices to engage with customers and make awareness about tourism products. When tourists are provided with better services and tourist experience, they become more loyal and satisfied. It is important to make the tourists satisfied for bringing them back to the same spot again and again.

The major challenge faced by tourism industry is the communication of travel packages to local and global audience. Digital marketing in this regards provides advertising methods and tools for proper communication of tourism products and services to potential tourists. Hence, this paper focuses on finding the role and impact of digital marketing with the help of primary data collected from consumers who has experienced digital platforms to plan or book their tours.

Keywords: Digital marketing, Tourism, tourist satisfaction, Tourism products, Tourism destinations.

INTRODUCTION

India is one of the most popular tourist destinations that attracts a large number of tourists in the world. Tourism plays a critical role in country's economic growth and prosperity. The world Travel and Tourism council says that in 2018, tourism in India has generated 16.91 lakh crore (9.2% of GDP) and it has also supported 42.67 million jobs of its total employment. Since tourism is considered as the major source of income by many people in India, it is important to understand the impact of digital marketing on tourism sector. Tourist is said to have loyalty to the destination only when the reality matches or goes above the expectations which is simply called satisfaction. In the present world anyone with internet knowledge and assess can plan trip to any part of the world. Sitting at home and collecting information from different tour sites helps travellers to plan their trip more conveniently. With a laptop, PC, or a smart phone almost everything is possible in the present world. After the introduction of smart phones and internet, it has become easier to book any travel packages, plan any trip to any part of the world. In this way digital marketing has a great influence on the tourism sector.

ONLINE ADVERTISING MARKET:

The online advertising market shows a steady growth in India. The main aim of marketing through online is to cover a large audience and communicate with them more easily. Online marketing has succeeded in settling the queries of potential travellers and provides more information time to time. In this fastest growing economy the term marketing has changed.

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PASSENGER AUTO RICKSHAW DRIVER'S PERCEPTION TOWARDS TRADE UNION: A COMPARATIVE STUDY ON RURAL AND URBAN AREA IN THIRUVANANTHAPURAM.

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ABSTRACT

Among different road transportation the most popular and cheapest transportation widely used by middle class people is three wheeled auto rickshaws. An auto rickshaw driver comes under the unorganized sector labour category. Frequently changing fuel rate, increase in the price of basic needy things, tax rates make the auto drivers life tragic. Traditionally the workers trade unions have targeted the welfare of people but today that are not fulfilled by them. Clearly the environment in which informal sector workers operate is considerably different from the prevailing environment in the modern economic scenario. Our society is not able to provide employment for emerging labour force as a whole thereby naturally people gravitated towards the self-employment. Auto rickshaw drivers' are self-employed, comes under unorganized labour sector which are very common in rural and urban area.

***Key words**: unorganized sector, self-employment, rural, urban*

INTRODUCTION

Transportation system provides a wide variety of choice to travel from one place to another. Different mode of transportation is air, water, road and rail. Among the most popular and widely used one is road transportation. No doubt to state the cheapest mode of transportation is road. There are different vehicles used in road transportation for private and public usage. In India for short distance travelling, easily available convenient vehicle is auto rickshaw. Auto rickshaw are modern version of pulled rickshaw or cycle rickshaw commonly used vehicle in rural and urban area act as a vehicle for hire and for private use in Kerala. In the 1930's Japan developed less expensive three- wheeled vehicles foremost. Bajaj Auto introduced the country's first auto rickshaw. The company get license to make 1000 auto per year initially from government. Government of Kerala undertaking Kerala Automobiles Limited incorporated in 1978 manufactures three wheelers with different engine model includes electric, diesel, petrol, LPG& CNG. It is suitable for both passenger and goods. Auto rickshaw drivers have a welfare board named KMTWWFB (Kerala Motor Transport Workers Welfare Fund Board) began in 1985 to provide the constitution of a fund to promote the welfare of private motor transport workers in the state. The welfare board provide following benefits for workers such as:

1. Marriage benefit Rs.20,000 will provided to the members
2. Scholarship will provide to children.
3. Maternity benefit Rs.3000 for female members
4. Natural death for nominee of deceased member Rs.50000 as natural death benefit.
5. Accident death, the nominee of member will get Rs.100000.
6. After completed 2 years of membership entitled to medical benefit.
7. Members will not having not less than 10 years of completed service shall eligible for pension

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AWARENESS AND PERCEPTION TOWARDS GREEN ACCOUNTING PRACTICES AMONG ACCOUNTING PROFESSIONALS WITH SPECIAL REFERENCE TO THE TOUR OPERATORS

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Abstract
Environment protection is the need of the hour because the earth's environment is worsening every day and the main reason is the activities of human beings. Every industry may face many challenges to maintaining corporate responsibility. Green Accounting is a recent concept and has various possibilities to deal with different issues related to corporate social responsibility and sustainable development. Green accounting practices can be effective only if the people deal with those practices is aware of green accounting and their perception regarding the same is positive. Hence, it is essential to study the level of awareness and perception of green accounting practices among accounting professionals. Tour operators can play a huge role in protecting the environment and reducing pollution by undertaking various green initiatives. Green accounting practices are one of them. This study tried to answer the question of whether accounting professionals are aware of green accounting practices in tour operators and whether their perception regarding the same is positive or negative. The study also identified various factors influencing accounting professionals to adopt green accounting practices in tour operators.

Keywords: Green Accounting, Environment Protection, Accounting Professionals, Tour Operators, Awareness, Perception.

Introduction

Every individual is responsible for minimizing environmental risks and ecological scarcity in our environment. Without a green environment and clean nature, we can't achieve sustainable development goals. Every industry and organization face various challenges to maintain social responsibility and ensure sustainable development due to environmental issues. Many individuals and organizations have implemented various initiatives and ideas for environmental protection. Green Accounting is one of them. Green accounting is a recent concept and the emergence of Green Accounting has a vital role in environmental protection. Green Accounting incorporates environmental sources and assets into the company's accounts. It is a type of accounting that attempts to factor environmental costs into the financial results of operations. Green Accounting helps in the computation of income by taking into account the economic damage and depletion of natural resources in an organization. The tourism industry has a huge impact on the environment because it is one of the major polluting industries on earth. So, it is essential to reduce the negative impact of this industry on the environment. Tour operators play an important role in the tourism industry by providing services to their customers. A tour operator is an organization, institution, or company that buys individual travel components separately from their suppliers and combines them into a package tour, which is sold to the public directly or through an intermediary. The present study focuses on understanding the level of awareness and perception of accounting professionals about green accounting practices in tour operators.

Statement of the problem

It is the responsibility of every individual to save nature and protect the environment at any cost. Green Accounting is one of the recent concepts for environmental protection and it deals with different issues related to corporate social responsibility and sustainable development. Tour operators play an essential role in the tourism industry. They deal with the planning, development, promotion, administration, and implementation of tourism products and services. Green Accounting

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GREEN INNOVATION IN TOURISM FOR ECONOMIC SUSTAINABILITY

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Abstract
The thinking that comes to our mind when we hear the word 'tourism' is roaming new places, interacting with new cultures and values, getting some great pictures, and creating the best memories for oneself. But along with these the tourism industry also has its own contributions to the field of global warming. In the present day, tourism alone contributes about 8% of the global greenhouse gas emissions. So to reduce the effects of the greenhouse effect scientists from all over the world have made green tourism a major factor. For understanding of green tourism, it is defined as the travel to natural areas like that of forests, which helps in the conservation of the environment and also helps in sustaining the well-being of the local people, and which also involves some education related to the environment.

Keywords: Green innovation, green tourism, economic sustainability

Introduction

With the rise of technology and innovation, a wide range of changes has been introduced in many sectors and it has developed and transformed many industries along with it. To reduce the effect of greenhouse originating from tourism the use of different technologies and smart tourism is not enough. The need of making the tourism industry more sustainable in accordance with green innovation has become an adequate factor. From an economic standpoint, it has been observed that eco tourism helps in generating higher economic benefits for the local people that of creating more employment chances, better and innovative infrastructure, and increasing the sales for the local stores.

Problem statement

The major difference that lies between ecotourism and other types of tourism is that ecotourism helps by creating a minimal impact on the life of the local people and also on the environment, while the other hand tourism does not have any concern regarding the environment or the life of the local inhabitants (Asadi et al. 2020). It is extensively observed that tourism has a wide range of challenges for the environment that is creating a lot of waste, using the land of the locals improperly, increase in pollution, and generating more pressure on the endangered species by destroying their natural habitats for the sake of constructing more attracting sites of tourism (Razzaq et al. 2021). Meanwhile, green tourism is creating a clear path for tourism in a better innovative way. With the help of green tourism, not only the generation of waste is getting reduced but also the natural home of the animals and other creatures are safe and the emission of greenhouse effects is also being lowered (Gurlek et al. 2018).

Aims and objectives of the study

The aim of the study focuses on the impact of green tourism on economic sustainability.
The study has the following objectives:
To find out the components involved with green tourism
To identify the factors involved with economic sustainability in terms of green tourism
To analyze the impact o green tourism on economic sustainability
To find out the challenges and recommend solutions while implementing green tourism

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A STUDY ON GREEN CONSUMERISM AND ETHICS IN GREEN MARKETING

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ABSTRACT
Any business's success depends on effective marketing, and this is especially true in the present era with its fierce competition. Given the limited resources and insatiable human want, green marketing has become inevitable. Therefore, it is important to use resources wisely for both the present and future generations. The role of green marketing is paramount in this regard. To please customers who choose items of good quality, performance, and convenience at cheap costs, while at the same time having no negative effects on the environment, green marketing is the process of designing products and services and advertising them. It covers a wide range of operations such product modification, altering the manufacturing process, altered promotion, and altered packaging that are intended to lessen the harmful effects. This paper is exclusively based on the secondary data. An attempt is made to shed the light on the new concepts namely green marketing and green consumerism. In order to maintain the environment for present and future generations, green consumerism places responsibility for developing things that are environmentally beneficial on manufacturers. It also covers the factors that affect and the moral dilemmas raised by green marketing.

Keywords
Green marketing, Consumer Practices, green consumerism, and ethics in marketing

Introduction
Green marketing is commonly termed as the process of evolving services and products and encouraging them to convince the consumers whose preference aims at the good quality of any product, the actual performance of the products, and how the product is more affordable than the other available products. Green marketing is also defined as the method of creating and maintaining products in such a way that it does not leave any harmful after-effects on the ecosystem. This kind of project contains a wide range of tasks like moderation of products, replacing how the product is processed, moderating the way of advertising, and evaluating the packaging style so that the dangerous effects of the products are reduced and also that it does not leave behind any of the harmful effects in the environments. Throughout the globe, all the corporations and industries are taking preventive steps to reduce the effect of the services and the products on the ecological and other atmospherically boundaries. As the needs and demands of humans are increasing by passing days the utilization of green marketing has become

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WORK STRESS MANAGEMENT AND ROLE OF HRM IN ORGANIZATIONS

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Introduction

Stress means body's reaction to a challenge or demand. It's a response to pressure. Medical researcher Hans Selye first used the term "stress" to describe the body's biological response mechanisms. He defined stress as "the nonspecific response of the body to any demand". It must be understood that in order for the stress to occur, the response should be non specific. According to Lazarus and Folkman (1984) "psychological stress is a particular relationship between the person and the environment that is appraised by the person as taxing or exceeding his or her resources and endangering his or her well being". To some extent pressure can be beneficial, it can motivate the employees to perform their work efficiently and it will help them to stay focused and productive. But too much pressure create stress which is harmful and can lead to major illness.

The stress created by desirable and successful effects is called "eustress" and the stress created by undesirable outcomes is known as "distress". It is primarily the distress form of stress which requires examination and steps to cope with it. Eustress is a positive, healthy and developmental stress response. Just as high level of stress is damaging to the physical and psychological well-being of the person, extremely low levels of stress are equally undesirable they cause boredom, and result in lack of stimulation, innovation and challenges. Thus moderate level of stress is necessary for higher level of performance.

Workplace environment place an important role to increase the level of stress. Happy and healthy environment keeps employees refresh and energetic to do their work with more efficiency. Singh Vikram and Chaudhary Suresh (2017) revealed in their study that there is relation between employee's workplace and behavior, productivity and performance. They discussed the term QWL (Quality of Work Life), if the employee get a good quality of work life he can enjoy his personal life as well which ultimately reduce stress.

Literature review

Daniels K, Gedikli C, Watson D (2017) interpret in their paper that if the initiatives of shared social activities is combined it may be enhanced employees welfare. In the comparative study of workplace of agriculture and IT sector by Prasad K.D.V, Vaidya Rajesh and Kumar V Anil (2016) revealed that there is moderate stress at both situations and one can get grips with this stress by developing some effective strategies by keeping in mind different factors of stress at work place. Karthik R. (2016) revealed in his study the stress level of employees in the personal and work condition. He says that stress can affect a person in two ways good or bad. The study explained that if there is moderate stress it can be helpful to do work more efficiently. He also discussed the measures and role of organization to reduce stress.

Yogeshwaram P. (2016) examined in his study that stress affect the employee in both ways physically and psychologically. It affects the work life and personal life as well. Work life balance needs the efforts made by all company, government, employee's family and employee himself. With the equal contribution of employer and employee one can overcome this issue.

Significance of the study

Nowadays workplace had become a high stress environment in many organizations. There are many factors that commonly cause work related stress such as long working hours, heavy workload, tight deadlines, over supervision, job insecurity, harassment, discrimination, poor relationship with colleagues, lack of job satisfaction etc. Stress at the workplace will lead to depression, anxiety, loss of interest in work, fatigue, high blood pressure, insomnia, increased use of alcohol and drugs, poor

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EMPLOYEES' PERCEPTION TOWARDS GREEN BANKING: A STUDY ON COMMERCIAL BANKS IN KERALA

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ABSTRACT
Environment protection is one of the significant duties of every citizen in the world to conserve natural resources and the existing natural environment to repair the damage to the environment. Nowadays, Banking industries have implemented various green initiatives to protect the environment and conserve the world's natural resources. Employees are the key people who contribute to the success of every business. Employees play a crucial role in conducting green banking activities in the banking sector. Hence, it is essential to study the employee's perception towards green initiatives in the banking sector. Commercial banks in Kerala have initiated several green banking activities for protecting the environment. For this study, the samples are selected from employees of Commercial banks in Kerala. This paper tried to answer the question of whether the employees are aware of the banking sector's green initiatives and their perceptions regarding the same. It also focused on the various challenges faced by employees while implementing green initiatives in the banking sector.
Keywords: Green initiatives, Banking sector, Perception, Employees, Commercial Banks.

INTRODUCTION
Protecting our environment is everyone's duty to conserve natural resources and the existing natural environment. Every citizen of India has a fundamental duty to protect and improve the natural environment including forests, lakes, rivers, and wildlife and should have compassion for living creatures. The financial and economic position of India is far superior to most other countries in the world. The banking sector is one of the important financial sectors in the Indian economy. The banks have implemented a lot of green initiatives for protecting the environment and conserving natural resources.

Green banking was introduced in the year 2009 in the State of Florida. In India, SBI (state bank of India) being the largest commercial bank took a lead towards setting higher standards of sustainability and undertook the foremost step the towards "green banking" initiative. Kerala's commercial banks have implemented numerous green initiatives to safeguard the environment. Employees are one of the most valuable assets of an organization and key to every business. This study titled "EMPLOYEES' PERCEPTION TOWARDS GREEN BANKING: A STUDY ON COMMERCIAL BANKS IN KERALA" tries to answer the questions of whether the employees are aware of green initiatives in commercial banks and what is their perception regarding various aspects of green banking. The various challenges faced by employees while implementing green initiatives are also addressed.

STATEMENT OF THE PROBLEM
Every industry has the responsibility to protect the environment and conserve the natural resources of the earth. The banking industry is one of the most essential parts of the economic system. As responsible financial organizations in our country, banks have to conduct financial transactions without adversely affecting the environment directly or indirectly. Hence, banks have implemented several green banking initiatives for environmental protection. Employees are the key personnel who

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Validating the Essence of Bhagavad Gita in Modern Times through TA

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Abstract

In this paper, the transaction between Arjuna and Lord Krishna in the age-old wisdom called Bhagavad Gita is being analysed along the lines of the Transactional Analysis theory of Eric Berne. There are two aims for the paper. 1. To analyse the transaction between Krishna and Arjuna in tune with the TA theory by Eric Berne. 2. To find out about the Universality of Human Behaviour by such correspondence and hence suggest the application of the wisdom of Gita in Counselling. The ego state of Arjuna before the discourse and later is analysed. The Processes used by Lord Krishna to make the ego state change in Arjuna are looked also into. The life script of Arjuna, the role of different Yoga systems etc are analysed. Three modes of material nature are compared and contrasted with the three ego states. Adult Autonomy as achieved by Arjuna and the state of Satwa is compared. Finally, the Universality of the Bhagavad Gita and the use of the Counselling tips got from the Bhagavad Gita are discussed.

Key terms:

Bhagavad Gita, Transactional Analysis, Ego state, Life script, Autonomy, Three Modes Of Material Nature

Paper

'Transactional Analysis (TA) is a theory of personality and a systematic psychotherapy for human growth and transformation,' according to the International Transactional Analysis Association. Transactional Analysis is a theory propounded by Eric Berne in 1957. Ego states, Three types of transactions, Life script, Life positions, and Games are the fundamental themes of Eric Berne's theory. Bhagavad Gita is the distilled spiritual essence of the Vedic scriptures. Vedic scriptures consist of 4 Vedas, 108 Upanishads 18 Puranas and two Itihasas, and the essence of the Vedic scriptures is a manual for human behaviour. Its 'distilled essence' is a guide to human behaviour. Written by Vyasa the Bhagavad Gita talks largely on the nature of the soul, yoga systems, the three modes of nature, and so on, within the framework of 18 chapters and 701 verses (shlokas). The Gita represents chapters 25-42 of the Mahabharata, which contains 100,000 shlokas.

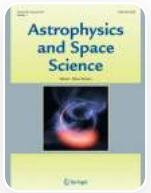
Bhagavad Gita is spoken in the war field by Lord Krishna to a depressed Arjuna has been referred to many times as psychotherapeutic intervention. (Murthy,1985). Bhagavad Gita is almost in its entirety the dialogue between Lord Krishna and Arjuna (the Pandava Prince) on the battlefield (war between the Pandavas and the Kauravas).. The discourse – one of the greatest philosophical and religious dialogues known to man – took place just before the outbreak of war, a great fratricidal conflict between the hundred sons of Dhrtharastra (known as Kauravas) and their cousins the Pandavas or sons of Pandu on the opposing side. (Prabhupad,1972).

The situation of Arjuna by the end of the first chapter is pitiable. *tatrāpaśhyat sthitān pārthaḥ pitṝīn atha pitāmahān/āchāryān mātulān bhrātṝīn putrān pautrān sakhīṁs tathā/śhvaśhurān suhṛidaśh chaiva senayor ubhayor api/*(After seeing within the midst of the armies of both parties, his fathers, grandfathers, teachers, maternal uncles, brothers, sons,

Characterization of ionospheric irregularities over the equatorial and low latitude Nigeria region

Research Published: 19 August 2022

Volume 367, article number 79, (2022) Cite this article



Aghogho Ogwala, Oluwole John Oyedokun, Andrew Ovie Akala, Paul Obiakara Amaechi, K. G. Simi, Sampad Kumar Panda, Cornelius Ogabi & Emmanuel Olufemi Somoye

Abstract

Ionospheric irregularity poses severe challenges to the highly dynamic satellite communication, navigation and tracking operations that rely on transionospheric satellite services like the operation of the Global Navigation Satellite System (GNSS). Although numerous studies on the effect of geomagnetic storms on the inhibition or suppression of irregularities across different longitudes have been documented, the prediction of equatorial ionospheric irregularities/scintillation over the Nigerian region still remains an unsolved scientific problem. Hence, this study characterizes storm-time ionospheric irregularities and comparison with the quiet-time baseline over the Nigerian equatorial region during the maximum phase (2012–2014) of the solar cycle 24. The ionospheric Total Electron Content (TEC) data from five geodetic GNSS stations across the equatorial region in Nigeria are considered to investigate the regional rate of change of TEC (ROT) and the rate of change of TEC index (ROTI). We also exploited the $\mathbf{E} \times \mathbf{B}$ vertical plasma drift (Vz) measurements from C/NOFS satellite and solar wind parameters from Advanced Composition Explorer (ACE) satellites in conjunction with the disturbance ionospheric electric currents (Diono) proxies from ground-based magnetometers to demonstrate the role of electrodynamics on development and modulation of ionospheric irregularities. In brief, we focused on regional ionospheric response characteristics during the initial phase, main phase and recovery phase of selected important storm events through comparison with the quiet-time ionospheric reference level over the region. The results show almost equal intensity of post-sunset ionospheric irregularities during quiet and disturbed geomagnetic days at most of the stations whereas the drift velocity was slightly higher during the quiet period. Moreover, the enhancement or suppression of ionospheric irregularities during the geomagnetic storm period demonstrates dependence on the local time of the storm commencement when the IMF-Bz and Dst southward orientation is at its minimum level. We emphasize the combined effect of the nominal quiet-time ionospheric electric field and storm-time Prompt Penetration Electric

Influence of structural variation on the optical properties of $Y_{2-x}Sm_xMo_3O_{12}$ phosphors

Published: 25 June 2022

Volume 33, pages 16837–16855, (2022) Cite this article

R. Satheesh, Meenu Venugopal & H. Padma Kumar

Abstract

$Y_{2-x}Sm_x(MoO_4)_3$ red phosphors have been synthesized using the traditional solid-state ceramic route and self-propagating solution combustion technique. The effect of synthesis methods on the structural and optical properties of the samples was studied and compared. High-temperature X-ray diffraction patterns of the undoped samples reveal the Pbcn orthorhombic $Y_2Mo_3O_{12}$ phase. Room-temperature diffraction patterns confirm a phase transformation in $Y_{2-x}Sm_xMo_3O_{12}$ phosphors from $Y_2Mo_3O_{12}.3H_2O$ to polycrystalline Pba2 orthorhombic $Y_2Mo_3O_{12}$ phase with Sm^{3+} substitution. This structural change occurred for $Y_{1.7}Sm_{0.3}Mo_3O_{12}$ for solid-state synthesized and for $Y_{1.9}Sm_{0.1}Mo_3O_{12}$ for combustion synthesized samples. HRTEM of combustion synthesized $Y_2Mo_3O_{12}$ and $Y_{1.9}Sm_{0.1}Mo_3O_{12}$ samples showed the presence of nano-crystallites with agglomeration. Bandgap variations with Sm^{3+} doping are in agreement with the observed structural changes in XRD. Intense orange-red emissions were observed for $Y_{2-x}Sm_x(MoO_4)_3$ samples due to radiative intraconfigurational f–f transitions from level $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$ levels of samarium ions. The optimum concentration of Sm^{3+} ions for maximum emission intensity and lifetime was for $Y_{1.7}Sm_{0.3}Mo_3O_{12}$ and $Y_{1.9}Sm_{0.1}Mo_3O_{12}$ samples prepared by solid-state and combustion synthesis, respectively. CIE color coordinates, CCT value, color purity, and quantum yield for bulk are compared with nano-samples. Optical properties of $Y_{2-x}Sm_xMo_3O_{12}$ phosphors showed strong dependence on structural variation with Sm^{3+} doping synthesized by two methods.

ScienceDirect

Journal of Luminescence

Volume 241, January 2022, 118486

Structural, optical and luminescence properties of $BaLaGa_3O_7$: x Eu^{3+} ceramic phosphors

B. Vasanthi [a] [b], N. Gopakumar [b], P.S. Anjana [a]

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Highlights

- The Photoluminescence (PL) and Mechanoluminescence (ML) properties of $BaLaGa_3O_7$ ceramic phosphor doped with different concentrations of Eu^{3+} ions have been prepared for the first time.

- The maximum photoluminescence and mechanoluminescence intensity is obtained for 0.05 mol % of Eu^{3+} ions.
- Chromaticity diagram shows that the wavelength emission is in the near red region.

Abstract

The undoped and Eu^{3+} doped $BaLaGa_3O_7$ ceramic phosphors have been prepared using solid state reaction technique. The structural studies have been done using X-ray Diffraction (XRD) and Fourier transform infra-red (FTIR) technique and the surface morphology analysis using Field emission scanning electron microscope (FESEM). The elemental analysis has been carried out using Energy Dispersive X-ray spectroscopy (EDX) and elemental mapping. XRD study reveals that all the prepared phosphors are single phase with tetragonal crystal structure. The FESEM and EDX spectra confirm the single phase nature of the phosphors. FTIR technique identifies the various vibrational modes present in the prepared phosphors. The UV–Visible analysis provides the absorption region and band gap energies of undoped as well as doped $BaLaGa_3O_7$ phosphors. The photoluminescence (PL) excitation spectra consist of sharp excitation peaks of Eu^{3+} ions at 374 and 394 nm. The emission spectra corresponding to excitation wavelengths of 374 and 394 nm have been carried out. Maximum PL emission is obtained for excitation at 374 nm and it provides excellent orange red emission. The decay profile of $BaLaGa_3O_7$:xEu^{3+} phosphors have been carried out. The mechanoluminescence (ML) property of the doped phosphors reveals good ML emission without any pre irradiation. The information about the trap depth parameters and charge carriers in the 1 kGy irradiated $BaLaGa_3O_7$ phosphor has been studied using the thermoluminescence (TL) glow curves. The $BaLaGa_3O_7$ phosphor is having kinetics of first order with activation energy 1.107 eV.

Introduction

The compound of general formula ABC_3O_7 where A=Ca, Sr, Ba, B = Y, La, Gd, C = Al, Ga are widely used in light emitting applications as well as lasing possibilities [1,2]. They exist in two structural forms, orthorhombic (C_{2V}) and tetragonal (C_{4V}) [3,4]. In ABC_3O_7, A and B

ScienceDirect

Journal of Molecular Structure

Volume 1263, 5 September 2022, 133132

Synthesis and characterization of biologically active novel structured cadmium barbiturate single crystal with good thermal stability

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Highlights

- A novel structured cadmium complex based on barbiturate ligand has been synthesized at room temperature by gel diffusion technique.

- SCXRD analysis reveals that the complex belongs to orthorhombic crystal structure with space group Ibam.
- The band gap of the CdB crystals was found to be 3 eV by tauc's plot and the corresponding refractive index obtained is 1.244.
- The crystal shows broad emission than that of its ligand (BA) in the entire visible region. The color corresponding to maximum emission of both ligand and CdB crystals were indicated by CIE chromaticity diagram.
- The response of CdB crystal against applied electric field is characterised by dielectric measurements.
- The antimicrobial activities of the complex CdB against various bacteria have been investigated and then compared it with the corresponding ligand (BA).The results showed that the complex had stronger antibacterial activities than the ligand.

Abstract

A novel structured cadmium complex based on barbiturate ligand has been synthesized at room temperature by gel diffusion technique. The prepared crystals were characterised by FTIR, PXRD, thermogravimetric and single crystal X-ray diffraction analysis. SCXRD analysis reveals that the complex belongs to orthorhombic crystal structure with space group Ibam. The optical properties were studied from UV-Visible and photoluminescence spectra. The band gap of the CdB crystals was found to be 3 eV by tauc's plot and the corresponding refractive index obtained is 1.244. The crystal shows broad emission than that of its ligand (BA) in the entire visible region. The color corresponding to maximum emission of both ligand and CdB crystals were indicated by CIE chromaticity diagram. The response of CdB crystal against applied electric field is characterised by dielectric measurements. The values of penn gap

Phase transformation induced structural, optical and photocatalytic investigations of TiO_2 nanoparticles

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Bulletin of Materials Science

Aims and scope

Submit manuscript

M S Gopika, S Jayasudha & Prabitha B Nair

Abstract

Titanium dioxide (TiO_2) nanoparticles were synthesised by the modified sol–gel method at different calcination temperatures. Samples were characterized using X-ray diffraction (XRD), high-resolution transmission microscopy, scanning electron microscopy, energy dispersive X-ray analysis (EDAX), Fourier transform infrared (FTIR) spectroscopy, Brunauer, Emmett and Teller surface area analyzer (BET) and diffuse reflectance spectroscopy (DRS). Phase transformation of TiO_2 nanoparticles from anatase to rutile phase with an increase in calcination temperature from 573 to 1173 K was observed from XRD analysis. Detailed structural analysis using size–strain plot and Halder–Wagner method was done for all samples. The formation of TiO_2 nanoparticles was confirmed from FTIR and EDAX spectra. The TEM image of the sample calcined at 673 K showed non-spherical shaped particles having particle sizes 13.16 ± 3.35 nm. The bandgap energy calculated from DRS decreases with an increase in calcination temperature, which supports phase transformation observed in XRD analysis. The photocatalytic degradation efficiency was evaluated by monitoring the degradation of Congo red (CR) azo dye under UV light and natural sunlight. The degradation of CR dye was confirmed by analysing the FTIR spectrum of the degraded sample. The sample calcined at 673 K, in the pure anatase phase, exhibited the highest photocatalytic activity.

Advances in Space Research
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Solar and interplanetary events that drove two CIR-related geomagnetic storms of 1 June 2013 and 7 October 2015, and their ionospheric responses at the American and African equatorial ionization Anomaly regions

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Highlights

- 1 June 2013 geomagnetic storm was driven by weak CME and HSSs, while 7 October 2015 storm was HSS driven.
- Storm at day side location had enhancement in plasma and poleward movement of EIA crests & vice versa.
- Daytime eastward PPEF intensifies plasma fountain to cause positive ionospheric response & vice versa.
- The season of storm's occurrence is a factor that also dictates ionospheric response to a storm.
- Stronger and well-developed EIA crests were observed over the American sector than African sector.

Abstract

This study investigates the sequence of solar and interplanetary events that drove the 1 June 2013 and October 2015 geomagnetic storms and how the American (68°–78°E) and African (32°–42°E) Equatorial Ionization Anomaly (EIA) regions responded to them. We constructed the EIA structures by using Total Electron Content (TEC) and ionospheric irregularities derived from Global Navigation Satellite System (GNSS) receivers along with the study locations. We also analyzed disturbed time ionospheric electric field ar model data alongside the GNSS data. The 1 June 2013 geomagnetic storm was driven by a combination of a weak CME and HS solar coronal holes, while the 7 October 2015 storm was solely driven by HSSs. Storm-time hemispherical asymmetry in ionospheric TEC and irregularities distributions was consistently observed. Storm with minimum SYM-H value at day-side locations caused enhancement in plasma ionization and pole-ward movement of EIA crests, while storm with minimum SYM-H value at night-side locations caused reduction in plasma ionization and equator-ward movement of EIA crests. The phase of responses of the ionosphere to geomagnetic storms depends on the local time of storm's onset and local time of the storm's main phase minimum which also

Influence of structural variation on the optical properties of $Y_{2-x}Sm_xMo_3O_{12}$ phosphors

Published: 25 June 2022

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R. Satheesh, Meenu Venugopal & H. Padma Kumar

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$Y_{2-x}Sm_x(MoO_4)_3$ red phosphors have been synthesized using the traditional solid-state ceramic route and self-propagating solution combustion technique. The effect of synthesis methods on the structural and optical properties of the samples was studied and compared. High-temperature X-ray diffraction patterns of the undoped samples reveal the Pbcn orthorhombic $Y_2Mo_3O_{12}$ phase. Room-temperature diffraction patterns confirm a phase transformation in $Y_{2-x}Sm_xMo_3O_{12}$ phosphors from $Y_2Mo_3O_{12}.3H_2O$ to polycrystalline Pba2 orthorhombic $Y_2Mo_3O_{12}$ phase with Sm^{3+} substitution. This structural change occurred for $Y_{1.7}Sm_{0.3}Mo_3O_{12}$ for solid-state synthesized and for $Y_{1.9}Sm_{0.1}Mo_3O_{12}$ for combustion synthesized samples. HRTEM of combustion synthesized $Y_2Mo_3O_{12}$ and $Y_{1.9}Sm_{0.1}Mo_3O_{12}$ samples showed the presence of nano-crystallites with agglomeration. Bandgap variations with Sm^{3+} doping are in agreement with the observed structural changes in XRD. Intense orange-red emissions were observed for $Y_{2-x}Sm_x(MoO_4)_3$ samples due to radiative intraconfigurational f–f transitions from level $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$ levels of samarium ions. The optimum concentration of Sm^{3+} ions for maximum emission intensity and lifetime was for $Y_{1.7}Sm_{0.3}Mo_3O_{12}$ and $Y_{1.9}Sm_{0.1}Mo_3O_{12}$ samples prepared by solid-state and combustion synthesis, respectively. CIE color coordinates, CCT value, color purity, and quantum yield for bulk are compared with nano-samples. Optical properties of $Y_{2-x}Sm_xMo_3O_{12}$ phosphors showed strong dependence on structural variation with Sm^{3+} doping synthesized by two methods.

ScienceDirect

Journal of Non-Crystalline Solids

Volume 576, 15 January 2022, 121242

Rare earth added barium alumino borosilicate glass-ceramics as sealants in solid oxide fuel cells

M.S. Salinigopal [a b], N. Gopakumar [b], P.S. Anjana [a], O.P. Pandey [c]

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Highlights

- 50BaO-(5-x)Al_2O_3-xR_2O_3–30B_2O_3–15SiO_2(x=0, 5 and r=Nd, Gd, La, Dy) have been synthesized using conventional melt quenching technique and converted to glass-ceramics by controlled crystallization of the parent glasses for the first time.

- The CTE of all the glasses and glass-ceramics lie within the range (11.60–12.81)×10^{-6}°C^{-1}, which matches with that of the other components of solid oxide fuel cell.
- The interaction study of glass-ceramics with Crofer22APU interface and Crofer22APU/Glass-ceramic/Crofer22APU showed no evidence of interfacial failure and cracks.
- The good thermal and interaction properties show that, the present glass-ceramics are suitable candidates as sealants in solid oxide fuel cells.

Abstract

Glasses with composition 50BaO-(5-x) Al_2O_3-xR_2O_3–30B_2O_3–15SiO_2 (x=0,5 and R=Nd, Gd, La, Dy) have been synthesized by conventional melt quenching method. Controlled crystallization has been carried out to convert these glasses to corresponding glass-ceramics. X-ray diffraction (XRD) technique has been used to identify the crystalline phases formed in glass-ceramics. Archimede's method has been used to measure the density of glass-ceramics. The co-efficient of thermal expansion of all glass-ceramics lie within the range (11.60 – 12.81) x 10^{-6}/°C, which matches with that of the other components of solid oxide fuel cell. The interaction study of glass-ceramics with Crofer22APU interface and Crofer22APU/Glass-ceramic/Crofer22APU showed no evidence of interfacial failure and cracks. Hence the prepared glass-ceramics can be considered as a suitable candidate for sealant materials in SOFC applications.

Introduction

Solid oxide fuel cell (SOFCs) is an emerging energy technology which has many advantages over existing technologies; high electrical conversion efficiency (over 60%), potential for carbon capture, no NO_2 emission, fuel flexibility, low noise, and suppleness for transportation and stationary applications. This technology may be a panacea for carbon capture visible of the separate fuel and air flow systems [1], [2], [3]. SOFC has lower manufacturing cost and better power density as compared to other fuel cells, but it requires

Research Article

Photocatalytic and antimicrobial activities of pure and Mn doped ZnO nanoparticles synthesised by *Annona Muricata* leaf extract

Vindhya P S, Kunjikannan R & **Kavitha V T**

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ABSTRACT

The present work aim to investigate the photocatalytic, antibacterial and antifungal activities of $Zn_{1-x}Mn_xO$ (x = 0.0, 0.03, 0.05 and 0.07) nanoparticles synthesised using the leaf extract of *Annona Muricata* via green synthesis method. The effect of Mn doping in the obtained nanopowder were studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), high-resolution transmission electron microscopy (HRTEM), selected area diffraction pattern (SAED), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and UV-visible spectroscopy techniques. XRD pattern confirms hexagonal wurtzite structure of ZnO nanoparticles. Incorporation of Mn into the ZnO host lattice was confirmed by XPS measurement. Morphology of nanoparticles shows irregular, spherical shapes with agglomeration. Presence of Zn, Mn and O elements in the EDAX reveals the perfect nature of nanostructures. The synthesised pure and Mn-doped ZnO nanoparticles were found to be significant antibacterial activity against gram positive *Bacillus*

Bio-fabrication of Ni doped ZnO nanoparticles using Annona Muricata leaf extract and investigations of their antimicrobial, antioxidant and photocatalytic activities

P S, Vindhya ; **R, Kunjikannan** ; **V T, Kavitha**

The present work aims to investigate the structural, optical, antimicrobial, antioxidant and photocatalytic activities of $Zn_{1-x}Ni_xO$ (x = 0, 0.03, 0.05 & 0.07) nanoparticles prepared by the green method using Annona Muricata leaf extract. The synthesised nanoparticles were analysed by XRD, FTIR, XPS, HRTEM- SAED, SEM- EDX and UV-Visible spectroscopy. The XRD pattern confirms Ni has been successfully incorporated into the hexagonal wurtzite structure of ZnO. XPS results demonstrate the binding energies of ZnO and Ni. The presence of Zn-O vibrational modes was identified by FTIR spectra. The morphology of prepared samples was investigated through SEM and TEM analysis. The presence of Zn, O and Ni elements in EDX spectra indicates the purity of the sample. The optical bandgap energy of ZnO nanoparticles decreases with an increase in Ni concentration. Antimicrobial activity of nanoparticles were carried out against s.aureus, B.subtilis and P.aeruginosa bacterial strains as well as the fungal strain of A.niger and C.albicans. ZnO nanoparticles have significant antioxidant activity against DPPH free radicals. Under solar irradiation, $Zn_{0.93}Ni_{0.07}O$ nanoparticles exhibit excellent photocatalytic degradation against malachite green (98.4 %) and methylene blue (94.9 %) dye solutions. Finally, these findings suggest an effective utilization of

phytochemicals present in the A.muricata leaf extract as a suitable source for biosynthesis of pure and Ni-doped ZnO nanoparticles utilised for biomedical and industrial waste water treatment applications.

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Leaf extract-mediated synthesis of Mn-doped CuO nanoparticles for antimicrobial, antioxidant and photocatalytic applications

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P. S. Vindhya & V. T. Kavitha

Abstract

The objective of the present investigation is the synthesis, characterization, antimicrobial, antioxidant and photocatalytic activities of pure and Mn (3%, 5% and 7%)-doped CuO nanoparticles fabricated using *Annona muricata* leaf extract. The obtained nanopowders were analysed by XRD, FTIR, XPS, HRTEM, SEM, EDX, SAED and UV–visible studies. XRD pattern reveals the monoclinic structure of CuO nanoparticles. FTIR was used to identify the functional groups present in the nanoparticles. XPS measurements confirm the binding energy, chemical state and chemical composition of Mn dopant ions in host CuO nanoparticles. The morphology of CuO nanoparticles is affected by Mn doping concentration, according to SEM and HRTEM analysis. EDX spectra reveal the purity and homogeneity of the sample. The optical properties of nanoparticles were investigated by UV–visible spectroscopy. The antimicrobial potential of pure and Mn-doped CuO nanoparticles was tested against pathogenic bacterial and fungal strains. Also, CuO nanoparticle exhibits respectable antioxidant activities. Furthermore, the photocatalytic effects of samples were tested for the MB dye degradation. Overall, this study shows that green synthesized pure and Mn-doped CuO nanoparticles can be used in biomedical as well as waste water management applications.

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INVASIVE EXOTIC PLANT SPECIES AND THEIR INFLUENCE ON THE ENVIRONMENT, ECOSYSTEM SERVICES, ECONOMY AND HEALTH: A SEARCH

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ABSTRACT

Invasive exotic plant species (IEPS) is recognized as threat to the native biodiversity and leads to the loss of habitat for the indigenous species on the earth. Invasions not only tear down the native plant species but have adverse impacts on economy and human health. Many documented records from Western countries connected with alien species revealed altered ecosystem services and socio-economic conditions via diverse mode of actions. Even though, the ecological impacts of alien species were documented, there is a dearth of analysis regarding their economic quantification, livelihood considerations, biotechnological aspects and human health risk assessments are the need of the hour. The noxious exotic invasive plants in India were *Ageratum conyzoides*, *Eupatorium adenophorum, Parthenium hysterophorus, Lantana camara, Mikania micrantha, Argemone mexicana* and *Eichhornia crassipes*. In this context, an attempt was made to enlist the alien species of Kerala and a review to account the impacts of invasive exotic plant species on various aspects of the environment globally. Results regarding the alien species search revealed the following species such as *Chromolaena odorata, Senna spectabilis, Hypoestes sanguinolenta, Maesopsis eminii, Eupatorium cannabinum, Mikania micrantha, Sphagneticola trilobata* and *Acacia mearnsii* were intruded in to various ecosystems of Kerala after the repeated floods. They directly affect the germination and survival of local species, damage the quality of soil and affect ground water availability. Nearly 80 species were noted as alien species in Kerala by many state level surveys. Research in the direction of impact of alien species on socio-economic cultural aspects of life and derailment of ecosystem is not yet seriously carried from Kerala. Further, there is a paucity of the ecological models/indicators to establish interrelationship among global environmental changes, biodiversity and health, warranting future researches.

Keywords: Alien species, Ecological impacts, Ecosystem, Invasion, Native species, Biodiversity.

1. INTRODUCTION

Invasive exotic plant species (IEPS) are considered to be the major direct driving force of loss of biodiversity across the earth. Management of invasive exotic plant species seems to be a challenge in the field of conservation of biological diversity. The alien species threatens the ecosystems, degrade the habitats and create issues to other indigenous species through invasion. It is treated as the second largest factor of species endangerment and extinction of biodiversity in an area. The ecological cost is often irrecoverable via loss of native species and ecosystems. It also causes high loss of economy, in terms of reduced crop yield and production of livestock, declined natural biodiversity, increased production costs and so on. Biodiversity has become one of the hottest areas at local, national and global scale. Biodiversity includes all forms of biological entities inhabiting the earth including microbes, wild plants and animals, domesticated animals and cultivated species and even genetic material like seeds and germplasm etc [1]. Invasive exotic plant species are species, native to one area or region, that have been introduced into an area outside their normal distribution, either by accidental or for on usage and

which latter gets colonized or invaded their new habitats, threatening the native biodiversity, ecosystems and habitats, and human wellbeing. Alien species invasion globally threatens biological diversity, ecosystem dynamics, resource availability, economy of an area and human health [2]. The spread of these species is considered as one of the high risk factor to the ecosystem. Accidental introductions happened via trade or travel across continents and import of various items such as timber, food grains, fodder etc.

Currently, the human centered landscapes are typically featured by intensive land-use pattern and increased scale of habitat destruction, often results in to contrasted mosaics of habitat. Fragmentation of the existing habitat is a major threat to biological diversity and ecosystem functioning. Decreasing existing habitat size and increasing isolation of habitat patches results in to decline in species richness and abundance, also changes in community structure. This process of habitat fragmentation and destruction may greatly change the landscape architecture and local ecosystem functioning. After habitat fragmentation, the surviving plant communities become more prone to invasion by non-native plant species. Many studies documented that floristic changes emerge after habitat fragmentation, which may be due to invasion by an alien weed. Forest study of Costa Rica reported that fragmented tropical dry forest were prone to invasion by weedy generalist plant species. When changes in community occur either through habitat alteration or through the invasion of alien species, local decline, and even extinction of native species may occur. The effect of fragmentation on species loss is now becoming well known in many parts of the earth. However, limited studies have viewed at the effects of fragmentation on the success of invaders and the subsequent effects of the invader on the native species resident in fragments. In this scenario, the objective of the review is to report the alien invasion of species threating to various aspects on the environment including health and economy. Further, a check list of exotic species was also prepared in this context from Kerala.

2. MATERIAL AND METHODS

Intensive floristic survey reports were screened in different areas of Kerala in such a way that each location could be studied in every season of the year. A comprehensive list of invasive exotic plant species and the information regarding the various issues of invasive exotic plant species of the area was prepared. The nativity, sources and mode of introduction of these alien invasive plants were noted from the available literatures. The native ranges of the species were recorded from published literatures. Plants were categorized according to their life forms as herb, undershrub, shrub, climber and tree. The studied habitats were wasteland, cultivated field, riverbank, pond bank, home garden, forest, roadside etc.

3. RESULTS AND DISCUSSION

3.1. Invasions of species by anthropogenic activities and natural means

The introduced invasive exotic plant species (IEPS) by human beings threaten the ecosystems, biodiversity and replaced many economically unique native plant species and thereby creating issues in agriculture and silviculture practices, upsetting the vegetation dynamics and nutrient recycling. Introductions of alien plants by human activities in the native habitats are the major reason for the drastic changes recorded within the indigenous native plant communities of the area [3]. Trade connected with commerce (especially imports) and extensive travel by people magnified the intensity of invasive alien species across the world. Current scenarios of transport have directly/indirectly increased the inadvertent migration of species, often resulted in to disastrous consequences [4]. Introduced or indirectly carried species reports like *Eucalyptus citriodora*, *Lantana camara, Acacia auriculiformis* and *Senna spectabilis* were the examples substantiating the degradation of natural ecosystems [5].

The natural invasion mainly depends upon the dispersal ability of the invading species. The time scale for natural invasion usually ranges from few to many years. Birds, animals, water and wind forms the agents for natural invasion. *Ageratum conyzoides* and *Parthenium hysterophorus* were examples for natural invasion [6]. After migration of an exotic plant species, there is a lag phase before an exponential phase of its fast spread. The species like *P. hysterophorus* that at a given period may seems to be non-invasive but suddenly spread vigorously.

3.2. Various types of environmental impacts by the invasive exotic plant species (IEPS)

3.2.1. Impacts of exotic species invasions on indigenous species

Study reports of past introduced plants illustrated that the impacts of invasive species are complex and may permanently alter the vegetation and community structures. Invasive exotic plant species inducts more

stress especially where communities are disturbed. Limited data was available on alien plant species threatened the undisturbed local indigenous plant communities. In Kerala, *Chromolaena odorata*, *Senna spectabilis*, *Hypoestes sanguinolenta, Maesopsis eminii, Eupatorium cannabinum, Mikania micrantha, Sphagneticola trilobata* and *Acacia mearnsii* were well recognized alien invaders which posed threat to indigenous plant communities including the protected areas under conservation and also the habitats from planes to hilly tracts (Table 1).

Table 1: List of alien invaders which posed threat to indigenous plant communities in Kerala

Sl. No	Plant name	Family, habit & origin	Threatens
1.	*Chromolaena odorata* (L.) R.M. King & H. Rob	Asteraceae, Climber South America and Central America	Threatens the species like *Sida cordifolia*
2.	*Senna spectabilis* (DC.) Irwin & Barneby	Caesalpinioideae, Tree, South and Central America	Intruded in to wildlife sanctuaries as well as in plantations
3.	*Hypoestes sanguinolenta* Hook.	Acanthaceae, Herb, Madagascar	High risk species to native plants
4.	*Maesopsis eminii* Engl.	Tree, Rhamnaceae, Africa	Inhibits the undergrowth of native species
5.	*Eupatorium cannabinum* L.	Herb, Asteraceae, Europe to Central Asia	High nuisance value around water ways
6.	*Mikania micrantha* Kunth.	Asteraceae, Climber, America	Herbivores face food scarcity as the native plant species
7.	*Sphagneticola trilobata* (L.) Pruski	Asteraceae, Runner, Mexico	Garden plant threatened
8.	*Acacia mearnsii* De Wild	Mimosoideae, Tree, south-eastern Australia	Ground water threatened

Disturbed and unattended habitats are more prone to the invasion when compared to the well-managed ecosystems and habitats. The habitats which have more diverse plant communities were highly competitive and resist invasion. Schmitz et al., [7] reported that the invasive trees of Florida such as *Schinus terebinthifolius*, *Melaleuca quinquenrvia* and *Casuarina* spp resulted in to major threats to the native vegetation. Similarly, the introduced different pine species created issues to natural habitats in Australia, New Zealand, and South Africa. It was reported that in Christmas Island at Australia 52.70% species have been found to be exotic like *Leucaena leucocephala, Muntingia calabura, Ricinis communis, Carica papaya* and *Psidium guajava* and most of them were confined to disturbed regions such as minefields, overburden dumps, and road sides [8].

The alien terrestrial species introduced in to the natural habitats are responsible for the extensive and unpredictable irreversible changes in those areas (Table 2). Many countries initiated techniques to utilize the exotic tree species for commercial, economic uses and for ornamental landscapes which further intensified more noxious invaders growth. These tree species have impacted the natural above-ground herbal and other native vegetation. Sometimes, under the alien conditions or in new invaded ecosystems, such type of species become naturalized and expands over other native ecosystems. Richardson et al., [9] reported that introduced pines in the Southern Hemisphere have affected large areas of natural grasses and thickets. It brought a lot of change in the dominant annual and perennial herbals and decreased the species composition and modified vegetation patterns and the nutrient cycles. The disturbed forest understories are more prone to invasion as compared to the undisturbed zones. Dogra et al., [10] reviewed that there are many species such as *Alliaria petiolata*, *Acer platanoides*, *Lonicera bella, Rhamnus cathartica* and *Berberies thunbergii* that established and dominated the low light forest understories in the Northwestern USA. The invasive species survive under the shade because rapid growth takes place in the microhabitats than exposed conditions.

3.3. Impact on the soil structure and its dynamics

Invasion by exotic plant species affects the dynamics and structure of the soil on a holistic scale and have immense impact on ecosystem functions like soil-mineral recycling. Since these effects result from differences in the mode of behavioural patterns between the exotic and native species, novel physiological characters such as nitrogen, phosphorus cycling may cause maximal alterations in the ecosystem function [11].

Table 2: List of Invasive Alien plant species in India

Plant species	Family, Habit & origin	Impacts
Acacia mearnsii De Wild.	Mimosoideae, Tree, South-eastern Australia	It rapidly grows to forms dense thickets and destroys the grazing lands.
Acanthospermum hispidum DC.	Asteraceae, Herb, Brazil	Troublesome annual weed of annual and perennial crops.
Aerva javanica (Burm.f.) Juss. ex Schult.	Amaranthaceae, Herb, Trop. America	It has only recently come to be regarded as a serious environmental weed.
Ageratum conyzoides L.	Asteraceae, Herb, Trop. America	Allelopathic, highly invasive, threat to croplands
Alternanthera tenella Colla.	Amaranthaceae, Herb, Trop. America	Rapid colonizer and harmful to forest ecosystem.
Alternanthera philoxeroides Mart.) Griseb	Amaranthaceae, Herb South America	By forming dense mats of interwoven stems over water or land, this invasive weed may threaten the native flora and fauna, reduce crops yields, block ships, and promote flooding
Argemone mexicana L.	Papaveraceae, Herb, Trop. Central & South America	Harm native flora through allelopathy
Asclepias curassavica L.	Asclepiadaceae, Herb, Trop. America	It is prolific in disturbed sites and competes with agricultural crops and indigenous species. This plant contaminates crop seed.
Blainvillea acmella (L.) Philipson.	Asteraceae, Herb, Trop. America	It is a common weed in cultivated fields, degraded forests.
Bidens pilosa L.	Asteraceae, Herb, Trop. America	The plant is thought to produce allelopathic toxins that affect a number of crops.
Blumea obliqua (L.) Druce	Asteraceae, Herb, Trop. America	The extinction of native species and has negative impact on crop production
Calotropis procera (Ait.) R.Br.	Asclepiadaceae, Shrub, Trop. Africa	It is noxious weed; hence it is controlled within the area. Establishing the weed has been advocated for environmental protection and as a nurse crop for more valuable species
Cardamine hirsuta L.	Brassicaceae, Herb, Trop. America	It is a fast-growing herb that often behaves as a weed in both disturbed and undisturbed sites
Cassia alata L.	Caesalpiniaceae, Shrub, West Indies	Introduced as an ornamental and became threat to local flora
Celosia argentea L	Amaranthaceae, Herb, Trop. Africa	It is a common weed of cultivated fields and scrub lands.
Chromolaena odorata (L.) King & Robinson	Asteraceae, Herb, Trop. America	Its foliage is reportedly flammable (contains essential oils), making it a threat to indigenous coastal forest patches, which are not resilient to fire.
Cleome viscosa L.	Cleomaceae, Herb, Trop. America	This species produces large numbers of sticky seeds that can be easily dispersed by wind and has the potential to spread much further into new habitats.
Chrozophora rottleri (Geis.) Spreng.	Euphorbiaceae, Herb, Trop. Africa	This plant species act as the main cause for threat to the native biological diversity.
Cleome gynandra L.	Cleomaceae, Herb, Trop. America	It is aggressive colonizer and is weed of village wastelands, dumping grounds, crop lands
Crotalaria retusa L.	Papilionaceae, Herb, Trop. America	The risk of new introductions as well as the probability of escape from cultivation is high
Croton bonplandianum Boil.	Euphorbiaceae, Herb, Temperate South America	Became threat to endemic flora and gradually destroys.
Cryptostegia grandiflora R.Br.	Asclepiadaceae, Herb, Madagascar	A threat to native biodiversity.
Cuscuta chinensis Lam.	Cuscutaceae, Herb, Mediterranean	It has proved locally invasive and damaging to fruit and ornamental trees.

Cytisus scoparius (L.) Link	Papilionaceae, Herb, Europe	It displaces native understorey vegetation and grasses, finally forming monospecific stands.
Crassocephalum crepidioides (Benth) S. Moore	Asteraceae, Herb, Africa	The plants pose a serious threat to flora and fauna.
Datura innoxia Mill.	Solanaceae, Shrub, Trop. America	It has the capacity to invade natural habitats and can be considered as potential threat for natural biodiversity.
Digera muricata (L.) Mart.	Amaranthaceae, Herb, SW Asia	Common weed of irrigated dry cultivated fields.
Echinops echinatus Roxb.	Asteraceae, Herb, Afghanistan	Serious aquatic weed, allelopathic in nature, causes hindrance in navigation, reduces water quality and algal growth
Eclipta prostrata (L.) Mant.	Asteraceae, Herb, Trop. America	It has never been reported as a serious weed but it is troublesome in several crops.
Eupatorium cannabinum L.	Asteraceae, Herb, Europe to Central Asia	Allelopatic effect causes serious threats to native flora
Euphorbia heterophylla L.	Convolvulaceae,:Herb, Trop. America	It is reported as an emerging weed in cotton and processing tomato.
Evolvulus nummularius (L.) L.	Convolvulaceae, Herb, Trop. America	It is found both in agricultural land and waste and fallow lands mainly as noxious weeds.
Gomphrena serrata L.	Amaranthaceae, Herb, Trop. America	Occasional weed of cultivated fields, habitation and forest openings.
Gnaphalium polycaulon Pers.	Asteraceae, Herb, Trop. America	It is a noxious species found in tanks, ditches and margins of river banks.
Hyptis suaveolens (L.) Poit.	Lamiaceae, Herb, Trop. South America	It is a major threat to native biodiversity, ecosystems and livelihoods.
Hypoestes sanguinolenta Hook.	Acanthaceae, Herb, Madagascar	It competes with the native flora and reduces its population.
Indigofera linifolia (L.f.) Retz.	Papilionaceae, Herb Trop. America	Invasion of the species threat natural habitat
Ipomoea carnea Jacq.	Convolvulaceae, Shrub Trop. America	The invasions of the species cause ecological disturbances that threaten native biodiversity.
Ipomoea obscura (L.) Ker.-Gawl.	Convolvulaceae, Herb Trop. Africa	Common weed in moist places of degraded forests and hedges.
Lantana camara L.	Verbenaceae, Herb Trop. America	Strongly allelopathic, serious threat to medicinal plants, responsible for forest fire
Lagascea mollis Cav.	Asteraceae, Herb, Trop. Central America	Common weed of forests, plantations, habitation, waste lands and scrub lands
Leucaena leucocephala (Lam.) de Wit	Mimosacceae, Herb, Trop. America	Runs wild in waste lands, scrub lands and fringes of plantations.
Macroptilium atropupureum (DC.) Urban	Papilionaceae, Climber, Trop. America	It is a weed species quite common but often scarce in crops.
Maesopsis eminii Engl.	Rhamnaceae, Tree, Africa	A threat to tropical forest conservation.
Malvastrum coromandelianum (L.) Garcke	Malvaceae, Herb, Trop. America	Common weed of cultivated fields, forest openings and habitation.
Merremia aegyptia (L.) Urban.	Convolvulaceae, Herb, Trop. America	A very good website detailing weed species
Melochia corchorifolia L.	Sterculiaceae, Herb, Trop. America	Common weed of moist places.
Mikania micrantha Kunth.	Asteraceae, Climber, Trop. America	Known for its allelopathic potential, highly invaded forest areas
Mimosa pigra L.	Mimosacceae, Shrub, Trop. North America	It has the potential to harm a wide number and variety of different types of primary production
Ocimum americanum L.	Lamiaceae, Herb, Trop. America	Common weed of waste lands and scrub lands.
Ocimum gratissimum L.	Lamiaceae, Herb, Africa	Species prefers wet and fertile conditions, but can tolerate drought after flowering and influence the natural habitat.
Oxalis corniculata L.	Oxalidaceae, Herb, Europe	Common winter season weed.
Parthenium hysterophorus L.	Asteraceae, Herb, Trop. North	Aggressive colonizer, highly allelopathic,

	America	allergic to animals and human being, threat cause to crops and other native flora
Passiflora foetida L.	Passifloraceae, Herb, Trop. South America	Common weed of forest fringes and bunds of cultivated fields.
Pedalium murex L.	Pedaliaceae, Herb, Trop. America	Occasional weed of waste lands, road sides and cultivated fields.
Pennisetum purpureum Schum.	Poaceae, Herb Trop. America	Posing a threat to the native species
Peristrophe paniculata (Forssk.) Brummitt	Acanthaceae, Herb, Trop. America	The native flora is facing severe threats from this species.
Peperomia pellucida (L.) Kunth.	Piperaceae, Herb, Trop. South America	Common winter season weed in gardens and on moist rocks near by habitation.
Pilea microphylla (L.) Liebm.	Urticaceae, Herb, Trop. South America	Pilea microphylla also known as rockweed, common weed of gardens and often as a pot weed.
Physalis pruinosa L..	Solanaceae, Herb, Trop. America	This alien invasive species is a serious threat to indigenous flora.
Portulaca oleracea L..	Portulacaceae, Herb, Trop. South America	Weed of moist fields and gardens.
Prosopis juliflora (Sw.) DC.	Mimosacceae, Shrub, Mexico	Aggressive and has not only successfully invaded several habitats but has also caused substratum degradation in these by causing loss of finer soil particles
Rhynchelytrum repens (Willd.) C.E. Hubb.	Poaceae, Herb, Trop. America	Occasional weed of disturbed places.
Senna spectabilis (DC.) Irwin & Barneby	Caesalpinioideae, Tree, South and Central America	The plant is posing a threat to wildlife and indigenous plants in the forest areas.
Sesbania bispinosa (Jacq.) Wight	Papilionaceae, Shrub, Trop. America	It has a tendency to naturalize and thus poses a threat of local dispersal.
Solanum americanum Mill.	Solanaceae, Herb, Trop. America	Occasional weed of cultivated fields and often found in forest fringes.
Sida acuta Burm.f.	Malvaceae, Herb, Trop. America	This plant has a pantropical distribution and is considered a weed.
Solanum torvum Sw.	Solanaceae, Shrub, West Indies	It is considered to be a serious threat to the productivity and sustainability of pasture.
Solanum seaforthianum Andrews.	Solanaceae, Climber, Brazil	This species is an aggressive invasive vine that has been widely cultivated as an ornamental.
Spermacoce hispida L.	Rubiaceae, Herb, Trop. America	Common weed of degraded forests, scrub and cultivated fields.
Spilanthes radicans Jacq.	Asteraceae, Herb, Trop. South America	Common weed of gardens and occasionally found in cultivated fields and forest fringes.
Sphagneticola trilobata (L.) Pruski	Asteraceae, Runner, Mexico	Plant is belongs to the top 100 of most alien invasive species in the world, which seriously threatens the biodiversity of its indigenous congener.
Stachytarpheta cayennensis (Rich) Vahl.	Verbenaceae, Herb, America	According to a risk assessment this species is regarded as being highly invasive and is a casual weed, a "garden thug", with effects on the local plant.
Synedrella nodiflora (L.) Gaertn.	Asteraceae, Herb, West Indies	Common weed of waste lands and gardens.
Tridax procumbens L.	Asteraceae, Herb, Trop. Central America	Common weed, along railway tracks, road sides, in cultivated fields and degraded forests.
Tribulus terrestris L.	Zygophyllaceae, Herb, Trop. America	Plants invade roadsides, pastures, fields, grasslands and degraded forests.
Triumfetta rhomboidea Jacq.	Tiliaceae, Herb, Trop. America	Common weed of forest openings, scrub and waste lands.
Turnera ulmifolia L.	Turneraceae Herb, Trop. America	Occasional weed of habitation and disturbed lands.
Urena lobata L.	Malvaceae, Shrub, Trop. Africa	It invades disturbed areas, pastures, eroded areas, and perennial crop plantations.

		Tolerates salt spray but does not grow in saturated soils.
Ulex europaeus L.	Papilionaceae, Shrub, Western Europe	It is an invasive shrub deemed as one of the most invasive species in the world.
Waltheria indica L.	Sterculiaceae, Herb, Trop. America	Abundant along railway tracks, road sides and in degraded forests.
Xanthium strumarium L.	Asteraceae, Herb, Trop. America	Occasional weed of cultivated fields and scrub lands.
Youngia japonica (L.) DC	Asteraceae Herb, Trop. South America	Occasional weed of cultivated fields and scrub lands.

(Source:C. Sudhakar Reddy, G. Bagyanarayana, K.N. Reddy & Vatsavaya S. Raju. 2008. Invasive Alien Flora of India. National Biological Information Infrastructure, Usgs, USA)

Kourtev et al., [12] studied the differences in earthworm densities and nitrogen dynamics in soils under exotic and native plant species. The invasion of *Berberis thunbergii* and *Microstegium vimineum* in hardwood forests of New Jersey, Europe has showed significant increase of pH in soils under the invasive plants when compared to soils under native shrubs (*Vaccinium* spp.). In addition, the available nitrate and net potential nitrification were remarkably higher in soils under the two exotic species. Sharma and Dakshini [13] reported the integration of plant and soil features and the ecological success of *Prosopis* species. The introduced *P. juliflora* was fast growing, highly aggressive and invasive, and causes substratum degradation in the semi-arid and arid areas of North and North-west India as compared to native species *P. cineraria*. This lack of integration amongst plant and soil characteristics and the ability to meet its nutrient requirements in all situations could be the basis of the phenomenal spread of *P. juliflora* across varying environmental conditions, in contrast to *P. cineraria* [13]. Correlations between habitats with contrasting levels of soil resource availabilities suggest that an increase in resource availability tends to increase invasion of non-native grassland communities than native plants. For example, nutrient enrichment has been consistently shown to increase the abundance of alien plant species and decrease the abundance of native ones.

3.4. Impact on economy due to invasion

Many introduced alien species for human welfare around the world are known to create environmental and economic havoc [14]. Therefore, people's views about alien spp. and their local ecological knowledge can be an effective mode to classify the exotic impacts. For example, *Acacia mangium*, an exotic species in northern Brazilian Amazon, is noted for its harmful effects to economy, environment and indigenous people through alteration of the water quality [14]. Similar reports were also noticed from India.

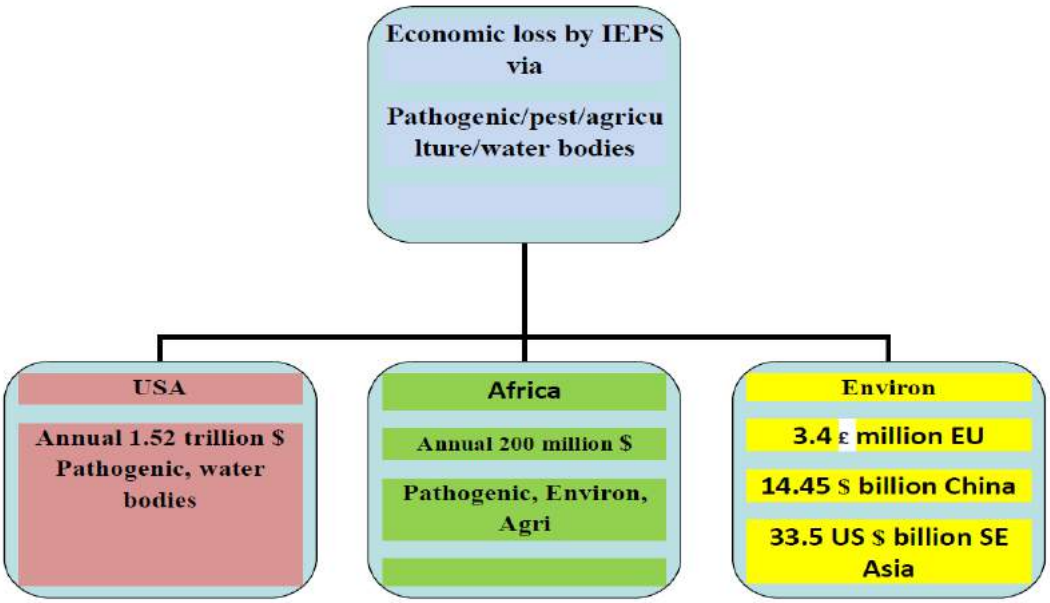
The invasion of aquatic species like *Eichhornia crassipes* in Lake Victoria has become a disaster for human welfare as it reduces fish growth and eco-tourism of the area [15]. Furthermore, the ecological niche models, and Global Climate Models have predicted a shift of water hyacinth, under climate change regime, towards European and Mediterranean regions indicating the serious economic implications of such invasion. Farming in Kuttanad depends on the entry of water into the fields. It has become routine for us to remove water hyacinth, locally known as *pola* or *kulavazha,* before preparing the fields for cultivation. The removal of weeds is labour and cost-intensive. The government provides us Rs. 4,880, but sometimes it is too meager an amount given the degree of infestation. The farmers also face difficulty in transporting machineries and harvested grains in boats through the weed-infested water channels in Kainakary. The plant chokes the life out of the freshwater ecosystem by preventing penetration of sunlight, required for the survival of underwater fauna. It also provides a breeding ground for mosquitoes, insects and disease pathogens. In Alappuzha, its overgrowth in Vembanad Lake, a designated Ramsar site, has affected the movement of passenger boats and houseboats. It causes damage to boats' engine. Fishing is another sector hit hard with large swathes of water bodies remaining carpeted with the plant. Efforts to remove the weeds from water bodies using various methods including physical, mechanical, chemical and biological have so far failed. In fact, the problem has virtually multiplied over the years. A sum of Rs. 30 crore earmarked under the first Kuttanad Package was "wasted" owing to the unscientific approach adopted. The locals in the area meet the major part of this expense by utilizing these weeds for making value-added products and thereby generating employment. Kottapuram, a village in

Thrissur district of Kerala, residents has found an innovative way to use the water weed to create jobs for poor underprivileged women.

In USA, the invaded *Tamarix ramosissima* plants has resulted in huge loss of water (1.4-3.0 billion cubic meters worth US$ 26.3-67.8 million) that deprives various human needs [15]. Similarly, *Melaleuca quinquenervia* in Florida, and *Eucalyptus* species in California, with their deep tap roots, use a huge quantity of the ground water.

In Southeast Asian context, human health sector alone suffered economic loss of US $1.85 bill ion from disease-spreading alien invaders. Negi et al., [16] attempted a long-term ecological monitoring on forest ecosystems in Indian Himalayan Region. The agriculture and health sectors together suffered an economic loss of US$33.5 billion due to the invasive species. Thus economic loss due to invaders was more pronounced in agriculture (approximately 90 % of monetary loss) than human health sector.

Shackleton et al., [17] documented in African region related with the alien species as high risk i.e. *Opuntia stricta*, was evaluated to cause the economic loss of US$ 500–1000 per household per year through participatory rural appraisal technique. Further, Sileshi et al., [18] reported that in the agriculture sector of African countries, alien invaders were evaluated to result in an economic annual loss of US$ 1 billion by causing damage to agriculture crops. Pejchar and Mooney, [15] evaluated *Myriophyllum spicatum*, an aquatic plant, in Lake Tahoe of Sierra Nevada (US), caused a recreational loss by 1%, which in monetary terms amounts to US$500 000 annually. Similarly, *Euphorbia esula* and pathogenic *Xanthomonas campestris* (citus canker) were known to cause economic loss of nearly US $200 million dollar annually [1]. It has been estimated that about US $ 600 million goes to minimize the loss caused by alien species to environment and agriculture (Fig.1).



Source [(Office of Technology Assessment.

Fig. 1: Quantification of alien species impacts in terms of economic loss driven by environmental alterations in terms of socio-ecological/economic aspects of human wellbeing of different countries - United states, China, Africa European Union, South East (SE) Asia

3.5. Impacts on the ecosystem services

Many alien/introduced exotic species are well known for their impacts on ecosystem services *viz,* aesthetic, recreational, cultural and regulatory [15]. Eiswerth et al., [19] recorded the adverse effect of alien species such as obstruction of the water navigation, they by the recreation and tourism services. Restrictions on trade of ornamental exotic species to avoid their harmful effects on environment have been reported to impact the aesthetic services of ecosystems [15]. Many alien species are also known to impact the regulatory ecosystem services i.e., hazards mitigation (e.g. landslide), water

treatment, pest management, pollination, climate change, etc., which are inextricably linked with agriculture and forestry [15].

The invasion of *Opuntia stricta* in African region adversely affected the environment and economy. It has also affected the livelihood of local people through reduction in fodder and livestock health [17]. Since the cultural values are confined to a specific community, their economic quantification is difficult [15]. The cultivation of multi-purpose trees and shrubs is encouraged widely in order to boost bioenergy and industrial sectors [20]. Although, multi-purpose plants provide several benefits to humans, the introduction of alien species as a multipurpose species like *Prosopis* sp. (mesquite) in South Africa can profoundly affect the ecosystem services [21].

3.6. Impact on invasion in diverse environment, protected areas and diversity hotspots

Hughes and Convey [22] reviewed the possible mechanism of protection of Antarctic terrestrial ecosystems from inter- and intra-continental transfer of non-indigenous species by human activities. Alien invasion of microbes, plants and animals may be occurred due to scientific explorations, industrial activities, tourism and cargo oriented travel of people [23]. Frenot et al., [24] reported the biological invasions in the Antarctic area and its impacts and implications. The red quinine tree was introduced in the treeless ecosystems of Galapagos highland, but recently it turned as invasive; thereby reduced the incoming solar radiation which in turn affected the endemic herbaceous species more adversely than non-endemic native species [25].

Foxcroft et al., [26] assumed that the well-managed protected areas, particularly those located on mountain hotspots, are resistant to plant invasion as evident from Kruger Natonal Park of South Africa. Now there is growing literature which reveals that the plant invasion is a major threat to forest biodiversity in protected areas also as is demonstrated in Gros Morne National Park in boreal Canada [26]. Najar et al., [27] analyzed the shola tree regeneration is lower under *Lantana camara* thickets in the upper Nilgiris plateau. Kannan et al., [28] warned on playing with the forest:invasive alien plant species, policy and protected areas in India.

Ecosystem functioning is derailed due to alien species to a greater extent in the geographically isolated islands than in the main lands [29]. It has been documented that such species affect the ecosystem functioning through (a) reduction in the diversity of native species and animals, (b) remarkable changes in physico-chemical soil features (mostly through allelopathy), and (c) enhancement in ecosystems response towards altered fire regimes [29]. Schindler et al., [30] and Heshmati et al., [31] documented the impacts of alien species to reduce the biodiversity of native plants, which may have adverse implications for environment functioning, ecosystem services and global climate change.

However, their proposed role in extinction was argued by invasion biologists and in order to invalidate it or ascertain it uniform dataset across the diverse habitats especially in the isolated islands are needed. Arya et al., [32] documented the ecological impact of planting indigenous plants instead of exotic Acacia trees in Anchal. Jones [33] studied the changes in cropping patterns, resilience and invasive plants of the home gardens of Kerala. Mangla et al., [34], recorded the impacts of exotic invasive plant accumulates native soil pathogens which inhibit native plants growth.

Competition between alien species vs native flora for resources regulating ecosystem functioning may lead to the invasion melt down. Simberloff and Von Holle, [35] meltdown hypothesis states that the establishment of one invasive species in a new environment makes it easier for other nonnative species to invade. The first impact of alien species is the reduction in biodiversity is common across the earth. Alien invaders are also affect the wildlife for example, Gan et al., [36] reported that the alien species *Spartina alterniflora* replaces native *Phragmites australis* and *Scirpus mariqueter* in wetlands of China, which eventually leads to the decline in avian populations due to the movement and feeding restrictions.

Eutrophication in the oligotrophic water bodies leads to intensify the strength of alien species. Similarly, alien species tend to spread at a faster rate, consequent upon the expansion of natural fire regime, which may also have adverse impacts on the ecosystem functioning. Pejchar and Mooney, [15] recorded that many alien species were found to alter the fire regimes in several terrestrial ecosystems that result in a huge socio-economic loss.

3.7. Impacts of the alien species on human health

Biodiversity and its changes are inextricably linked with the human health, both in positive and negative sense like malaria transmission, positive health effects of diversity in nature and green spaces etc [37, 2]. Positive

implications include their applications in vector borne control and ethno-medicinal uses. For instance, a mosquito repellent was extracted from *Lantana camara* [37]. *Ambrosia artemisiifolia, Parthenium hysterophorus, Ailanthus altissima, Acacia, Acer, Casuarina, Eucalyptus, Helianthus, Platanus and Xanthium* were some of the alien species which cause allergy in human beings.

Lake et al., [38] tried to prioritize the impacts of alien species on human health, through direct exposure, as vectors or through transfer of toxins in edibles. *Lantana camara* provides a favourable habitat to tse-tse fly which causes sleeping sickness. Likewise, brush tail possum transmits bovine tuberculosis to live-stock and deer in New Zealand, affecting human health indirectly through food-chain; whereas *Parthenium hysterophorus* serves as a vector of Malaria. Similarly, *Ixodes scapularis* is a vector of *Borrelia burgdorferi*, which causes the Lyme disease in humans.

The prominent aquatic alien species like *Phragmites australis* and *Typha* assist in the colonization and multiplication of vector-borne pathogens, particularly West Nile virus [39]. *Eichhornia crassipes* is a high risk alien species, helping in the spread of schistosomiasis [37]. *Arundo donax* another top ranked alien species posing severe threats to the global environment and health. Trade of such aquatic plants facilitates the spread of disease causing vectors and increases the health risks from vector borne diseases [37]. Water blooms like cyanobacteria that release the cyano-toxins like microcystin, hepatotoxins, saxitoxins, lynbyatoxin and anatoxins are teratogenic (embryotoxic), carcinogenic, and promote tumours. These bio-toxins enter into food chain through the edible species of aquatic ecosystems like water chestnut, fishes etc. Besides the bacterial invaders, there are several other alien species which release diverse chemical toxins for example, grayanotoxins of *Rhododendron ponticum*, which contaminates honey with hazardous toxins. Similarly, the sap of *Ailanthus altissima* upon direct contact effectuates myocarditis, glochids of *Opuntia stricta* cause the eye irritations, retrorsine, an alkaloid of pyrrolizidine group from *Senecio inaequidens, Cortaderia selloana*, *Spartina anglica*, *Caesalpinia decapetala,* and *Rosa rugosa* causes skin cuts and injuries owing to their sharp edge and silicate crystal depositions on leaves. Several ornamental alien species also pose health issues as they emit toxins in the environment. For example, Allergen-specific immunotherapy is considered the most effective tool for managing human health issues due to such allergic species, whereas the adoption of ecological breeding measures like cross-breeding, and understanding the invasion biology of the may be useful for reducing their health impacts. However, species specific focused studies are needed to provide an insight of health hazards, emanating from the exposure alien species for developing better mitigation strategies [40].

3.8. Invasion is it a nuisance? The quest of management implications

Biologists in the field of invasion of alien species are now realizing that not all the alien species impose threats to environment [41]. Pejchar and Mooney [15] reported that 99% of the selected alien species were used globally as food crops directly or indirectly. Even, certain species like *Lantana camara* and *Ageratum conyzoides* were reported to have some ethno medicinal roles in primary health care [20].

IUCN's (2003) clearly states that management of alien species is a priority issue and must be mainstreamed into all aspects of managements of forests and protected areas. Both positive as well as negative ecosystem services must be clearly identified to elucidate their cost-benefit to guide the stakeholders and policy makers [17]. In biodiversity conservation, identifying/ prioritizing alien species has been given the top priority. In this respect, 10% of coastal/ marine areas and 17% of terrestrial and inland water areas are conserved through the diverse targets/action plans. Further, attention is needed for the management of global protected areas, which cover the 14.9 %, of the terrestrial realm.

4. CONCLUSION

The invasion of exotic species is the major concern throughout the earth and has adverse impact on vegetation and agricultural system. There are multiple features which influence the invasion process of alien species. Various mechanisms of invasion of alien species have been proposed. Studies highlighted that antibiosis has major role in establishment and rapid invasion of alien species. Studies documented that the allelochemicals leached from the exotic species are the major factor to compete them with habitat and environment for successful invasion. Similarly, different strategies have been also discussed regarding control of the invasive plant species including biological, cultural and chemical practices. The consequences of invasion are, diverse across the states. Public awareness related to environmental change and biodiversity loss related to alien invasion is mandatory. Sustainable utilization of

land and to counter the invasive species on the native flora and biodiversity is to be designed. The rate of spread of alien species in each of the climatic zones is different. There is also a need to give adequate resources and strategies through which ideal management can be done to control the invasion process in future.

Conflict of interest

The authors report no conflict of interest

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Research Paper

Qualitative Detection of Triterpenes and Quantification of Betulinic Acid from Hexane Extract of *Simarouba glauca* Leaves by Gas Chromatography-Mass Spectrometry and High-Performance Thin Layer Chromatography

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The present study focuses on the efficiency of high-performance thin layer chromatography and gas chromatography-mass spectrometry analysis in qualitative and quantitative analysis of triterpenoid from the terpene fraction of hexane extract of *Simarouba glauca* leaves. The total terpenoid content of the hexane extract was assessed which shows that 73.69 % of the extract content is terpenoid. The terpene fraction extracted in petroleum ether from the hexane extract of *Simarouba glauca* leaves was subjected to gas chromatography-mass spectrometry and high-performance thin layer chromatography analysis. Gas chromatography-mass spectrometry analysis results indicated seventeen compounds out of which only one was triterpene (Squalene an important bioactive triterpenoid). In high-performance thin layer chromatography the separation was achieved by using hexane:ethyl acetate in a 5:5 proportion as mobile phase and anisaldehyde sulphuric acid reagent was used for derivatization which imparted violet color to the triterpenoid containing bands. Detection and quantification of betulinic acid and other triterpenes was done by densitometric scanning at 525 nm. Betulinic acid produced compact spots at Rf 0.66. Linear range of betulinic acid was prepared using concentrations 1-7 µg/spot with a correlation coefficient R2 and standard deviation of 0.96004 %±19.68 % respectively. The results indicated the presence of 10 triterpenoids showing different Rf values including betulinic acid. This study confirmed the presence of betulinic acid in the terpene fraction of the hexane extract of *Simarouba glauca* leaves.

Key words: *Simarouba glauca*, betulinic acid, high-performance thin layer chromatography, gas chromatography-mass spectrometry, squalene

Simarouba glauca (*S. glauca*) DC. also known as paradise tree or bitter wood, is an evergreen small to medium sized and shade tolerant tree. It is well known for its medicinal properties and is used as a traditional medicine in different parts of the world. The leaves and bark are used in the treatment of various diseases. Lakshmi *et al.*[1] reported the *in vitro* antibacterial, anti-oxidant, hemolytic and thrombolytic activities of *S. glauca*. Researchers have discovered a range of medicinally active compound in the plant. The leaf extracts have shown anticancer properties against different cancer cell lines like T lymphoblast (MOLT-3), human immortalised myelogenous leukemia (K-562), erythroleukemia (KG-1) and human urinary bladder (T-24) cell lines[2,3]. Rivero-Cruz *et al.*[4] isolated four alkaloid derivatives from *S. glauca* having cytotoxic activity against human colon cancer, human oral epidermoid cancer, human hormone-dependent prostate cancer and human lung cancer cells. But the major groups of compounds which contribute to the anticancer properties of *S. glauca* were identified as triterpenes and their derivatives known as quassinoids. Tricaproin isolated from this plant inhibits the growth of human colorectal carcinoma cell lines by targeting class I histone

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deacetylase[5].

The quassinoids shows strong anticancer property. The identified phytochemicals include glaucarubol, glaucarubinone, scopoletin, canthin-6-one, squalene, tricaproin etc. which possess various biological activities and many of which have been patented[6-10]. Recent works have reported and isolated many different triterpenes from various parts of *S. glauca* but the presence of betulinic acid which is a well-known triterpene having various biological activities is not yet reported from this plant. Betulinic acid is a pentacyclic triterpene acid which is found in the bark of various species of plants. As a natural compound it shows wide range of pharmacological activities because of its low toxicity which includes inhibition of Human Immunodeficiency Virus (HIV), antibacterial, antimalarial, anti-inflammatory and antioxidant properties. Betulinic acid shows potent anti-maturation activity against HIV-I[11]. Fulda *et al.*[12] identified betulinic acid as a new cytotoxic agent against neuroectodermal tumor cells including neuroblastoma, medulloblastoma, glioblastoma and Ewing's sarcoma cells, which represent the most common solid tumors of childhood. Park *et al.*[13] reported that the anticancer effect of betulinic acid is mediated through reactive oxygen species dependent cell cycle arrest and apoptosis. Betulinic acid extracted from the leaves of *Vitex negundo* demonstrated antibacterial activity against *Bacillus subtilis* at a concentration of 1000 ug/disc with a zone of inhibition of 18.8 mm2[14]. *In vitro* antiplasmodial activity (half maximal inhibitory concentration (IC_{50})) of the betulinic acid was studied and isolated from the root bark of the Tanzanian tree against chloroquine-resistant (KI) and sensitive (T9-96) *Plasmodium falciparam* were found to be 19.6 ug/ml and 25.9 ug/ml respectively[15]. Recio *et al.*[16] reported the analgesic and anti-inflammatory activity on betulinic acid isolated from *Diospyros leucomelas*. Zuco *et al.*[17] studied the anticancer activity of betulinic acid for selective tumor growth inhibition without damaging the normal cells. The present study was aimed to find out the qualitative and quantitative detection of various classes of triterpenes by using Gas Chromatography-Mass Spectrometry (GC-MS) and High-Performance Thin Layer Chromatography (HPTLC) with special emphasize on betulinic acid.

MATERIALS AND METHODS

Plant collection:

The leaves of *S. glauca* were collected from College junction, Kollam district (8°52'43'' N latitude and 76°36'10'' E longitude) in the month of September 2018 as shown in fig. 1.

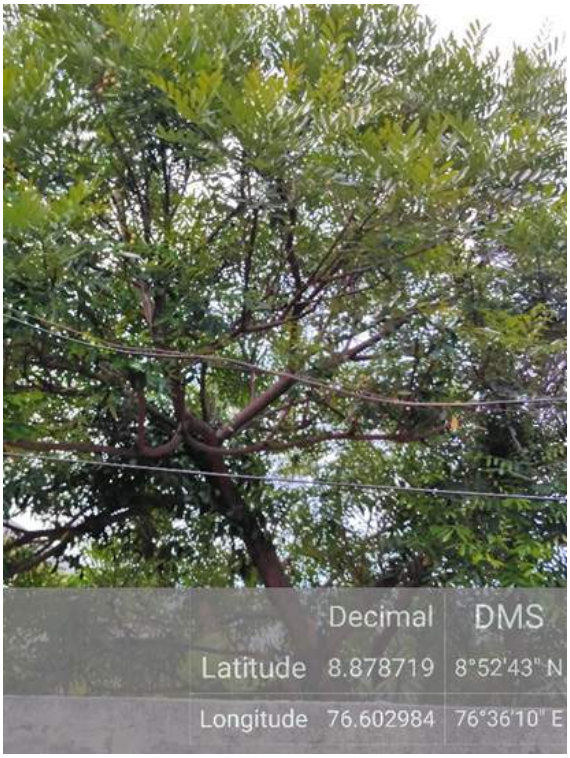


Fig. 1: Photograph of *S. glauca* plant from which the leaves were collected

Extraction in n-hexane:

All chemicals and solvents used were of analytical grade and obtained from Nice® Chemicals Ltd. 30 g of dried leaf powder was subjected to Soxhlet extraction with 250 ml of hexane. Extraction was carried out for 9 cycles and temperature was maintained at 65°. The color of the extract was dark green. The extract was collected and cooled at room temperature filtered through filter paper and poured in glass petri dishes and then evaporated at 40° using hot air oven. Dried extract was kept in desiccator for 2 d and stored at 5° in airtight containers until further use.

Preparation of standard solution:

Betulinic acid was used as a standard both for qualitative detection of triterpenes and for the quantitative detection of the betulinic acid in the plant extract using in HPTLC. For this purpose, Betulinic acid ≥98 % high-performance liquid chromatography grade was purchased from sigma and a 100 µg/ml solution was prepared by transferring 0.1 mg of accurately weighed betulinic acid into 1 ml ethyl acetate and mixing it thoroughly.

Extraction and quantification of terpenes:

The total terpenoid was extracted using standard protocol[18]. 100 mg of dried hexane extract was taken and soaked in 9 ml of ethanol for 24 h. The extract after filtration, was extracted with 10 ml of petroleum ether using separating funnel. The ether extract was separated in pre-weighed glass vials and waited for its complete drying. Ether was evaporated and the yield (%) of total terpenoids contents was measured by the formula

Percentage yield=$(wt_i\text{-}wt_f/wt_i)\times100$

Where,

wt_i represents initial weight of the dried plant extract (100 mg) and wt_f weight of the terpene fraction left after complete drying of ether. The dried terpenoid fraction (0.24 g) was dissolved in 10 ml hexane and used for GC-MS and HPTLC analysis.

Anisaldehyde-sulphuric acid reagent:

Place 170 ml of methanol in 200 ml glass bottle and cooled it down in ice cube water bath. To the ice-cold methanol, 20 ml of acetic acid and 10 ml of sulphuric acid were added slowly and carefully and mixed well. Allow the mixture to cool to room temperature, then added 1 ml of anisaldehyde.

GC-MS analysis of terpene extract:

The GC-MS analysis was carried out using a 7890A Gas chromatograph equipped and coupled to a triple axis mass detector, DB-5MS 30 m×0.250 mm×0.25 mm thickness capillary column. The instrument was set to an initial temperature (oven temperature) of 40° for 5 m. At the end of this period, the rate of increase of temperature was 5°/min. Final temperature maintained was 280° for 10 m, 3 ul of sample was injected and the injector temperature was maintained at 280°. For GC-MS detection an electron ionization system with ionization energy 80 eV was used and helium was used as a carrier gas at a constant flow rate of 1 ml/m and pressure 7.0699 psi. The quantification of the components was based on the total number of fragments of the metabolites as detected by the mass spectrometer. The identification of the chemical components was carried out based on the Retention time (Rt) of each component compared with those of the National Institute of Standards and Technology 08 mass spectral libraries.

HPTLC analysis of terpene extract:

Chromatography conditions: Chromatography was performed on a 10×10 cm reactivated HPTLC Silica gel 60 F254 plates (Merck, Darmstadt, Germany). 10 µl, 30 µl, 50 µl and 70 µl of the samples and standard were separately applied to the plate by spotting on HPTLC plate using automatic TLC applicator Linomat-V with N_2 flow (CAMAG, Switzerland), with a band width of 8 mm and 8 mm from the bottom. Scanning was performed with CAMAG scanner III at 525 nm with a speed of 20 mm/s. A slit dimension of 5×0.45 was employed. Linear ascending development was carried out in a 10×10 cm CAMAG twin glass tank pre-saturated with the mobile phase at room temperature. 10 ml of hexane:ethyl acetate in a 5:5 proportion was used for chromatographic development.

Detection and quantification: After development, plates were dried with a hair dryer and then derivatized in 200 ml of anisaldehyde sulphuric acid reagent in immersion device CAMAG and heated at 105° for 5 min. The concentration of betulinic acid present per spot of the plant extract applied was calculated from the standard curve obtained from the HPTLC analysis.

RESULTS AND DISCUSSION

The results indicated that terpenes are the most dominant class of phytochemicals present in the leaves of *S. glauca*. The terpene content determined was 73.69 mg/100 mg which accounts for about 73.69 % of the total phytochemical content. The GC-MS analysis results indicated the presence of seventeen compounds out of which seven were terpenes. The chromatogram represents the peaks of detected compounds shown in fig. 2. Out of the seven terpenes three sesquiterpenes, two monoterpenes, one diterpene and one triterpene were identified (Table 1). The Rt, compound name and molecular formula are presented in Table 2[19-23]. The triterpenoid identified in GC-MS analysis was squalene. Squalene is a very important bioactive triterpenoid. Many steroids like cholesterol are squalene derivatives. An entire class of triterpenoids is represented as squalene group many of which have important bioactivities. Studies have suggested that squalene has a potential to decrease fibrosis induced as a result of atherosclerotic diet have been reversed by hydroxytyrosol and squalene, natural products from the minor fraction of virgin olive oil[24]. Squalene has been shown to have anti-oxidant activity in mammary epithelial tumor cells[25]. Studies have reported the anticancer property of squalene[26]. Ganbold *et al.*[27] reported a new amphiphilic squalene derivative improves metabolism of adipocytes differentiated from diabetic adipose-derived stem cells and prevents excessive lipogenesis.

The chromatographic analysis after derivatization with anisaldehyde sulfuric acid reagent showed the presence of 10 bands in violet color with different Retention factor (R_f) values indicating the presence of ten different compounds (fig. 3). Triterpenes produce violet and blue color when treated with anisaldehyde sulphuric acid reagent and heated at 105°[28]. The standard triterpene used here for validation was betulinic acid which also developed a violet color. Thus, ten different triterpenes were detected. Quantitative analysis of the betulinic acid was done by scanning the plates at 525 nm using CAMAG TLC scanner III equipped with win-CATS-V 1.2.3 software (CAMAG). The identification of betulinic acid was confirmed by superimposing the Ultraviolet (UV) spectra of the samples and standards within same R_f 0.66 window (Table 3). A calibration curve for betulinic acid was plotted with four known standard concentrations 1 µg, 3 µg, 5 µg and 7 µg by spotting 10 µl, 30 µl, 50 µl and 70 µl of the standard solution on HPTLC plate respectively with a band width of 8 mm. Each concentration peak area in the plant extract was plotted against the concentration of betulinic acid spotted or injected. The linear regression of standard curve was determined with R_2=0.96004 %±19.68 % as shown in fig. 4.

The standard triterpene betulinic acid produced a violet-colored band R_f (0.66). All four concentrations of plant extract showed the presence of spot at Rf value 0.66 corresponding to betulinic acid. The results clearly indicate the presence of betulinic acid in the hexane extract of *S. glauca* leaves. The concentration of betulinic acid obtained in 10-70 µl of the fraction is provided in Table 4. The concentration of betulinic acid did not show a steady increase with the increasing concentration of the terpene fraction applied but the presence was confirmed by the presence of the same R_f value 0.66 band corresponding to betulinic acid in all the sample concentrations (fig. 5). As described, triterpenes produce violet color after derivatization with anisaldehyde sulphuric acid reagent followed by heating so the other nine bands which produced violet colour and showed absorbance at 525 nm similar to betulinic acid were identified as triterpenes as shown in fig. 6[28].

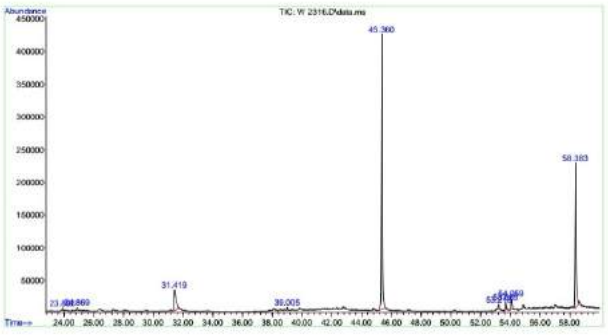
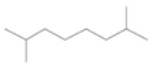
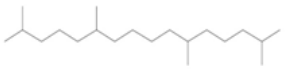
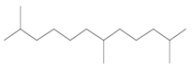
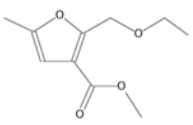
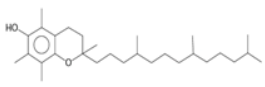
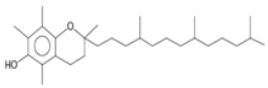


Fig. 2: GC-MS chromatogram of terpene fraction extracted in petroleum ether from hexane extract of *S. glauca* leaves. The peaks with their corresponding Rt are depicted in the chromatogram

TABLE 1: THE PHYSICAL PROPERTIES OF THE COMPOUNDS DETECTED IN THE GC-MS ANALYSIS OF THE TERPENE FRACTION OF *S. glauca* LEAVES

Sl. no	Name of the compound	Rt	Molecular formula	CAS No
1	Octane,2,7-dimethyl-	23.891	$C_{10}H_{22}$	1072-16-8
2	Decane,2,9-dimethyl-		$C_{12}H_{26}$	1002-17-1
3	Octane, 3,5-dimethyl-	24.873	$C_{10}H_{22}$	15869-93-9
4	Undecane,4,7-dimethyl-		$C_{13}H_{28}$	17301-32-5
5	Dibutyl phthalate	31.415	$C_{16}H_{22}O_4$	84-74-2
6	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester		$C_{16}H_{22}O_4$	17851-53-5
7	Hexadecane,2,6,11,15-tetramethyl-	39.009	$C_{20}H_{42}$	504-44-9
8	Dodecane,2,6,11-trimethyl-		$C_{15}H_{32}$	31295-56-4
9	1,2-Benzenedicarboxylic acid, diisooctyl ester	45.362	$C_{24}H_{38}O_4$	27554-26-3
10	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester		$C_{16}H_{22}O_4$	4376-20-9
11	Squalene	53.214	$C_{30}H_{50}$	7683-64-9
12	2,6,10,14,18,22-Tetracosahexane,2,6,10,15,19,23-hexamethyl-(all-E)-		$C_{30}H_{50}$	111-02-4
13	1-pyrrolidinebutanoic acid,2-[(1,1-dimethylethoxy) carbonyl]-α nitro-,2,6-bis(1,1-dimethylethyl)-4-methoxyphenyl ester, [S-(R*,R*)]-	53.684	$C_{28}H_{44}N_2O_7$	124201-86-1
14	3-furancarboxylic acid, 2-(ethoxymethyl)-5-methyl-methyl ester		$C_{10}H_{14}O_4$	35339-98-1
15	Acetamide, N-(4-methylphenyl)-N-[4-methyl-2-[[2-(phenyl amino) phenyl] methyl] phenyl]-	54.06	$C_{29}H_{28}N_2O$	52812-78-9
16	Vitamin E	58.38	$C_{29}H_{50}O_2$	59-02-9
17	dl-α-Tocopherol		$C_{29}H_{50}O_2$	10191-41-0

TABLE 2: THE NAME OF THE IUPAC NAME, STRUCTURE, MOLECULAR WEIGHT AND BIO-ACTIVITY OF THE TERPENES DETECTED IN TERPENE FRACTION OBTAINED FROM HEXANE EXTRACT OF *S. glauca* LEAVES IN GC-MS ANALYSIS

Name of the compound	Structure	M.W	Activity
Octane,2,7-dimethyl- (monoterpene)		142	No biological activity reported
Hexadecane,2,6,11,15-tetramethyl-(diterpene)		282	Molecular indicator for the anaerobic oxidation of methane[19]
Dodecane,2,6,11-trimethyl-(sesquiterpene)		212	No biological activity reported
Squalene 2,6,10,14,18,22-Tetracosahexane,2,6,10,15,19,23-hexamethyl- (all-E)- (triterpene)		410	Antioxidant and antitumor
3-furancarboxylic acid, 2-(ethoxymethyl)-5-methyl-methyl ester (monoterpenoid)		198	No biological activity reported
Vitamin E (sesquiterpene)		430	Dietary supplement important antioxidant protection of vision and health of blood, brain and skin[20-22]
dl-α-Tocopherol (sesquiterpene)		430	Antioxidant and anticarcinogenic[23]

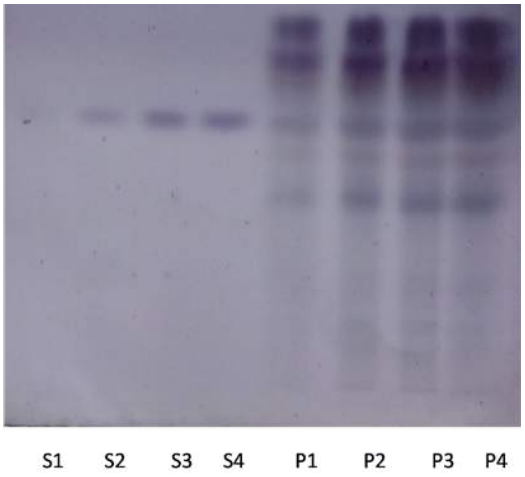


Fig. 3: HPTLC chromatogram of betulinic acid and terpene fraction extracted in petroleum ether from hexane extract of *S. glauca* leaves. The chromatogram after derivatization in anisaldehyde-sulphuric acid reagent under 525 nm. S1-S4 tracks represent standard Betulinic acid 1 µg, 3 µg, 5 µg and 7 µg/spot concentrations and P1-P4 represent terpene extract 10 µl, 30 µl, 50 µl and 70 µl/spot.

TABLE 3: THE RF VALUE, ABSORBANCE AREA AND % AREA OF TEN PEAKS CORRESPONDING TO TRITERPENES OBTAINED FROM THE TERPENE FRACTION OF *S. glauca* LEAVES AFTER DERIVATIZATION WITH ANISALDEHYDE SULPHURIC ACID REAGENT AT 525 nm

Peaks	R_f value	Inference
1	0.1	unknown
2	0.13	unknown
3	0.14	unknown
4	0.24	unknown
5	0.26	unknown
6	0.47	unknown
7	0.58	unknown
8	0.66	Betulinic acid
9	0.77	unknown
10	0.82	unknown

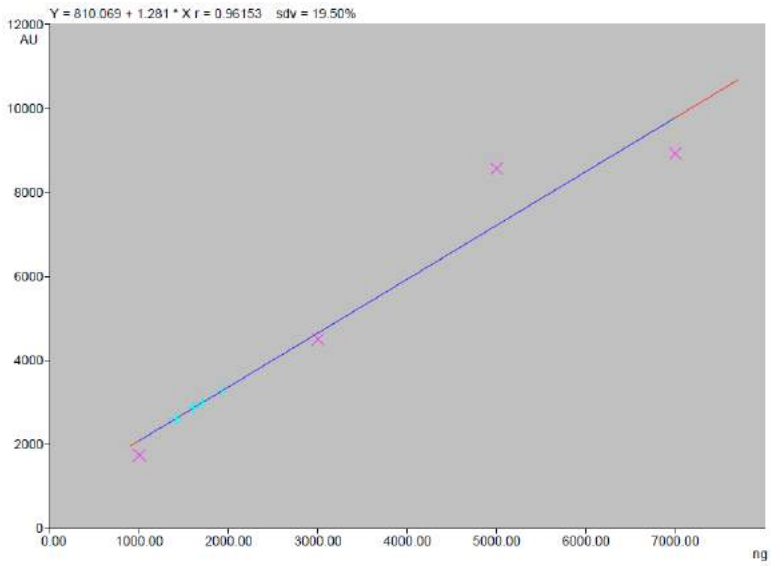


Fig. 4: Calibration curve of standard betulinic acid prepared using concentrations 1-7 µg with a correlation coefficient R^2 and Standard deviation of 0.96004±19.68 % respectively

The present study was intended to detect different triterpenoids present in the terpene fraction extracted from hexane extract of *S. glauca* leaves using GC-MS and HPTLC. HPTLC method was used to qualitatively and quantitatively detect the presence of betulinic acid from the leaves extract of *S. glauca*. Although many triterpenoids and quassinoids have been detected from different parts of *S. glauca*, no study has concentrated on qualitative and quantitative detection of betulinic acid from leaves of *S. glauca*. In the present study the GC-MS analysis was not found to be an effective tool to detect triterpenoids as only one triterpene squalene was detected in GC-MS. This may due to heat stable nature of most of the triterpenoids, in contrast to monoterpenes and diterpenes which are more heat liable. But HPTLC results clearly indicate the presence of ten triterpenoid including betulinic acid which was not detected in GC-MS analysis. The betulinic acid was confirmed by the presence of corresponding R_f value similar to the standard betulinic acid. The densitometric chromatogram did not show an increase in betulinic acid concentration with the increasing concentration of the terpene fraction.

To conclude, the present study indicates that GC-MS is not an effective tool for detection of triterpenes when compared to HPTLC as HPTLC showed the presence of ten triterpenes while GC-MS could detect only one triterpene (Squalene). The identification of these triterpenes requires further analysis using either Mass Spectroscopy (MS) in combination with HPTLC or other techniques like Liquid Chromatography Mass Spectroscopy (LCMS). The study for the best of our knowledge newly reports the presence of betulinic acid in the terpene fraction extracted using petroleum ether from hexane extracts of *S. glauca* leaves. Thus, leaves of *S. glauca* can be used as a source for the extraction of betulinic acid which is a potent anti-cancer agent. Future works can focus on the extraction and identification of different triterpenes from the hexane extracts of *S. glauca* which will help to find out the other biologically active triterpenes and similar or modified versions of betulinic acid which can be exploited for the therapeutic purpose.

TABLE 4: THE CONCENTRATION OF BETULINIC ACID OBTAINED FROM THE DENSITOGRAM

Plant extract (µl)	Concentration of Betulinic acid obtained from peak height (µg)	Concentration of Betulinic acid obtained from peak area (µg)
10	1.833	1.608
30	1.983	1.925
50	1.722	1.706
70	1.503	1.403

Note: The concentration of betulinic acid obtained upon loding 10-70 µl of the terpene fraction obtained from hexane extract of *S. glauca* leaves, calculated according to the peak height and peak area

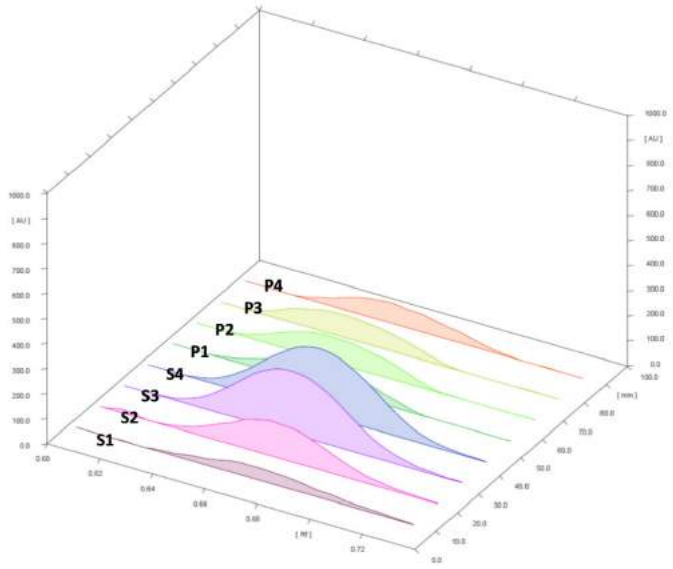


Fig. 5: 3D-Densitogram of the terpenoid fraction extracted in petroleum ether from hexane extract of *S. glauca* leaves showing the peaks of betulinic acid obtained in different concentrations of extract (10 µl, 30 µl, 50 µl and 70 µl) along with the standard betulinic acid concentrations

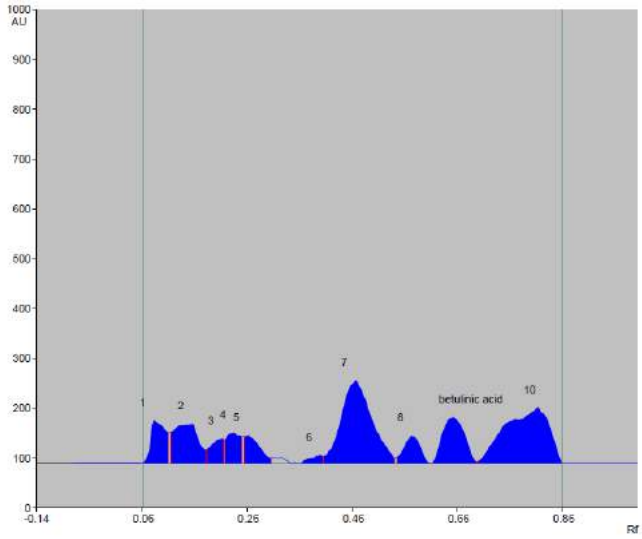


Fig. 6: Densitogram of the terpenoid fraction extracted in petroleum ether from hexane extract of *S. glauca* leaves showing ten peaks corresponding to different bands of triterpenes including betulinic acid after derivatization with anisaldehyde sulphuric acid reagent at 525 nm

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Conflict of interests:

The authors declared no conflict of interests.

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Research Article

Assessment and impact of alien species - *Mimosa invisa* L. on the biodiversity and pattern of vegetation at Dhoni hills, Western Ghats of Palakkad, Kerala-A case study

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Abstract
Mimosa invisa is a widely adapted weed from tropical America that has invaded the Dhoni hills of Palakkad District, Kerala. They were established as monocultures in grasslands, agricultural fields, plantations and forest areas of Palakkad, causing threats to other species. In this juncture, the present study was conducted to evaluate the impact *of Mimosa invisa* on the natural biodiversity and floristic compositions of native species of Dhoni hills, Palakkad. Vegetation analysis was carried out using random-systematic design and gradient methods, including the importance value index, species richness, dominance index, diversity, similarity and dissimilarity index, using standard protocols, followed by soil parameters such as pH and nutrient content and phenols in the invaded and uninvaded areas. It was noticed that in the *Mimosa* invaded area, the mean species number and the α diversity declined by 32.10% and 41.21%, respectively. Similarly, fresh and dry plant weight displayed remarkable variation (decreased by 35.9 and 49.9%, respectively) in the intruded zones. Out of 135 species recorded, 63 species were common in the control and intruded zones. Eleven species were growing exclusively in the invaded areas. The total phenolic content was 45%, the ion conductivity was 32%, the % of organic carbon and organic matter was 51%, the nitrogen content was 55.7%, and the phosphorus, potassium and sodium contents were 48, 38.5 and 24.4%, respectively, in the invaded soil compared to the control. Similarly, the calcium, magnesium and chloride contents were increased by 38.4, 30.6 and 33.5% respectively. Hence, it could be concluded that the invasion of *M. invisa* drastically affected the productivity and diversity of the invaded areas in the Dhoni hills of Palakkad.

Keywords: Biomass, Biodiversity, Dhoni Hill, Invasive species, *Mimosa invisa*

INTRODUCTION

Biological invasion threatens biodiversity, ecosystem dynamics, resource availability, the national economy and human health worldwide (Ricciardi *et al.,* 2000). It is a pervasive and costly environmental problem. Over the last half of the last century, it has become the focus of intense management and research activities worldwide. Invasion of native communities by exotic species has become the most intractable ecological problem in recent years (Sharma *et al.,* 2005). Invasion of exotic species is a global-scale problem experienced by natural ecosystems and is considered the second largest threat to biodiversity globally (Global Invasive Species Programme, 2005). In India, especially in the dry deciduous forest region, no information is available on demographic instability caused by the exotic species *Mimosa invisa*. *Mimosa* is ranked at the top of the highest impacting invasive species and is considered one of the world's 100 worst invasive alien species (Geographic Information System in of plant (GISP) taxonomy, 2005). According to Sharma *et al.* (2005), the invasive species have spread in almost all areas of dry deciduous regions. In India, tropical forests account for

approximately 86% of the total forest land (Mahato *et al.,* 2021), while dry forests account for 38.2% of the total forest cover (Padmakumar *et al.,* 2018). Natural forests are under immense pressure due to various human-induced activities. In Dhoni hills, the establishment of cement factories, quarrying for limestone and thermal power stations have resulted in a rapid population increase, which has caused deforestation and the conversion of natural forests into marginal croplands. *Mimosa* has strong allelopathic properties, and they interrupt the regeneration of other plant species in their invaded area by decreasing seed germination, reducing early growth rates and selectively increasing the mortality of other plant species, which ultimately results in the reduction of species diversity and decline of species (Uko *et al*., 2020).

Mimosa invisa is a shrubby sprawling annual plant that behaves as a perennial vine in certain years. The stem is bunching, often scrambling over other plants, four-angled and the angles with a line of sharp, hooked prickles. *M. invisa* scrambles vigorously over other plants, forming dense tangled thickets up to 2 m high (Wang *et al.,* 2019). They are nitrogen fixers and rapidly growing species. Their sharp, recurved thorns make stock reluctant to graze on them, as it is difficult to penetrate the stands. It is difficult to harvest crops infested with *M. invisa* because of their thorns. They are commonly seen along roadsides and in moist waste places. They cause major problems in plantations of coconut, tea, rubber, sugarcane, pineapple, and other croplands and pastures. In this scenario, the present study aimed to compare the impact of *M. invisa* invaded and non invaded areas on the flora and soil parameters of Dhoni hills, Palakkad, and Kerala.

MATERIALS AND METHODS

Study area

. The western Ghats mountain range covers 160,000 km² in a stretch of 1,600 km parallel to the western coast of the Indian Peninsula, traversing the states of Karnataka, Goa, Maharashtra, Gujarat, Kerala, and Tamil Nadu. The western ghats are interrupted by the Palakkad gap, approximately 30 km wide. They reappear abruptly as the Annamalai Palani block, whose high plateau attains a height of 2695 m, the highest point in South India, the Anamudi peak. Dhoni hills is one of the fast-changing areas of the Palakkad district situated between 76°21' to 77° east longitude and 10° 15' to 11°15' north latitude. It is situated at the foot of the Western Ghats and on the Palakkad gap. The altitude ranges from 90 m to 1525 m above mean sea level. The climate in the area is subtropical. The average rainfall in this area is approximately 1800 to 3510 mm. The minimum temperature in the hills is 10°C in winter, and the maximum is40°C in summer. Dhoni Hills was the study area. Tropical thorn forests, tropical dry forests, subtropical broad-leaved forests and tropical evergreen forests are the potential vegetation of this area.

Methodology

Vegetational analysis

The vegetation analysis study was performed using the random-systematic design and gradient methods of Barbour *et al.* (1999). To study the impact of *M. invisa* on other plant species, a vegetational analysis was performed from October 2009 to March 2010. Three-invaded sites of *M. invisa* were selected randomly from Dhoni hills. A noninvaded area with *Mimosa* was also selected as a control to compare the diversity, species richness and composition of vegetation in the intruded and nonintruded zones. A 200 m^2 study spot with 20 quadrats of 2 m^2 size was constructed in random mode for the present evaluation. Entire species in the intruded and nonintruding zones were screened to quantify their importance value index (IVI) (Mishra, 1968). In addition, species richness, dominance index, diversity, similarity and dissimilarity index were analysed. The evenness of the intruded and non intruded zones was also quantified and matched to pinpoint species loss due to the *M. invisa* invasion. To avoid conceptual and technical problems and to obtain precision, only a few indices, such as Margalef's richness, Hill's evenness, Shannon's diversity, and Simpson's index of dominance, were used in the study (Ludwig and Reynolds, , 1998). The vegetation other than invasive species in the study area was uprooted, and their fresh and dry biomass (after oven drying) was measured (Noumi, 2015).

Soil analysis

Parameters such as pH variation, soil electric conductivity, phenolic content, organic carbon and related matter, and available minerals such as N, P, K, Na, Ca, Mg and Cl were analysed between the *M. invisa* intruded and non intruded zones. The soils were gathered after eliminating litter of the top layer (3.5 – 5.5 cm) from each zone. The soil samples were filtered, dried in the shade and kept until further studies. The soil pH and electrical conductivity were recorded after placing the soil extract in a 1:2 ratio (soil: water w/v) by applying a digital pH-sensitive meter and an EcoScan Con 5 digital conductivity meter. The soil phenolics were quantified following the Buondonno *et al.* (2014) protocol. Organic carbon and organic matter were estimated by the rapid titration method of Walkey and Black (1934). Available N was estimated using the alkaline potassium permanganate method of Castro *et al.* (2008). Available phosphorus was determined by the method of Koralage *et al.* (2015), Na^+ and K^+ were estimated as per the method of Fardous *et al.* (2010), and available Ca^{2+}, $Mg^{2+}$and Cl^- were determined by the method of Black (1973).

Statistics analysis

SPSS ver. 10.0 Origin 6 and Micorstat were used for statistical analysis of each experiment. The significance of paired treatment was determined using Student's 2 sample *t*-test. The significance ($P < 0.05$ or $P < 0.01$) of the variation in the soil characteristics of the control and *Mimosa* intrusion zones was evaluated using a *t*-test.

RESULTS

Influence of *Mimosa invisa* on the diversity of species

The intrusion of *M. invisa* significantly (0.01%) affected Dhoni hills' diversity and vegetation composition, Palakkad. The present study revealed 123 plant species in the *Mimosa* uninvaded area. In contrast, 74 in the intruded zone (Table 1), i.e., the species number, declined by 38.8%in the intruded area compared to the control plot. Margalef's index of species richness, α-species diversity and evenness index were determined to be 48.6, 41.3 and 20.9%, respectively, in the *M. invisa* intrusion zones. Similarly, the number of abundant species (A1 & A2) was recorded in the *M. invisa* intrusion zones. The index of dominance has maximal values in the intruded zones, which suggests that communities were homogenous, with one species dominant compared to more heterogeneity in the uninvaded areas. The similarity index of communities in the invaded and noninvaded areas was only 51.4%, clearly indicating diversity loss due to the invasion of the exotic species *M. invisa*. Comparison of fresh and dry plant weight from the intruded and nonintruded zones also displayed remarkable variation (decreased by 35.9 and 49.9%, respectively) in the intruded zones.

Influence of *M. invisa* intrusion on the composition of flora

The composition of flora narrates the distribution pattern of species in aspecific habitat.In the current study, the flora compositions of the *M. invisa*-intruding and non intruded zones were compared. A total of 135 plant species of 51 flowering families were noticed during the current study. Thirty-eight families were noticed in the control zone compared to 23 in the *M. invisa*-intruding zones. Out of 135 species recorded, 63 species were uniform in control and intruded zones (Table 2). Eleven species were growing exclusively in the *M. invisa* invaded areas. *M. invisa* was found to be a major plant species in the invaded area in addition to *Cynodon-dactylon*, *Eclipta alba*, *Tribulus terrestris*, *Barleria cristata, Holarrhena antidysenterica* and *C. carandas*, while *Adhatoda vasica* was a well-established plant species in the control areas along with *C. dactylon*, *E. alba, B. cristata, C. carandas, Andrographis paniculata*, *Aspargus aspera,* and *Phyllanthus amarus*. In both study areas, the number of herbal species was quite high when compared to other life forms. Even though the number of herbal species was lower than that of other species habits in the intruded zones, it is plausible to suggest that herbs were affected more than other habits of species (Table 2). The sequence of species in both zones of the study was in the declining order of their IVI values, and it revealed that the species became less consistent in the *M. invisa* intruded zones (Fig. 1). Significant medicianal herbals were noticed in the control zones, such as *Vitex altissima, E. alba, A. paniculata, C. dactylon, A. aspera, A. vasica* and *C. carandas* (Fig. 2). The invasion of *M. invisa* mostly affected medicinal plants such as *Vitex altissimia, E. alba, A. paniculata, C. dactylon, A. aspera, A. vasica* and *C. carandas*. The IVI values of medicinal herbals seemed to be marginal in the intruded zones compared to the nonintruded zones. The IVIs of *A. vasica* and *V. altissimia* in the control zone were 8.6 and 5.6%, respectively, but both were not noticed in

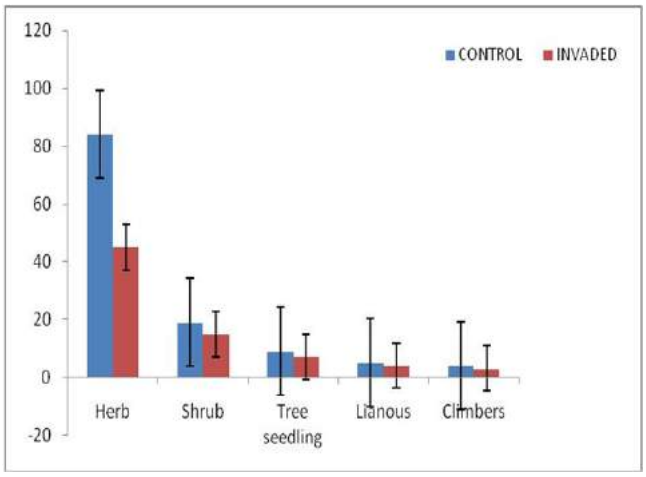

Fig. 1. *Comparison of different forms of plants in control and Mimosa invisa-invaded areas*

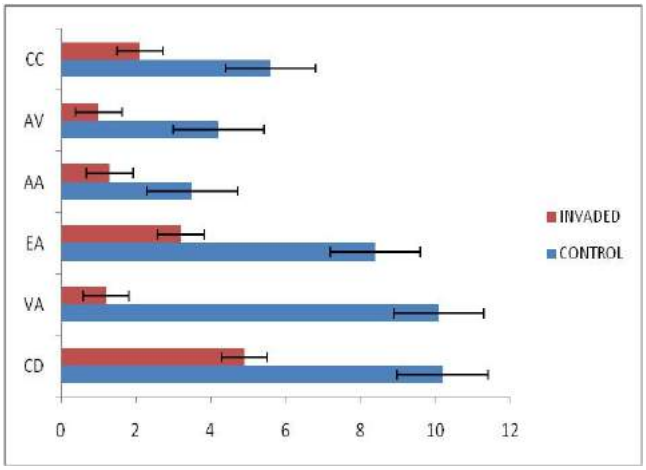

Fig. 2. *Impact of Mimosa invisa on the IVI (%) of some medicinal plant species. All values are significant at the 5% significance level after applying two population tests*

Table 1. Impact of *M. invisa* invasion on plant diversity and biomass.

Sl No.	Parameters	Control	Invaded	% decrease over control
1	Total Species	121	74	(-) 38.8
2	Average Fresh Biomass (g/m^2)	919.6	589.2	(-) 35.9
3	Average Dry Biomass (g/m2)	671.1	335.96	(-) 49.9
4	Margalef Index of Richness (R1)	7.2	3.7	(-) 48.6
5	Simpson's Index of Dominance (λ)	0.05	0.14	(+) 64.3
6	Shannon's Index of Diversity (H')	4.1	2.2	(-) 46.3
7	Diversity Number (N1)	21.5	10.4	(-) 51.6
8	Diversity Number (N2)	15.2	5.9	(-)61.2
9	Index of Evenness (Es)	0.91	0.72	(-) 20.9
10	Similarity Index (51.4)			
11	Dissimilarity Index (48.6)			

All values are significant at the 5% significance level after applying a two-population *t* test; (−) shows a lower value, and (+) shows a high value at the invaded site.

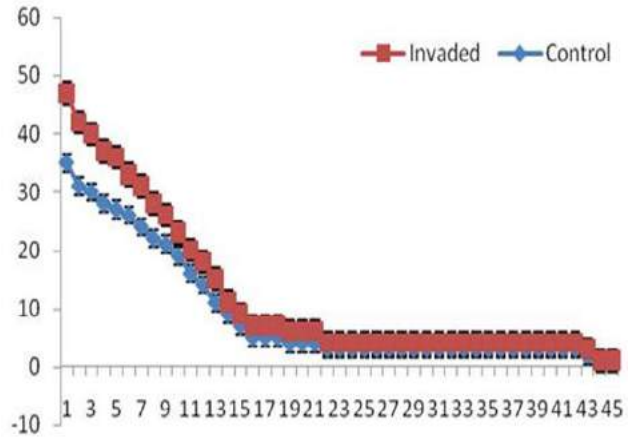

Fig. 3. *Distribution of common species in the control and Mimosa-invaded sites (decreasing order of importance value index).*

the top 10 species in the intruded zones. The IVI of *C. dactylon* in the invaded area was reduced by 44%, *E. alba* and *C. carandas* by 60.7 and 62.8%, and *A. aspera* by 52%. In addition, the sequence of species commonly noticed in both zones was represented in the declining order of their IVI values, and it displayed that the species become less consistent in the *M. invisa* intruded zones (Fig. 3).

Changes in soil nutrients

The total phenolic content in the *M. invisa*- intruding soil zone was 45% higher than in the control zone (Table 3). The soil pH of the control and intruded soil was almost 7; it was marginally lower in the control zone, while in the *M. invisa* intruded zone, it was 7.8. The ion conductivity was 32% higher in the *M. invisa* intrusion zone than in the control zone. % of organic carbon and organic matter inclined in the intruded zone by nearly 51%. The increase in the available nitrogen content was the highest among all other nutrients. It increased by 55.7% in the invaded area. The amounts of available phosphorus, potassium and sodium were 48, 38.5 and 24.4% higher, respectively, in the *M. invisa*-invaded soil than in the control soil. Similarly, the available calcium, magnesium and chloride also increased in the *M. invisa* -invaded soils; the increase was 38.4, 30.6 and 33.5%, respectively, in the invaded soil compared to the control soil (level of significance 0.01%).

DISCUSSION

Plants are the primary producers of the ecosystem, so it is important to protect them from various threats to sustaining all other biotas. Significant loss of the native medicinal plants in the invaded areas in the present study showed that they became less productive than the plants in the control area (Fig. 1,2 & 3). Biomass is directly related to the productivity of the plants (Table 1). The influence of the invaded species in the intruded zones of the Dhoni hills altered the physiological nature of the biological species and decreased the species diversity and dependent animals (Table 2). Dogra *et al*. (2009) also noticed a similar trend of the impact of three invasive species in the Shivalik hills, Himachal Pradesh. Uko *et al.* (2020) also recorded that *M. invisa* caused severe losses of yield reductions in cassava, maize, plantations and other arable crops (60-90%) in Nigeria and caused fire hazards during the dry season in infested fields. It formed large swathes of impenetrable prickly thickets that are difficult to irradicate.

It is time to record the impact of intrusion of alien species in terms of quantitative data of invasion influence on the diversity needed (Franz Essl *et al.,* 2020). In the present study, *M. invisa* seems to be a dominant alien species on the Dhoni hills and near plantations in Palakkad. They have increased density and abundance in the invaded habitats, resulting in the extinction of many

Table 2. Floristic composition of the vegetation in the control and *A. conyzoides*-invaded areas (alphabetical order). Total species = 135; Total species in control site = 121.Total species in invaded site = 74; Common species = 42

Sl. No	Name of the species	Family	Control	Invaded
1	*Abrus precatorius* L.	Fabaceae	+	-
2	*Acacia auriculiformis.*	Mimosaceae	+	+
3	*Acalypha indica* L.	Euphorbiaceae	+	+
4	*Acalypha wilkesiana* M.Arg.	Euphorbiaceae	+	-
5	*Acanthus ilicifolius* L.	Acanthaceae	+	-
6	*Achyranthes aspera* L.	Amaranthaceae	+	+
7	*Acorus calamus* L.	Araceae	+	-
8	*Adenanthera pavonina* L.	Mimosaceae	+	+
9	*Adhathoda beddomei* Clark.	Acanthaceae	+	-
10	*Adhathoda vasica* Nees.	Acanthaceae	+	-
11	*Aerva lanata* Juss.	Amaranthaceae	+	+
12	*Alpinia calcarata* Rosc.	Zingiberaceae	+	+
13	*Alstonia scholaris* R.Br.	Apocynaceae	+	+
14	*Amaranthus caturus* Heyne.	Amaranthaceae	-	+
15	*Amaranthus caudatus* L.	Amaranthaceae	+	-
16	*Amaranthus gangeticus* L.	Amaranthaceae	+	-
17	*Amaranthus spinosus* L.	Amaranthaceae	+	+
18	*Amaranthus viridis* L.	Amaranthaceae	+	-
19	*Andrographis paniculata* Nees.	Acanthaceae	+	-
20	*Antidesma menasu* Miq.	Euphorbiaceae	-	+
21	*Aristolochia indica* L.	Aristolochiaceae	+	+
22	*Asparagus racemosus* Willd.	Liliaceae	+	-
23	*Bacopa monnieri* (L)pennel.	Scrophulariaceae	+	-
24	*Barleria cristata* L.	Acanthaceae	+	+
25	*Barleria montana* Nees.	Acanthaceae	+	-
26	*Begonia sps.*	Begoniaceae	+	-
27	*Biophytum sensitivum* (L)DC.	Geraniaceae	+	+
28	*Boerhaavia diffusa* L.	Nyctaginaceae	+	+
29	*Calotropis gigantea* R.Br.	Asclepiadaceae	-	+
30	*Capsicum anum* L.	Solanaceae	+	+
31	*Capsicum frutescens* L.	Solanaceae	+	-
32	*Cardiospermum halicacabum* L.	Sapindaceae	+	+
33	*Carrisa carandas*	Apocynaceae	+	+
34	*Cassia siamea* Lam.	Caesalpiniaceae	+	+
35	*Cassia tora* L.	Caesalpiniaceae	+	+
36	*Cayratia pedata* Juss.	Vitaceae	+	+
37	*Centella asiatica* (L)Urban.	Apiaceae	+	-
38	*Cissus quadrangularis* L.	Vitaceae	+	+
39	*Cissampelos perera*	Menispermaceae	+	_
40	*Cleome viscosa* L.	Capparidaceae	+	+
41	*Clerodendron inermae* Gaertn.	Verbenaceae	+	+
42	*Clerodendron infortunatum* L.	Verbenaceae	+	+
43	*Clerodendron serratum* (L)Moon.	Verbenaceae	+	-
44	*Coccinia indica* W&A.	Cucurbitaceae	+	+
45	*Costus speciosus* S.M.	Zingiberaceae	+	-
46	*Crotalaria sps.*	Papilionaceae	+	+
47	*Croton tiglium* L.	Euphorbiaceae	-	+
48	*Curculigo orchioides* Gaertn.	Amaryllidaceae	+	-
49	*Curcuma canannoorensis.*	Zingiberaceae	+	-
50	*Cuscuta reflexa* Roxb.	Convolvulaceae	+	+
51	*Cyathula prostrata* Bl.	Amaranthaceae	+	+
52	*Cyclea peltata* Hf&T.	Menispermaceae	+	+
53	*Cymbopogon citratus*(DC)Stapf.	Poaceae	+	-
54	*Cynodon dactylon* (L)Pers.	Poaceae	+	-
55	*Cyperus rotundus* L.	Cyperaceae	+	+
56	*Datura stramonium* L.	Solanaceae	+	+
57	*Derris trifoliata* Lour.	Fabaceae	-	+
58	*Desmodium gangeticum* DC.	Fabaceae	+	-
59	*Dioscorea pentaphylla* L.	Dioscoreaceae	+	-
60	*Eclipta alba* Hassk.	Asteraceae	+	-

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Table 2. Contd…...

61	*Elephantopus scaber* L.	Asteraceae	+	-
62	*Emilia sonchifolia* DC.	Asteraceae	+	+
63	*Euphorbia hirta* L.	Euphorbiaceae	+	+
64	*Euphorbia pulcherima* Willd.	Euphorbiaceae	-	+
65	*Euphorbia splendens* Boj.	Euphorbiaceae	-	+
66	*Evodia roxburgiana* Benth.	Rutaceae	+	-
67	*Gloriosa superba* L.	Liliaceae	+	+
68	*Glycosmis pentaphylla* Corr.	Rutaceae	+	+
69	*Gmelina arborea* Roxb.	Verbenaceae	+	+
70	*Grewia microcos* L.	Teliaceae	+	+
71	*Grewia tiliaefolia* L.	Teliaceae	+	+
72	*Helicteres isora* L.	Sterculiaceae	+	+
73	*Hemidesmus indicus* R.Br.	Asclepiadaceae	+	+
74	*Holarrhena antidysenterica* Wall.	Apocynaceae	+	-
75	*Hydrocotyl asiatica* R.Br.	Apiaceae	+	-
76	*Indigofera prostrata* Willd.	Fabaceae	+	+
77	*Indigofera tinctoria* L.	Fabaceae	+	+
78	*Impatiens concinna* L.	Rubiaceae	+	-
79	*Ipomaea companulata* L.	Convolvulaceae	+	-
80	*Ipomaea hederacea* (L)Jacq.	Convolvulaceae	+	-
81	*Ixora coccinea* L.	Rubiaceae	+	+
82	*Ixora brachiata* Roxb.	Rubiaceae	+	-
83	*Jacquemontia caerulea* Choisy.	Convolvulaceae	-	+
84	*Jasminum malabaricum* L.	Oleaceae	+	-
85	*Jatropa curcas* L.	Euphorbiaceae	+	+
86	*Jussieua* sps.	Onagraceae	+	-
87	*Kaempferia galanga* L.	Zingiberaceae	+	-
88	*Leucas aspera* Spr.	Lamiaceae	+	-
89	*Maranta arundinacea* L.	Marantaceae	+	-
90	*Melastoma malabathricum* L.	Melastomaceae	+	+
91	*Melochia corchorifolia* L.	Sterculiaceae	+	-
92	*Mimosa pudica* L.	Mimosaceae	+	-
93	*Mucuna pruriens* Baker.	Fabaceae	+	+
94	*Murraya Koenigii* Spreng.	Rutaceae	+	-
95	*Mussaenda frondosa* L.	Rubiaceae	+	-
96	*Naravelia zeylanica* DC.	Rananculaceae	+	+
97	*Naregamia alata* W&A.	Meliaceae	+	-
98	*Ocimum basilicum* L.	Lamiaceae	+	-
99	*Ocimum gratissimum* L.	Lamiaceae	+	-
100	*Oldenlandia corymbosa* L.	Rubiaceae	+	-
101	*Oldenlandia umbellata* L.	Rubiaceae	+	-
102	*Olea dioica* Roxb.	Oleaceae	+	+
103	*Oxalis corniculata* L.	Oxalidaceae	+	-
104	*Passiflora foetida* L.	Passifloraceae	+	+
105	*Paveta indica* L.	Rubiaceae	+	+
106	*Pergularia extensa* N.E.Br.	Asclepiadaceae	+	+
107	*Phyllanthus amarusi* L.	Euphorbiaceae	+	-
108	*Piper betle* L.	Piperaceae	+	+
109	*Piper longum* L.	Piperaceae	+	-
110	*Piper nigrum* L.	Piperaceae	+	-
111	*Plumbago rosea* L.	Plumbaginaceae	+	-
112	*Plumbago zeylanica* L.	Plumbaginaceae	+	-
113	*Pothos scandens* L.	Araceae	+	+
114	*Premna latifolia* Roxb.	Verbenaceae	-	+
115	*Prunus avium* L.	Rosaceae	-	+
116	*Pseudarthria viscida* W&A.	Fabaceae	+	+
117	*Quamoclit pinnata* Boj.	Convolvulaceae	+	+
118	*Rauwolfia serpentina* Benth&Kurz.	Apocynaceae	+	-
119	*Sida cordifolia* L.	Malvaceae	+	+
120	*Sida retusa.*	Malvaceae	+	+

Contd…...

Table 2. Contd…...

121	*Sida spinosa* L.	Malvaceae	+	+
122	*Solanum melongena* L.	Solanaceae	+	-
123	*Smilax zeylanica* L.	Liliaceae	+	-
124	*Sphaeranthus indicus* L.	Asteraceae	-	+
125	*Spilanthus calva* W.	Asteraceae	+	+
126	*Tabernae montana divericata.*	Apocynaceae	+	+
127	*Thunbergia grandiflora* Roxb.	Acanthaceae	+	+
128	*Tinospora cordifolia* (Willd)Miers.	Menispermaceae	+	+
129	*Tinospora malabaricum.*	Merispermaceae	+	+
130	*Tribulus terrestris* L.	Zygophyllaceae	+	+
131	*Trichosanthes anguina* L.	Cucurbitaceae	+	-
132	*Triumfetta rhomboidea* Jacq.	Tiliaceae	+	-
133	*Turnera ulmifolia* L.	Turneraceae	+	-
134	*Tylophora asthmatica* W&A.	Asclepiadaceae	+	+
135	*Urena lobata* L.	Malvaceae	+	-

Table 3. Comparison of selected physico-chemical properties of soil collected from areas invaded by *Mimosa* and free from it (control)

Sl. No	Parameters	Control	Invaded
1	Phenolics (ig/100 g soil)	12.4 ± 1.05	21.8 ± 0.98**
2	pH	6.8 ± 0.01	7.5 ± 0.02**
3	EC (iS)	130.4 ± 1.8	190.6 ± 4.05**
4	Organic Carbon (%)	0.5 ± 0.03	0.97 ± 0.08**
5	Organic Matter (%)	0.85 ± 0.02	1.7 ± 0.1**
6	N (kg/ha)	91.79 ± 2.5	214 ± 7.6**
7	P (ppm)	65.53 ± 2.8	123 ± 1**
8	K (ppm)	88.39 ± 4.08	143 ± 2.79**
9	Na (ppm)	40 ± 4.21	53.05 ± 3**
10	Ca (g/100 g)	4.17± 0.28	6.7 ± 0.3**
11	Mg (g/100 g)	2.2 ± 0.3	3.2 ± 0.8**
12	Cl (g/100 g)	3.5 ± 0.18	5.1 ± 0.34**

native species. Dai *et al.* (2020) recorded the synergistic effect of alien plant invasion processes in native species. They also prepared a road map for future conservation of the crop species. Demertzis and Iliadis (2018) predicted the plausible impact of climate change on biodiversity in the ecological consequences of invasive species in Greece. Manoharan *et al.* (2019) proved that gene expression profiling enhanced the defense responses of invasive weeds compared to their native congener during pathogenesis. Rutherford *et al.* (2021) analysed the speciation dynamics of codistributed *Angophora* species in a varying landscape versus alien species. Sun *et al*. (2021) established the plant-soil feedback during biological invasions: effect of litter decomposition from an invasive *Sphagneticola trilobata* on its native congener (*S. calendulacea*). Xie *et al.* (2020) proved that hybridization with natives augments the threats of introduced species in *Sonneratia* mangroves. Zhang *et al.* (2021) analysed the transcriptome profiling of *Arabidopsis thaliana* roots in response to the allelopathic effects of *Conyza Canadensis.* Zhu *et al.* (2018) reviewed the invasive *Hydrocharis morsus-ranae* vs the native species in North America. Dai *et al.* (2022) documented global changes and plant invasions in different eco-climatic zones. All these findings substantiate the present data of the invasion of *M.invisa* at Dhoni hills.

According to Semwal *et al.* (2007), the increasing abundance of invaders decreases species diversity. Much effort has been put into identifying determinants constraining broad-scale variability in species richness. It is apparent that the factors influencing the patterns of species richness vary with the geographical extent and sample resolution (Shukla, 2009). Therefore, only by multiple analysis scales for different locations and at various spatial scales can general explanations of broad-scale species richness, diversity, and distribution patterns be provided (Semwal *et al.,* 2007).

M. invisa is a strong invader; its abundance, cover, and density threaten natural biodiversity. The decrease in plant mass and allied indices of the ecosystem features, such as α-diversity, abundant species, and Margalef's index, in the intruded habitats reflect that these zones were less productive and stable than the non-intruded zones. Certain species in the intruded areas were lost. Meanwhile, some are competing to survive. The lack of seedlings of trees in the intruded zones revealed that *M. invisa* allelopathically prevented their

establishment. Thus, *M. invisa* inhibits the growth of other plant species directly by creating its own niches. The intrusion of *M. invisa* also changed the soil physico -chemical features, i.e., the soils in the intruded zones had a high nutrient content to facilitate the growth of the intruded species. The data revealed that the values of most soil nutrients seemed to be better in the *M. invisa*-intruding zones than in the control. pH showed a minimal change compared to other features. Similarly, the total phenolics of a proven allelochemical seemed to be higher in weed-intruded soil when compared to the control. Phenolics leached from the herbals as volatile molecules from the aerial parts and roots, volatilization or microbial degradation. These allelochemicals prove the allelopathic property of plants and regulate the biotic communities of soil (Shukla, 2009). Many studies suggest that allelopathy may contribute to the ability of particular alien species to become dominant in native plant communities (Abd El-Wahab *et al.,* 2008). Several aggressive weeds, such as *Eichhornia crassipes, Centaurea stoebe* ssp.*Micranthos*, *Alliaria petiolata,* exhibit the phenomenon of allelopathy as a mechanism of interference that provides them with a competitive advantage over other plants (Mahato *et al.,* 2021).

The present study revealed more availability of minerals and other nutrients in the *M.invisa*-intruded soils than in the nonintruded zones (Table 3). These higher values established the concept that more availability of minerals and other nutrients enhanced the susceptibility to the invasion of other communities. As reported by Padalia *et al.* (2010), the factors other than allelopathy might be operating in nature, which favours the rapid establishment and persistence of dense stands of invasive alien species such as *Chromolaena odorata, Fallopia japonica*, *Conyza bonariensis, Lantana camara, Acacia nilotica* sp. *indica, Parthenium hysterophorus, Opuntia stricta* and *Trianthema portulacastrum*. Furthermore, the absorption of phenolics and allelopathic compounds by soil particles and their microbial breakdown may account for the outcome of the present observations (Gupta *et al*., 2006), which are further affected by different soil factors, such as soil texture, organic carbon and organic matter. (Kobayashi, 2004).

Conclusion

The invaded dominance of *M. invisa* at Dhoni hills, Palakkad altered the structural types of vegetation into a homogeneous land, reducing the diversity of flora, most likely including many medicinal species. It altered the soil regimes, such as pH, organic matter, mineral content and phenols, and often encroached on water bodies. Globalization has increased by introducing alien species to new areas with deleterious effects on ecosystems and displaced native plants, degraded ecosystems, and negatively impacted human health. Plant invasions may result in the homogenization of biological systems worldwide and global biodiversity loss. Similarly, allelochemicals such as phenols leached from the alien may regulate the growth of native species but can have potential value in agriculture. Future research should use multiple environmental stressors to address their impacts on environment/ecosystem services and socioeconomic and human health.

Conflict of interest

The authors declare that they have no conflict of interest.

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Research Article

Antimetastatic potential of anthocyanins from *Cordyline australis* (G. Forst.) Endl. Red star variety on MCF onco cell lines

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Abstract
Breast cancer is the second most deadly diagnosed lifestyle disease among women. Surgery and chemotherapy are the current treatments of choice; nevertheless, toxicity connected with this underscores the urgency of the demand for the human-friendly drug. 50% of current synthetic drugs available commercially today are either direct or indirect descendants extracted from herbs. Anthocyanins possess many pharmacological activities, including anticancer potential. However, no study on anticancer activity of anthocyanins from *Cordyline australis* has been reported. Anthocyanins were extracted from fresh leaves using ethanol as solvent. The total anthocyanin was quantified and fractionated by Ultra Performance Liquid Chromatography. Cytotoxicitic effect was carried on diverse cancer cell lines like MCF 7, HCT-116, Caco-2 and SW480 using MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide assay. Based on MTT data, MCF 7 cells were further analyzed by LDH assay, Glutathione-S- transferase (GST), Quercetin reductase, Cytochrome P450 and Caspase 3, 8 and 9 activities. The obtained results were analyzed using ANOVA with a level of significance. Results obtained from MTT assay revealed that the anthocyanin extract carried significant toxic ($p < 0.05$) specificity against MCF 7 cells (65 ± 2.1 toxicity at 50 µg/ml) when compared to the other onco cells. Remarkable LDH leakage (50.2% vs 50 µg/ml), GST (3.0±0.002 U/mg protein), QR (4.4±0.054 U/mg protein), Cyt P450 activities (0.291±0.01 U/mg protein) were noticed. Caspase 3 (157%), 8 (142%) and 9 (147%) displayed profound activities. These *in vitro* findings of specific anticancer effects noticed on *C. australis* anthocyanin extract require further evaluation using animal models. Finally, the obtained findings open up the possibility of developing a lead antimetastatic anthocyanin candidate against deadly breast cancer.

Keywords: Antimetastatic, Anthocyanin, Caspase, Cytochrome P450, Glutathione-S- transferase (GST), Lactic dehydrogenase, Quercetin reductase

INTRODUCTION

Breast cancer is one of the most prevalent types of cancer, with the highest incidence among all cancer types that occurs in women. Despite advancements in research, screening and treatment, the mortality rates associated with it remain high and metastasis is the leading cause of mortality (Zhou *et al.*, 2017). The study of phytochemicals extracted from fruits, vegetables and herbals has been focused, indicating that phytonutrients have a significant role in oncotherapy (Han, 2005). Anthocyanins are the most abundant flavanoid constituents in vegetables and fruits. They are water-soluble and their occurrence is ubiquitous in the plant world (Wang and Stoner, 2008; Liu, 2021).

Over the years, researchers have revealed that anthocyanins are non-toxic natural pigments with antioxidant and anti-inflammatory potentialities. The conjugated bonds present in anthocyanin structures absorb light at 500 nm wavelength and are responsible for diverse colours such as blue, bright red and purple found in berries, grapes, apples, purple cabbage and corn (Wang and Stoner, 2008). Anthocyanins also possess antimicrobial, antiviral, antiallergic, anticarcinogenic, antimutagenic, and antiproliferative effects and therefore play significant roles in preventing and lowering

the risk of cardiovascular disease, diabetes, arthritis and various cancers (Liu, 2021; Diaconeasa, 2018).

Anthocyanins have exhibited *in vitro* and *in vivo* anti-carcinogenic efficacies against multiple cancer cells. Their chemopreventive activities include radical scavenging, stimulation of phase II detoxifying enzymes, reduction in cell proliferation, angiogenesis & invasiveness, and induction of apoptosis and differentiation (Wang and Stoner, 2008). Anthocyanins with *ortho*-dihydroxyphenyl, on their B-rings possess the most obvious anticancer potentiality by targeting RTKs (EGFR, PDGFR and VEGF/VEGFR) / Ras-MAPK and PI3K/Akt signal cascade pathways, inhibit the cancer cell growth and metastasis. Similarly, anthocyanins regulate the functionality of gene expression through apoptotic pathways.

Anthocyanin extract provides an adjuvant therapeutic effect for breast cancer. According to Tan (2020), anthocyanins from the skin of grapes increase intracellular ROS levels leading to apoptosis in MCF-7 breast cancer cells and also arrests the cells in the G2/M phase. Mazzoni (2019) reported that anthocyanin extract from Alba strawberry induces apoptosis and cell death of breast cancer cells by downregulating AMPK expression and lowering breast cancer. Li (2009) reported that fruit extracts of *Eugenia jambolana*, contain 3.5% anthocyanins, which causes proapoptotic effects only on breast cancer cells and not on normal breast cells. Cya-3-O-sam, the anthocyanin fraction obtained from the fruits of the deciduous shrub, *Acanthopanax sessiliflorus*, inhibits the metastasis of breast cancer cells by causing the suppression of neovascularization and the gelatinolytic potential of MMP-9 (Lee, 2013).In this scenario, the present study attempted to evaluate the anti-metastatic efficacy of anthocyanins from Red star variety of *Cordyline australis.*

MATERIALS AND METHODS

Plant material

C. australis (G.Forst.) Endl. (Figure 1) is an erect monocot shrub endemic to New Zealand. The height varies from 5-8m, leaves are narrow and linear with bronze-red colour. Upper leaves are erect, while the lower leaves are horizontal and drooping, forming star burst-shaped clusters. Leaves of Red star variety of *C. australis,* collected from Thiruvananthapuram District of Kerala, were used for the present study.

Assay of total anthocyanin content (TAC)

Anthocyanins were isolated with ethanol and quantified as per the method of Young and Abdel-Aal (2010). The absorbance was read at 520 nm against distilled water as the blank. The data were expressed as µg of cyanidin 3-glucoside (Cy 3-glu) equivalents / g of fresh weight.

Fractionation and quantification of anthocyanin by Ultra Performance Liquid Chromatography (UPLC)

Sixteen anthocyanin standards such as cyanin chloride (cyanidin-3,5-di-o-glucoside chloride), delphinidin chloride (3,30,40,5,50,7-hexahydroxyflavylium chloride), cyanindin-3-o-glucoside chloride, delphin chloride (delphinidin-3,5-di-o-glucoside chloride), cyanindin-3-o-rutinoside chloride, delphinidin -3-o-glucoside chloride, delphinidin-3-o-sambubioside chloride, delphinidin-3-o-galactoside chloride, delphinidin-3-o-rutinoside chloride, malvin chloride (malvidin-3,5- di-o-glucoside chloride), malvidin-3-o-glucoside chloride, peonidin-3,5-di-o-glucoside chloride, peonidin-3-o-glucoside chloride, petunidin-3-o-glucoside chloride, peonidin-3-o-rutinoside chloride and pelargonidin 3-o-glucoside chloride were used for the study. 1 mg/mL stock solutions for all the standards were prepared and standard curves in the concentration range between 1 to 200 ppm were made. The extract was concentrated using a rotavapor at 37 °C and the dried extract was dissolved in 1 mL methanol. UPLC of these anthocyanin extracts was performed using Waters Acquity Ultra Performance. LC system, equipped with a quaternary pump system following the protocol of Sharma *et al*., 2020. Eluent A comprised 5% (v/v) formic acid and eluent B comprised HPLC grade acetonitrile. Gradient elution was employed to carry out separation for 6.8 min. The extraction and quantification of anthocyanins were performed by comparing the retention times of anthocyanin peaks in the sample extracts with the standards and calibration curves.

Cells and culture conditions

Human cancer cell lines such as MCF 7, HCT-116, Caco-2 and SW480 (ATCC) were purchased from National Centre for Cell Science (NCCS), Pune and were maintained with Dulbecco's Modified Eagle Medium (DMEM) medium as specified above. On the day before the treatment, the cells were seeded in six-well plates at a density of 5 x 10^5. Then the cells were replaced with fresh DMEM with & without 10% FBS (serum-free conditions) and then treated with 10, 20, 30

Fig. 1. *Plant material Cordyline australis (G.Forst.) Endl.*

and 50 µg/ml of anthocyanin extracted from the leaves of *C. australis.*

Cytotoxicity and apoptosis assay

Cytotoxicity was assessed by MTT reduction assay as per the protocol of Greeshma *et al*., 2020. Cancer cells were isolated and digested using trypsin into single cell suspension during the logarithmic phase of growth. They were seeded into the 96-well plate at a 2.0 × 104 per well density. Cells were divided into three groups: blank control group (culture medium only), control group (cells without extract treatment) and treatment group (cells treated with various doses of extracts). After 24 h, various concentrations of anthocyanin extracts were added and incubated with the cells. After another 24 h, 20 µl 5 mg/ml MTT solution was added to each well and incubated for 4 h. DMSO (100 µl) was added following the removal of the supernatants. The crystals were thoroughly dissolved and the absorbance value of each well was measured at 570 nm by enzyme -linked immunosorbent assay (ELISA). The % of inhibition was calculated as per I%= (1-average absorbance value of the treatment group)/ average absorbance value of the control group) × 100%.

Lactate dehydrogenase (LDH) assay

Lactate dehydrogenase (LDH) cytotoxicity assay kit was used to evaluate the cell membrane damage. The assay was based on the activity of LDH leached from the damaged cells into the medium (Kaja, 2017). Cells were plated in the 96-well plates (1×10^4 cells / well) and incubated for 24 h. To the cells with different dosages (10, 20, 30 and 50 µg/ml),*C. australis* anthocyanin extract was introduced and incubated for another 24 h. 1% Triton of lysis solution was added to the control cells at 45 min prior to the centrifugation and was selected as positive control. Centrifugation was carried out at 1200 rpm for 5 min and 100 µL of the supernatant from each well was transferred to 96-well culture plate and OD was read at 490 nm. The LDH leakage % of positive control was recorded as % of $(OD_{test}-OD_{blank})/(OD_{positive}-OD_{blank})$, where OD_{test} is the OD of the control cells or cells exposed to anthocyanin, $OD_{positive}$ is the OD of the positive control cells and OD_{blank} is the OD of the wells without cells.

Isolation and assay of enzymes

The treated and control MCF 7 cells were homogenized at 4°C in phosphate buffer (pH 7.0, 0.1 mol/L potassium phosphate) using hand held homogenizer. Subsequently, the cells were centrifuged for 20 min at 4°C and 10,000 X g. The supernatant was re-suspended in phosphate buffer.

Glutathione-S- transferase (GST) activity was recorded in the cytosol with Spectrophotometer as per the method of Habdous *et al*. (2003) using 10 mmol/L 1-chloro-2,4-di nitrobenzene (CDNB) as substrate. In the reaction mixture, incubation of 0.2 to 30 mg tissue cytosol protein was carried out briefly. The reaction mixture attained a final volume of 1 ml and included 0.1 mol/L potassium phosphate buffer (pH 6.5), 6.2 mmol/L glutathione, and 10 mmol/L CDNB. The reaction was initiated upon the addition of CDNB. The velocity of formation of S-(2-chloro-4-nitrophenyl) glutathione was noted for every 30 sec for 3 min. at 340 nm, at 25°C. One unit of enzyme activity = 1 nmole conjugate formed/min/mg protein. The molar extinction coefficient for CDNB was 9.6 nmol/ml.

Quercetin reductase (QR) activity in the cytosol was assayed using 12 mmol/L DPIP (2,6-dichloroindophenol) as substrate (Prochaska and Santamaria, 1988). The total volume in the cuvette included 0.06 to 0.28 mg tissue cytosol protein incubated with 25 mmol/L Tris-HCl (pH 7.4), 0.7 mg BSA, 1% Tween 20, 5 µmol/L FAD, and 0.2 mmol/L NADPH and 0 or 10 µmol/L dicoumarol at 25°C, to which 40 µmol/L DPIP was added to start the reaction. The reduction of DPIP was measured at 600 nm, for 3 min, with readings taken every 15 sec. The dicoumarol sensitive part of the activity was taken as a measure of the QR activity.

Cytochrome P450 (CYP1A1) activity was evaluated in the cells as per Manson *et al.* (1997) method with 7-O-ethoxyresorufin as the substrate. Total volume of the reaction mixture was 3 ml, which includes 25 µl cell protein, 0.1 mol/L potassium phosphate buffer (pH 7.4), 50 mmol/L NADPH and 0.75 mmol/L ethoxyresorufin. The sample buffer and ethoxyresorufin were incubated at 37°C in a water bath for 4 min with shaking at low speed. After 4 min, 100 mmol/L NADPH was added to initiate the reaction. The formation of resorufin was read at an excitation wavelength of 550 nm and emission wavelength of 581 nm, for 2.3 min. at 20°C. The protein concentration of each tissue was measured using the method of Lowry *et al.* (1951). Data were expressed as U/mg protein.

Caspase-3, -8, and -9 colorimetric assays

Quantitative estimation of human caspase-3, 8, and 9 was carried by Caspase-family Colorimetric Substrate Set Plus as per the manufacturer's (Biovision, Milpitas, CA, USA) instructions. Cells (10^6/ml) were incubated with different doses of BAA extract (IC_{10}, IC_{20}, and IC_{50}) for 24 h before treatment (Pu, 2017). The treated and untreated cells were harvested and centrifuged at 1000 rpm for 5 min and the pellets were lysed by adding a cold lysis buffer and incubated on ice for 10 min. After that, the cells were again centrifuged at 5000 rpm for 2 min and from the lysate 50 µl was transferred to a microplate; 50 µl 2x reaction buffer containing 10 Mm DTT was added to the reaction mixture followed by 5 µl of caspase p-nitroaniline (pNA) substrate, then each well was incubated at 37°C for 1–2 h. The absorbance

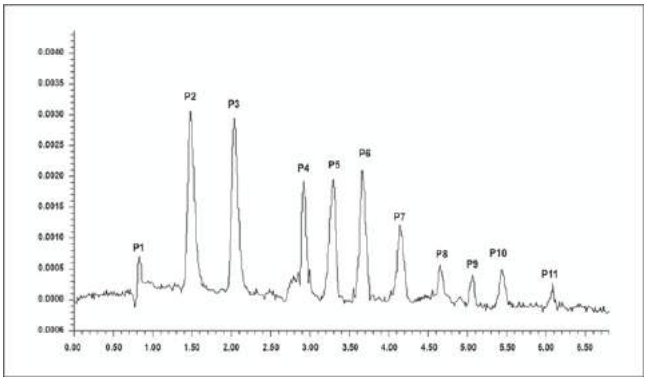

Fig. 2. *Ultra performance chromatography (UPLC) chromatogram*

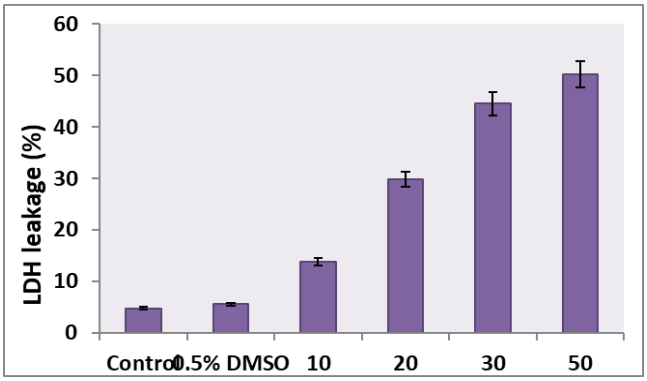

Fig. 3. *LDH leakage (%) induced in MCF 7 cells by the anthocyanin extract*

of coloured product was noted on a FLUO star Omega microplate reader at a wavelength of 405 nm.

Statistical analysis

Results were analyzed using version 7 of GraphPad Prism, using ANOVA, and differences were considered statistically significant at the level of p-values ≤ 0.05.

RESULTS AND DISCUSSION

Anthocyanins and anthocyanin-rich plant extracts have exhibited antimetastatic activity against multiple cancer cell types under *in vitro* conditions (Erikade Arruda Nascimentoa *et al*., 2022). Cell proliferation was arrested by the anthocyanins by inhibiting various cell cycle stages (inhibits cell cycle regulator proteins like p53, p21, p27, cyclin D1, cyclin A, etc.) (Anantharaju *et al*., 2016). Many researchers studied the antimetastatic potentials of anthocyanins on normal vs. cancer cells and found that they selectively block the growth of cancer cells with a relatively marginal effect on the growth of normal cells (Zorita Diaconeasa *et al*., 2020).

The total anthocyanin content of the ethanolic extract from *C. australis* was 27.4 mg/ml. UPLC analysis (Fig. 2) showed characteristic 11 anthocyanin peaks with remarkable level of delphinidin-3-o-galactoside (P2- 29.2 ppm) followed by delphinidin-3-o-glucoside (P3- 25.7 ppm), cyanindin-3-o-glucoside (P4- 20.4 ppm), and cyanindin-3-o-rutinoside (P5- 18.2 ppm). Delphinidin-3-o-rutinoside (P6-18.65 ppm), peonidin-3, 5-di-o-glucoside (P7), petunidin-3-o-glucoside (P8), pelargonidin 3-o-glucoside (P9), peonidin-3-o-glucoside (P10), peonidin-3-o-rutinoside (P11) and malvidin-3-o-glucoside (P1) were the minor peaks recorded.

MTT assay

The antimetastatic potential of anthocyanin extract was done by MTT assay on the selected cancer cell lines such as MCF 7, HCT-116, Caco-2 and SW480. The anthocyanin extract displayed concentration-dependent inhibition of cell proliferation on MCF 7 cell lines. No significant inhibition/cytotoxic impact was noticed with HCT-116, Caco-2 and SW480 onco cell lines. The IC_{50} value of MCF-7 cells was found to be 28.4 ± 0.32 µg/ml (Table 1).

LDH leakage assay

Generally, the cell membranes damage by chemicals/ drugs leads to intracellular leakage of LDH molecules into the culture medium. Thus, the leakage of LDH indirectly reflects the cell membrane integrity, which may be associated with necrosis. Necrosis refers to cell death that will provoke an inflammatory response in surrounding cells by leaking intracellular contents (Adigun *et al.,* 2021). As shown in Fig. 3, the LDH leakage % induced in MCF-7 cells remained 13.8 % at a lower dosage (10 µg/ml) compared with a higher concentration of 50 µg/ml (50.2 %). The values were statistically significant at 1%.

The present data revealed that the cells showed morphological deformities of apoptosis rather than necrosis. Helm *et al*. (2017) noted that the drastic loss of membrane integrity may not be used as an index to differentiate apoptosis from necrosis cell death. Meanwhile, Forkasiewicz *et al.* (2020) documented the direct involvement of LDH over expression and subsequent

Table 1. Percentage of inhibition on selected onco cell lines by the anthocyanin extract of *Cordyline australis*

Cell lines	10 µg/ml	20 µg/ml	30 µg/ml	50 µg/ml
MCF 7	11.98 ± 0.59	37.3 ± 1.08	54 ± 1.7	65 ± 2.1
HCT-116	0.061 ± 0.04	0.095 ± 0.02	0.11 ± 0.003	0.12 ± 0.006
Caco-2	0.04 ± 0.003	0.08 ± 0.004	0.1 ± 0.005	0.1 ± 0.001
SW480	0.062 ± 0.007	0.099 ± 0.001	0.1 ± 0.002	0.1 ± 0.007

outbreak of apoptosis.

Quinone reductase (QR), glutatione-S- transferase (GST) cytochrome P450 assay

C. australis anthocyanin extract displayed significant impacts on QR activity i.e. concentration-dependent relationship in MCF 7 cell lines when compared to the control (Table 2) ($p < 0.05$) i.e., from 1.01±0.002 (control) to 4.4±0.054 U/mg protein at 50 µg/ml. Similarly, glutathione S-transferase activity (GST) also enhanced above the mean control activities (0.54±0.004 - 3.0±0.002 U/mg protein). Cytochrome P450 also showed a dose dependent performance i.e., the control activity level was 0.15±0.001, while at 50 µg/ml it was increased to 0.291±0.01 U/mg protein.

Generally, polyphenols inhibit the CYP1A1 and CYP1A2 activities, thereby protecting the cells from carcinogenic activators. In the present study, anthocyanins activated phase I and II metabolizing enzymes such as Quinone reductase (QR), glutatione-S- transferase (GST) cytochrome P450 and there by regulated the metastasis in MCF 7 cell lines (Table 2). Seelinger *et al*. (2008) reported the role of luteolin against tumors via inhibiting angiogenesis. Tumor necrosis factor-related apoptosis-inducing ligand (TRAIL) belongs to TNF cytokine category. TRAIL was used to evaluate antimetastatic potential. The binding of TRAIL, TRAIL-R1, the death receptor 4 (DR4) and TRAIL-R2 (DR5) triggers the apoptotic signals through the formation of trimerization of TRAIL-R1 and/or TRAIL-R2 (death-inducing signaling complex) leading to recruitment of caspase-8 to the intracellular death domain (DD) of the receptors, which induces a caspase cascade and finally apoptotic death of malignant cells (Manoj, 2012). In the present study, 4, 6 and 2 folds increase in the activity of QR, GST, CYP 2 A1 in MCF 7 cells were observed when compared to control (Table 2). In most antimetastatic studies, phase I and II metabolizing enzymes have not been evaluated to confirm their efficacy against cancer cell lines (Choudhari Amit *et al.,* 2020). This is the first report on *C. australis,* anthocyanin vs QR, GST, CYP 2 A1 enzyme activities. Remya Krishnan and Murugan (2013) reported the potentiality of flavonoids from the liverwort *Marchantia* in the above enzymes in SW 480 cells. The present data was almost at par with the activity displayed by flavonoids of liverworts.

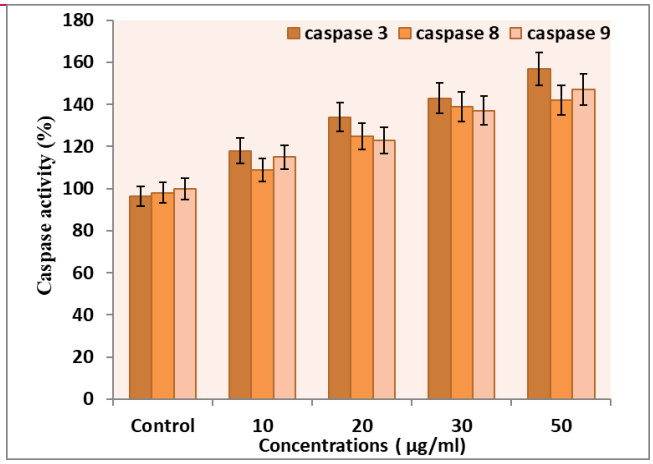

Fig. 4. *Caspase 3, 8, 9 activities (%) induced in MCF 7 cells by the anthocyanin extract of Cordyline australis*

Induction of caspase activity

The hallmark of apoptosis occurs through the activation of the caspases and tracing its pathway induced by antimetastatic drugs may offer crucial input in modeling better treatment strategies in cancer. In the present study, the activation of caspase 3, 8, and 9 was analyzed at 24 h with various dosages of anthocyanin extract. MCF7 cells, following exposure to anthocyanin extract, showed profound elevation of effector caspases - caspase 3 activities at 30 and 50 µg/ml concentrations. In addition, the anthocyanin extract was able to induce caspase 8 activity. Interestingly, the caspase 9 initiator caspase activity was also increased in MCF7 cells treated with anthocyanin (Fig. 4).

The two basic reactions involved in apoptosis are intrinsic (mitochondrial) and extrinsic (death receptor) pathways. The effector caspases - caspase-3/7 is involved in the final execution of death, while caspase 8 and 9 are initiator caspase regulates the intrinsic pathway. Caspase 3, 8 and 9 activities were evaluated to understand the mechanism of action induced by the anthocyanin extract, which revealed that the extract induced concentration-dependent increases in caspase 3, 8 and 9 activities in MCF 7 cell lines. Activation of the extrin-

Table 2. Activities of QR, GST, CYP 2 A1 in MCF 7 cells treated with different concentrations of the anthocyanin extract of *Cordyline australis*.

Concentration (µg/mL)	0	10	20	30	50
QR (U/mg protein)	1.01±0.002	1.66±0.03	2.89±0.03	3.77±0.06	4.4±0.054
GST (U/mg protein)	0.54±0.004	1.2±0.089	2.12±0.003	2.81±0.005	3.0±0.002
CYP2A1 (U/mg protein)	0.15±0.001	0.20±0.013	0.25±0.007	0.287±0.001	0.291±0.01
GSH (µmol / g)	0.59±0.004	1.8±0.007	2.6±0.043	3.5±0.045	4.4±0.005

sic apoptosis pathway was carried out through a ligand binding to a death receptor, which in turn performs recruitment, dimerization and activation of caspase 8 with the help of adapter proteins (FADD/TRADD). Apoptosis is initiated by activated caspase 8 either directly by cleaving and consequently activating executioner caspase (3, 6, and 7) or by activating the intrinsic apoptotic pathway through cleavage of BID to induce efficient cell death. Various cellular stresses can cause activation of the intrinsic mitochondrial apoptosis pathway, leading to the release of cytochrome c from the mitochondria and the formation of the apoptosome, comprised of APAF1, ATP, cytochrome c, and caspase 9, resulting in the activation of caspase-9, which inturn initiates apoptosis by cleaving and subsequently activating executioner caspases (McIlwain, 2013; Brentnall, 2013; Liu 2017).

Ediriweera *et al*. (2016) analyzed the anticancer activity of the bark hexane extract from *Mangifera zeylanica* in terms of cytotoxic and apoptosis and also its bioassay-guided fractionation to identify phytochemical constituents. The present cytotoxic data was more significant than the bark extract of *M. zeylanica.* Patil and Kim (2017) validated the efficacy of silver and gold nanoparticles in terms of antibacterial and anticancer activities. Deng *et al*. (2015) reviewed polyphenols of leaf and bark extracts of *Solidago canadensis* and its biological features. Elansary *et al*. (2020) compared antimicrobial, antioxidant and anticancer potentialities of *Malus baccata* var. gracilis and *M. toringoides* bark polyphenols. The viability data of the polyphenols was less than that of anthocyanin extract of *Cordyline australis.* Elansary *et al*., (2020) profiled the polyphenols of *Quercus* spp with their pharmaceutical potentials. Cosarca *et al.* (2019) recorded aqueous extracts of spruce and beech bark as a source of polyphenols, tannins, antioxidants and correlated the components with the *in vitro* anti-tumor potential against two different cell lines. The present study of anthocyanins from *C. australis* profoundly substantiates the above research outputs.

Conclusion

Increasing *in vitro* experimental data from various research documents have proved that anthocyanins can interfere with multiple signal pathways to exert their antimetastatic activities. However, most of these experiments were performed under *in vitro* conditions. The present study also attempted the anticancer efficacy of anthocyanin extract from the Red star variety of Cordyline australis. The ethanolic extract showed 11 anthocyanin fractions (Delphinidin-3-o-galactoside, Delphinidin-3-o-glucoside, Cyanindin-3-o-glucoside, Cyanindin-3-o-rutinoside, Delphinidin-3-o-rutinoside, Peonidin-3, 5-di-o-glucoside, Petunidin-3-o-glucoside, Pelargonidin 3-o-glucoside, Peonidin-3-o-glucoside, Peonidin-3-o-rutinoside & Malvidin-3-o-glucoside) and displayed its potentiality against MCF 7 cells in terms of inducing phase I and II enzymes, LDH leakage, caspase activates. Future studies should explore the connection between the intake of anthocyanin by the cells and its anticancer efficacy using *in vivo* animal models.

Conflict of interest

The authors declare that they have no conflict of interest.

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RESEARCH ARTICLE

Phylogenetic relationships of Indian *Memecylon* L. (Melastomataceae) based on nrDNA ITS and cpDNA *rbc*L sequence data

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Abstract. *Memecylon* (Melastomaceae) is a large genus of the Old-World predominantly woody species. Many species of *Memecylon* are used for timber, ornamental and medicinal purposes. The objective of the present study was to undertake a phylogenetic analysis of Indian *Memecylon* based on nuclear ribosomal DNA internal transcribed spacer (nrDNA-ITS) and *rbc*L sequence data. Sampling included 26 species and one variety (20 endemics) representing 67% of the total Indian species. Molecular phylogeny data for analysed species revealed that the Indian *Memecylon* is monophyletic. Monophyly is strongly supported in the ITS, *rbc*L and ITS + *rbc*L combined analyses. *Memecylon* species are grouped in a major clade with strong support in ITS sequence data and moderate support in combined ITS + *rbc*L analyses.

Keywords. India; *Memecylon*; phylogenetic relationships; monophyly.

Introduction

The genus *Memecylon* L. (Melastomataceae) is confined to the Old-World tropics, and comprises ~300 species (Bremer 1979; Stone 2014). In India, the genus is represented by *ca.* 53 species (Das *et al*. 2016, 2018a, b), of these, 37 are found in peninsular India (Andhra Pradesh, Karnataka, Kerala and Tamil Nadu) and 16 including three varieties occur in Andaman and Nicobar Islands. Two species, namely *M. edule* and *M. ovatum* are widely distributed in different parts of India (Das *et al*. 2018a, b). The genus *Memecylon* was proposed by Linnaeus based on *M. capitellatum* as type species, the specimen of which was collected from Sri Lanka (Ceylon). *Memecylon* is a Greek word meaning 'edible fruit' of strawberry trees. The members of the genus are evergreen and predominantly woody shrubs and some of them are small to medium sized trees (figure 1). The flowers are characteristically coloured from white to blue and hence *Memecylon* is called as 'blue-mist' genus.

Memecylon species are generally distributed in all types of habitats ranging from deciduous, semi evergreen, evergreen and montane sholas with a wide range of altitude from sea level to 2500 m. Several species are economically important as they are used for timber, ornamental, and medicinal purposes (Sivu *et al*. 2012; Stone 2014). The species are variable in nature and often the morphological key developed by the conventional taxonomy is of limited use in determining the species resulting in taxonomic ambiguity in many taxa.

The characters which have been used by the traditional taxonomists like floral characters are not much variable and

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Figure 1. *continued*

hence have less diagnostic importance at species level. Some key characters like branchlets, leaf morphology, inflorescence position, peduncle shape, leaf base shape, and prominence of disc-rays have been found useful in delimiting species boundaries. Leaf morphology alone has been used in distinguishing species like *M. gracile*, *M. agastyamalaianum* and *M. subramanii* (Sivu 2012).

Cogniaux (1891) monographic work on the genus *Memecylon* is the only comprehensive work available till date. Later, only a handful of revisionary studies have been done in Africa (Engler 1921; Jacques-Félix 1978a, b, 1979), Madagascar (Perrier de la Bâthie 1932, 1951; Jacques-Félix 1985), Sri Lanka (Bremer 1979, 1988), Borneo (Bremer 1983), peninsular Malaysia and Thailand (Maxwell 1980; Hughes and Wijedasa 2012).

Clark (1879) presented the first comprehensive taxonomic account of the family Melastomataceae in India that included 40 species of *Memecylon* including 27 varieties. Gamble (1919) in his *Flora of presidency of Madras*, provided a comprehensive account of the genus *Memecylon* occurring in the peninsular India. Despite the above works, information on the closely related species of Indo-Malesian region is limited.

Renner (1993) and Clausing and Renner *et al.* (2001) presented a classification for the family Melastomataceae and Memecylaceae and supported the monophyly of the genus *Memecylon*. Stone (2006a, b, 2014) carried out detailed systematic work on African and Madagascan taxa and ascertained the monophyly of the genus based on internal transcribed spacers (ITS) and external transcribed spacers (ETS) sequences. Stone (2014) also provided a revised infrageneric classification of the genus for tropical Africa and Madagascar. With limited sampling from Indo-Malesia, the combined phylogeny reveals that the three strongly supported clades of the group is paraphyletic with poor support.

The unexplored area of research for the group which includes divergence time, biogeography and character evolution has recently been investigated using phylogenomic approach (Amarasinghe *et al.* 2021). Their evolutionary and biogeography study revealed African origin of the woody plant group in the Eocene epoch and towards the east migration and subsequently colonization in Paleotropics, namely long distance dispersal (LDD). The character evolution within the group revealed that a large number of morphological characters exhibit homoplasy and some were phylogenetically informative (prominence of veins, inflorescence position petal colour etc.).

Figure 1. Endemic *Memecylon* species. (a) *M. agastyamalaianum*, (b) *M. courtallense*, (c) *M. flavascens*, (d) *M. mundanthuraianum*, (e) *M. kollimalayanum*, and (f) *M. ponmudianum.* (g) *M. sahyadrica*, (h) *M. randerianum*, (i) *M. sisparense*, (j) *M. sivadasanii*, (k) *M. subramanii*, (l) *M. terminale.*

While revising the Indian *Memecylon*, we examined all the herbarium specimens deposited at Central National Herbarium (CAL), Madras Herbarium (MH) and Tropical Botanic Garden Thiruvanthapuram (TBGT) and searched published literature (Cogniaux 1891; Clarke 1879; Renner *et al.* 2007-2014). Understanding the systematic relationships within *Memecylon* is required to assess the evolutionary relationships and solve the persisting taxonomic conflicts as pointed out by Stone (2014) for African species. Hence, the present work was undertaken to assess the phylogenetic relationships in the genus *Memecylon* and to test if the Indian species are monophyletic.

Material and methods

Sampling of the Indian Memecylon *and their outgroups*

Field trips were undertaken in different parts of India with greater focus on Western Ghats of peninsular India (table 1 in electronic supplementary material at http://www.ias.ac.in/jgenet/). Leaves were preserved in silica gel for molecular studies. In the present study, we sampled 26 species including two unnamed species and one variety. *Memecylon* species and remaining sequences were retrieved from GenBank from previous studies of Renner *et al.* (2001) and Stone (2014). The outgroup taxa belong to the genera *Mouriri*, *Spathandra*, *Warneckea* and *Lijndenia* (Stone 2014).

DNA data generation, phylogeny estimation and evolutionary rate analyses

The genomic DNA was extracted from silica-dried leaves and leaf fragments from herbarium specimens using a DNeasy Plant Mini Kit (Qiagen, Amsterdam, The Netherlands). The extracted DNA was evaluated for its quality and concentration using 1 kb standard on 1% agarose gel. DNA amplification and sequencing of the ITS region was performed using the primers ITS5 and ITS4 (White *et al.* 1990). The polymerase chain reaction (PCR) was performed with standard methods

using Promega PCR master mix (Promega Corporation, Madison, USA) in 25 μL volumes containing 50 U/mL *Taq* DNA polymerase (supplied in a proprietary reaction buffer (pH 8.5)), 400 μM dNTPs and 3 mM $MgCl_2$. To this, 2 μL of a 10 pM solution of each primer, 2 μL of genomic DNA and milli-Q water were added to make a total volume of 25 μL. PCR amplification was performed with 35 cycles (denaturation for 1 min at 94°C, annealing for 1 min at 49° C, and 1 min of extension at 72°C followed by a last cycle of final extension for 5 min at 72°C). Another region *rbc*L consists 824 bp excluding primer sequences within 1434 bp (57%) ribulose-1,5-bisphosphate carboxylase/oxygenase large subunit gene (CBOL 2009, Peterson *et al*. 2014). The primers *rbc*La-F (5′-ATGTCACCACAAACAGAGACTAAAGC-3′) as forward and *rbcLa*-R (5′-GTAAAATCAAGT CCACCRCG-3′) as reverse, (Integrated DNA Technology, USA) were used for highest level amplification of target region (Kress and Erickson 2007). Thermal cycling programme followed was: 98°C for 45 s; 36 cycles consisting of denaturation at 94°C for 10 s, annealing at 55°C for 30 s, and synthesis at 72°C for 40 s; final extension 72°C for 10 min. Reaction conditions for *trn*L-*trn*-F includes initial denaturation at 95°C for 45 s. followed by 35 cycles of denaturation at 95°C for 10 s, annealing at 50°C for 30 s, and an extension at 72°C for 45 s followed by final extension at 72°C for 10 min. PCR products were checked for the presence of appropriate bands on a 0.8% agarose gel, purified, and sequenced at AgriGenome, Kochi, Kerala, India. The sequences comprised of cpDNA *rbc*L and nrDNA ITS5, 5.8S, and ITS4 regions. Forward and reverse sequences were edited and aligned using the computer program Geneious® 10.2.2 (Drummond *et al*. 2010). All sequences were deposited in GenBank (table 1 in electronic supplementary material). A partition homogeneity test (PHT) between the ITS and *rbc*L sequences was performed with PAUP 4.0b10* (Swofford 2001).

Phylogenetic analysis

Phylogenetic analyses were done using MrBayes v. 3.2.3 X64 (Ronquist *et al*. 2012) and RAxML v. 8.1.18 (Stamatakis *et al*. 2008; Stamatakis 2014) on CIPRESS Science gateway v.3.3 (Miller *et al*. 2010). In Bayesian analyses, parameters for the evolutionary model were estimated by ModelTest (Kalyaanamoorthy et al. 2017) and the state frequency parameter for stationary nucleotide frequency of the rate matrix was fixed. The number of chains was set to four with three heated and one cold chain. Two runs were executed in parallel. Analyses were run for 1,300,000 generations until stationarity (standard deviation below 0.01). In each run, trees were sampled every 1000 generations with a sample frequency of 10. The parameters were summarized after excluding 25% of the samples based on the inspection of log-likelihoods of sampled trees after stationarity. The potential scale reduction factor (a convergence diagnostic) approached 1.0 for all the parameters suggesting good sampling from the posterior probability distribution with no spread. Trees were summarized yielding a cladogram showing posterior probabilities and clade credibility for each split and a phylogram with mean branch lengths. RAxML was run under GTR-GAMMA model. The RAxML bootstrap (BS) values were calculated using 1000 random iterations. The following criteria were used to evaluate the posterior probability (pp): 50–80, low; 81–94, moderate; 95–100, strong. The following criteria were used to assess bootstrap support percentages (BP): 50–70%, low; 71–84%, moderate; 85–100%, strong.

Results

Multiple sequence alignment analyses

***Internal transcribed spacer alignment*:** Twenty-eight sequences were newly generated in the present study (table 1 in electronic supplementary material). The sampling represents the maximum diversity of the Indian *Memecylon*. The ITS1 + 5.8s +ITS2 alignment has 159 sequences (including outgroups) with 771 characters, 528 distinct patterns, 322 parsimony-informative sites, 97 singleton sites, 345 constant sites, percentage pairwise identity was 91.2%, GC content was 53%, all INDELS constitute 13% of the aligned sites. The 5.8S region was similar in size (∼165 bp) in all the taxa. ModelFinder hosted at IQ-TREE reveals the Best-fit model for the ITS dataset to be TN+F+I+G4 chosen according to Bayesian information criterion (BIC).

***rbcL alignment*:** Thirty-six sequences were newly generated and added to a matrix of retrieved GenBank sequences along with 108 GenBank retrieved sequences accounting for a total of 144 sequences (including one outgroup taxa), with 718 nucleotide sites. Total number of constant sites in the alignment was 679 (= 94.5%). Number of variable sites in the alignment was 19 only and there were 86 number of distinct pattern sites. ModelFinder hosted at IQ-TREE reveals the best-fit model according to BIC calculations is JC+I.

***Combined ITS +rbcL alignment*:** In the combined analyses, the dataset was reduced to a total of 163 concatenated sequences including newly sequenced ITS and *rbc*L loci along with outgroups and relevant GenBank sequences. The PHT resulted in a P value = 1 – (0/100) = 1.000000, indicating that no significant incongruence was found between the ITS and *rbc*L datasets. The short sequences with less information and more ambiguity were removed. The alignment had 1498 nucleotide sites. Of the total combined (ITS + *rbc*L) loci, 1145 were constant sites (= 77 %), number of parsimonious informative sites were 213 and number of distinct site patterns was 401. The best-fit model estimated according to the BIC scores is TN+F+I+G4. However, while analysing GTR+G was selected as it was the best available model on CIPRESS Science Gateway.

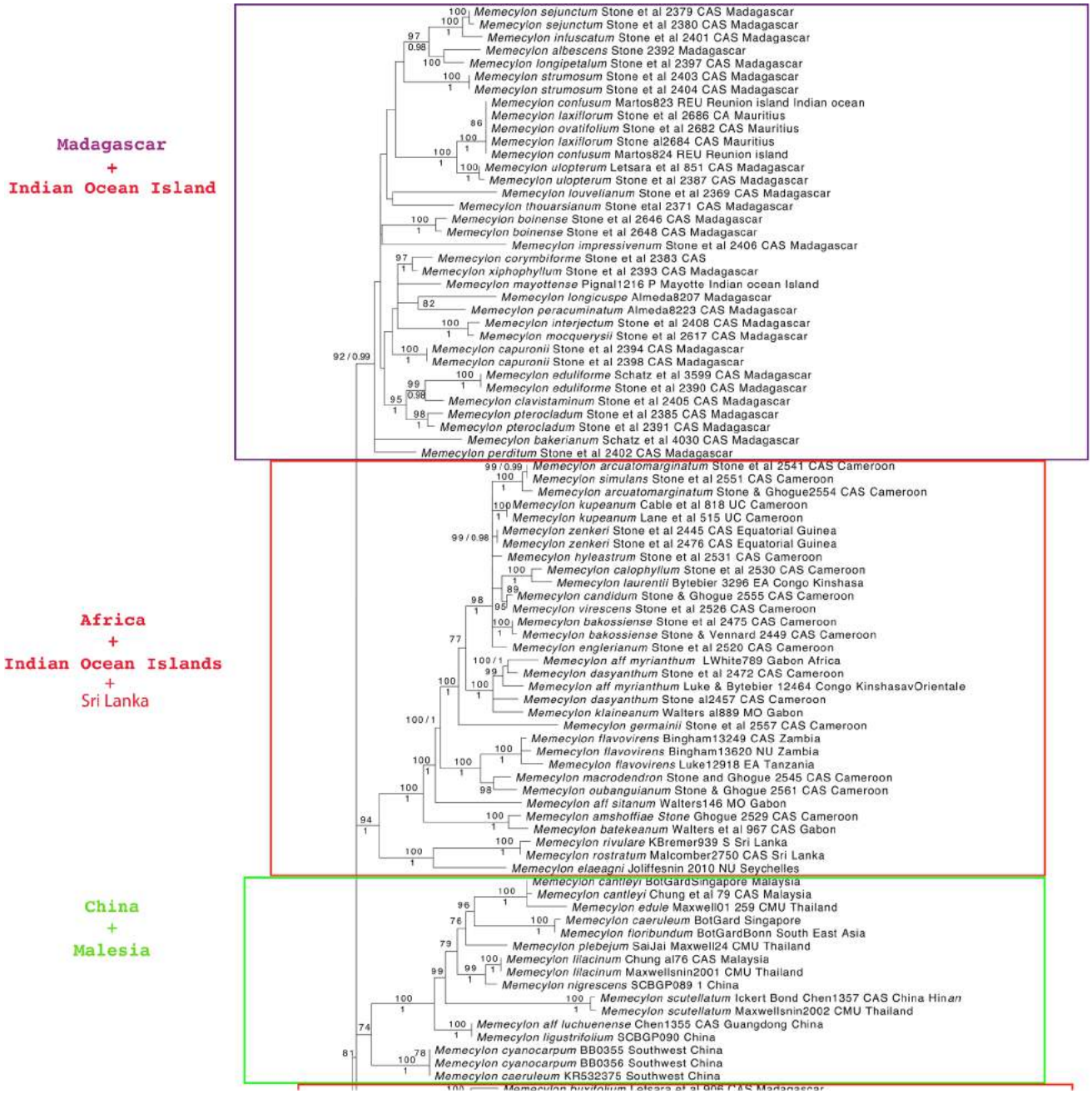

Figure 2. *continued*

ML and Bayesian phylogeny estimates

The genus *Memecylon* is recovered as a monophyletic group and the topology obtained after incorporating Indian species is congruent to previous studies (Renner *et al*. 2001; Stone 2014; Amarasinghe 2021). The topologies of the Bayesian majority-rule consensus trees are mostly congruent to the best ML tree from RAxML for ITS (nrDNA) and *rbc*L (cpDNA) DNA (figures 2 and 3; figure 1 in electronic supplementary material). Among the individual trees, ITS phylogeny (figure 2) is better resolved than combined ITS + rbcL tree (figure 3), in the individual cpDNA *rbc*L tree, the relationship between the species is unclear pertains to low variability of the region (figure 1 in electronic supplementary material). The ingroup taxa in the ITS and ITS + *rbc*L phylogenies resolve into six major well-supported clades just after splitting from the last common ancestors, namely (i) African (BP 100; PP 1); (ii) India+Sri Lanka+Malaysia (BP 100; PP 1); (iii) Madagascan + African (BP 97; PP 1); (iv) China + Malesia (BP 74; PP -); (v) Africa+Indian-Ocean Island + Sri Lanka (BP 94; PP 1); and (vi) Madagascan + Indian Ocean Island (BP 92; PP 0.99) (figures 2 and 3). All the Indian species analysed in the present study, collected from peninsular India are recovered monophyletic and placed in India + Sri Lanka + Malaysia clade

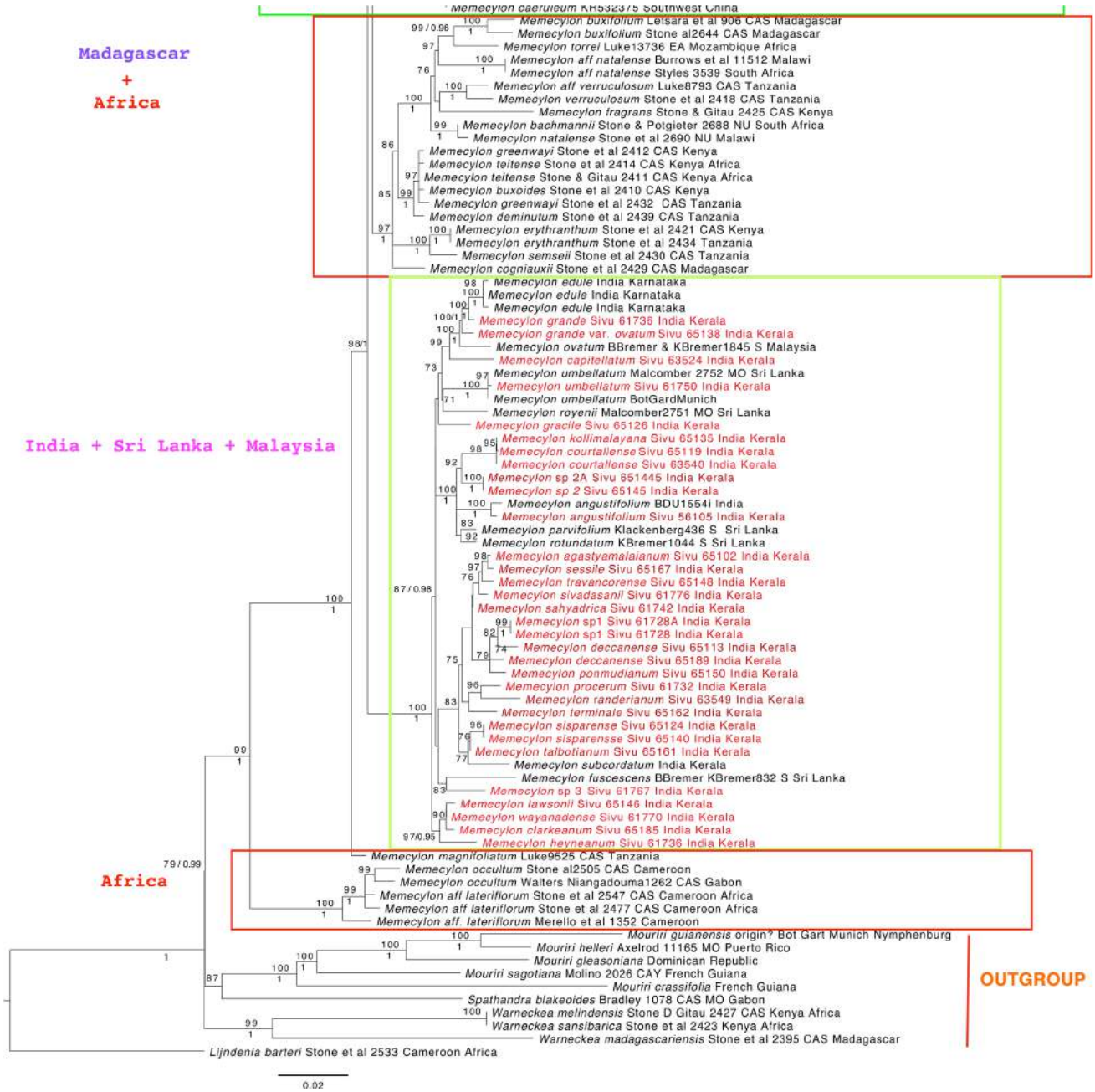

Figure 2. Best ML out-group rooted tree retrieved after analysing combined dataset of 163 sequences from ITS and *rbc*L comprising 1490 characters, assuming independent, best fit nucleotide substitution models for each of two sequence partition. The scale bar of 0.02 represents the average number of nucleotide substitutions per site. RAxML bootstrap values ≥75% indicated above the branches, Bayesian posterior probability values ≥0.95 below the branches.

(figures 2 and 3). The cases of in-congruency is *Memecylon* sp. 3 (India, Kerala) sister species to *M. fuscescens* (Sri Lanka) (BP 83; PP-) is placed as sister to *M. gracile* (BP 83; PP-) in ITS phylogram (figure 2) and in combined ITS +rbcL phylogram (figure 3) it is placed in polytomy along with all Kerala *Memecylon* spp. clade (BP 83; PP-). *M. magnifoliatum* from Tanzania, eastern Africa was recovered as basal to India + Sri Lanka + Malaysia clade, systematic position is consistent (figures 2 and 3). For all *Memecylon* spp. from rest of the tropics basal species were form central Africa (*M. occultum*, *M. aff. lateriflorum*).

The ITS+rbcL tree (India + Sri Lanka + Malaysia clade) (100 BS; 1 PP)

The clade is represented by 28 Indian species and one variety along with the six species from Sri Lanka and one

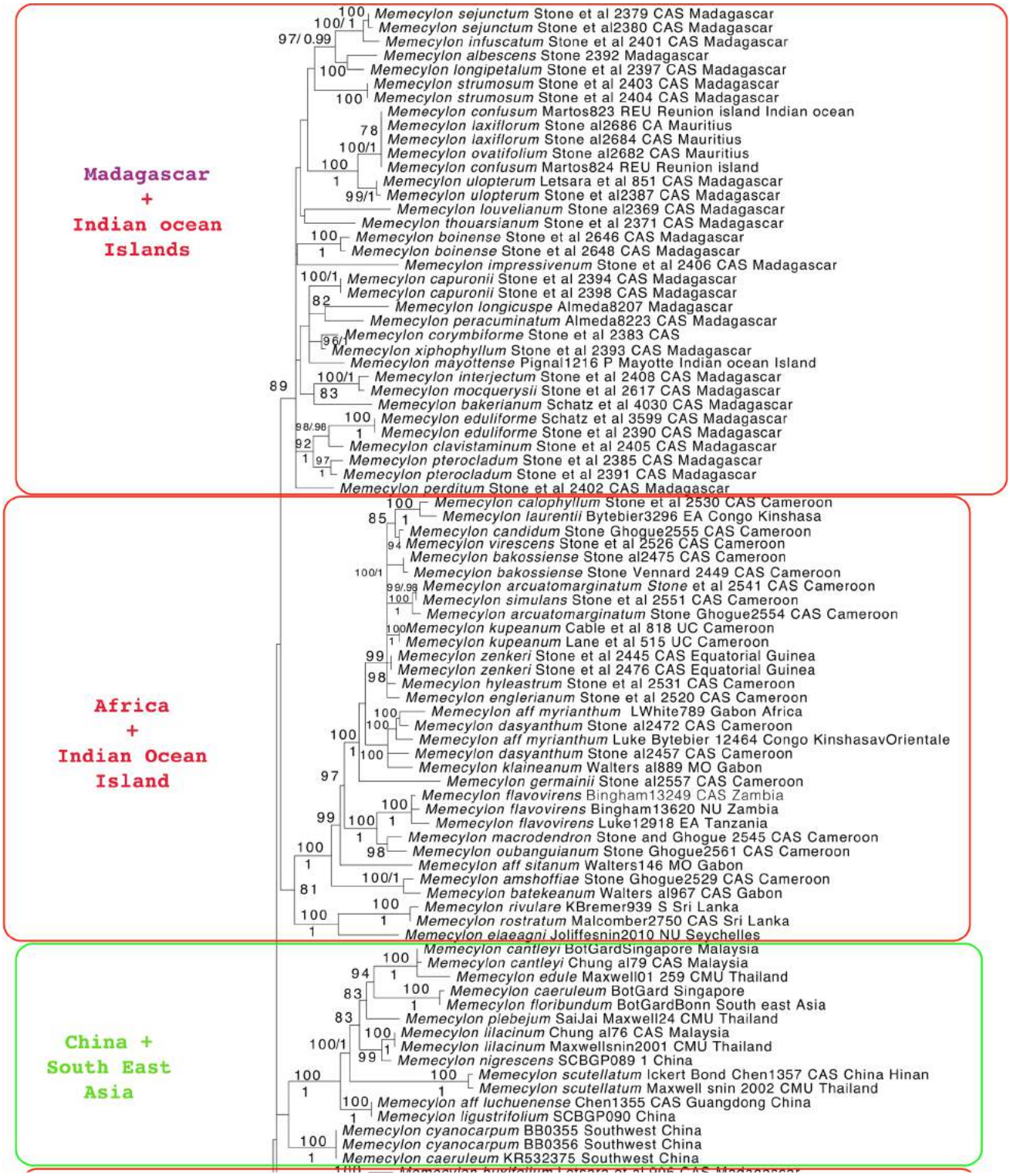

Figure 3. *continued*

species, namely *M. ovatum* from Malaysia. *M. clarkeanum* and *M. lawsonii* and *M. wayanadense* (only rbcL sequence) are in a polytomy (BP 90; PP -), which is in turn sister to *M. heyneanum* (BP 97; PP 0.95).

Kerala clade (83 BS; - PP) comprises of all the species analysed and collected from Kerala. The clade consists of *M. agastyamalaianum* sister to *M. sessile* (BP 98; PP -), *M. travancorense* is recovered sister (BP 97; PP-)

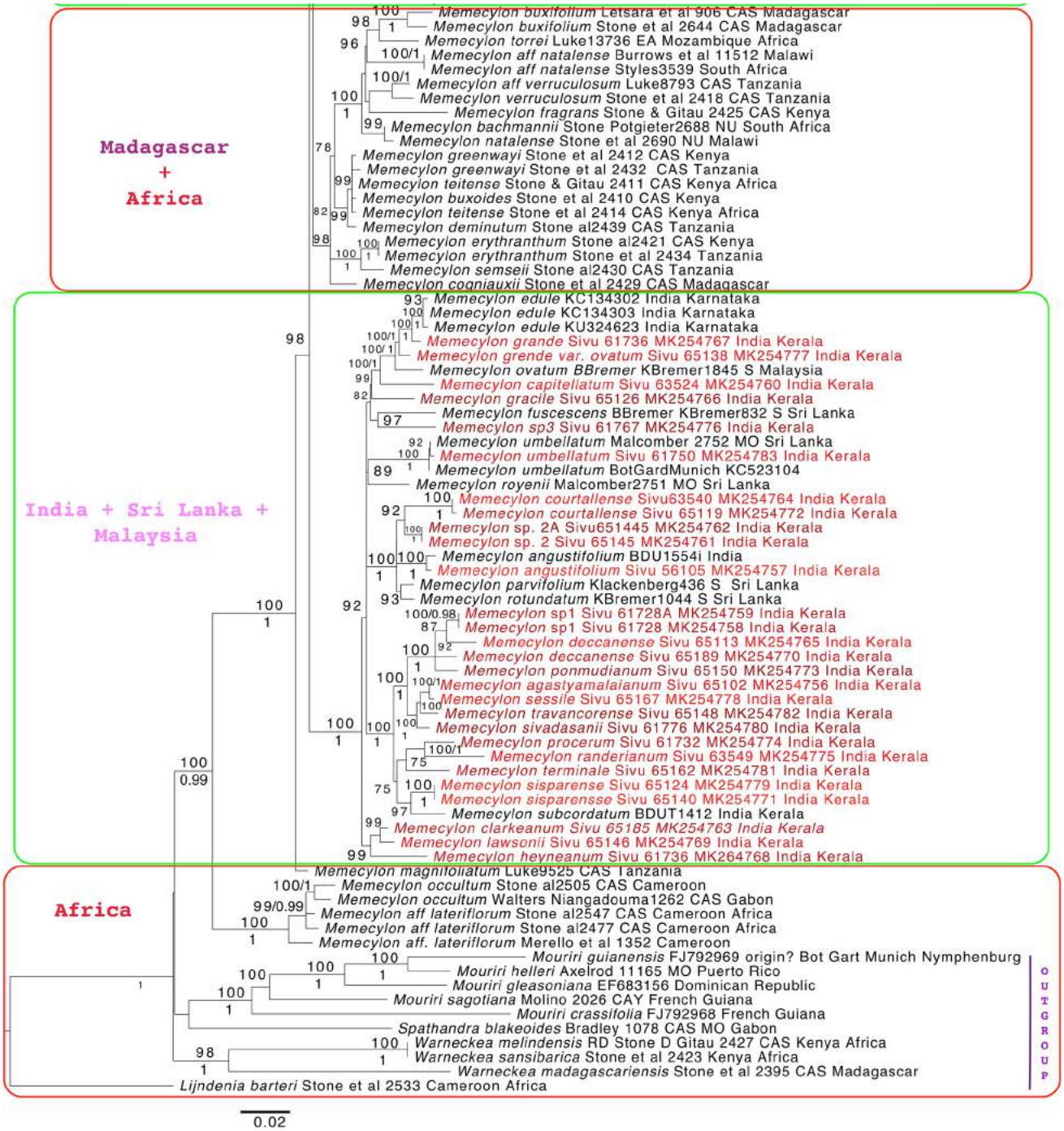

Figure 3. Best ML tree retrieved after analysing 771 nucleotide sites from 168 accessions including outgroups taxa. ITS sequence data includes accessions from previous studies and data generated in the present study. The outgroups were selected from previous studies by Stone (2014). RAxML bootstrap values ≥75% indicated above the branches, Bayesian posterior probability values ≥ 0.95 below the branches. The newly generated sequences for the *Memecylon* accessions are marked with red.

M. travancorense and *M. sessile. M. sivadasanii* is sister to all the before mentioned species in the Kerala clade. In the same clade there are a few unnamed taxa, two accessions of *Memecylon* spec. nov. 1 (BP 99; PP 1) is recovered sister to *M. deccanense* (BS 82; PP 0.98). Along with *M. deccanense* some more species are in polytomy like *M. ponmudianum* (BS 79; PP-). *Memecylon procerum* is recovered sister to *M. randerianum* (BP 96; PP-), *M. terminale* is sister to *M. procerum* and *M. randerianum* but has low support value in combined phylogram (figure 3) while good support (BP 75;

PP-) in only ITS phylogram (figure 2). Two accessions of *M. sisparense* (BP 96; PP -) is embedded in a clade (BP 76; PP-) along with *M. talbotianum*. *M. subcordatum* (Kerala) obtained from GenBank is sister (BP 77; PP-) to *M. sisparense* and *M. talbotianum.*

Another newly analysed species but not described here is *Memecylon* sp. 2 is recovered sister (BS 93) to two accessions of *M. courtallense* and one accession of *M. kollimalayana* in polytomy (BS 95; PP 1). *M. angustifolium,* an endemic species, is placed in the same clade (BS 100; PP 1) along with *M. curtallense* in polytomy. *M. parviflolium* and *M. rotandatum* are sister species (BP 92; PP -) from Sri Lanka*,* both the species are also placed as sister in the same clade in polytomy.

Another well supported clade (BP 73; -PP) comprising of three accessions of widely distributed species *M. edule* (BS 100; PP 1). *M. grande* and one variety of *M. grande* var. *ovatum* is sister to *M. edule* (BP 100; PP 1). This in turn is sister to *M. capitellatum* (BP 99, - PP). In the clade consisting *M. umbellatum* from various localities (India, Sri Lanka, Munich Botanical Garden) is recovered monophyletic (BP 100; PP 1) and *M. royenii* collected for Sri Lanka is recovered sister to *M. umbellatum* with a moderate support (71 BS, - PP) in combined phylogram (figure 3).

Discussion and conclusion

This is first molecular systematic study of the Indian *Memecylon*, which includes 26 species of the 37 species found in peninsular India. *Memecylon* is monophyletic. Indian members nest within a strongly supported clade comprising of members occurring in India and species from Southeast Asia. Monophyly of the Indian species is evident from the fact that the species from the peninsular India sampled and analysed are grouped in one major well supported clade (figures 2 and 3).

The combined as well as individual analyses reveal that the branches of the trees are short and weakly supported at the base which could be due to rapid radiation and decrease in rate of speciation. This assumption has also been made in some previous studies (Rabosky and Lovette 2008; Morlon *et al*. 2010; Venditti *et al*. 2010). The strong geographic structure, whereby well-supported subclades (in most cases) are each associated with a particular region, can be attributed to the phylogenetic niche conservatism in combination with limited or historically contingent opportunities for long-distance dispersal (Donoghue 2008). A similar pattern of strong geographic structuring has been found in phylogenetic studies of other species-rich, tropical groups, e.g., *Begonia* (Forrest *et al*. 2005; de Wilde *et al*. 2011), *Impatiens* L. (Janssens *et al*. 2006), *Piper* L. (Jaramillo *et al*. 2008), *Miconia* (Goldenberg *et al*. 2008), neotropical Melastomateae (Michelangeli *et al*. 2013) and the genus *Indigofera* (Schrire 2009).

This is the first inclusive study using nuclear and chloroplast sequences to estimate the phylogenetic relationships in the Indian *Memecylon*. The phylogenetic results reveal several insights into the history of the genus, many of which were supported by Stones's high bootstrap percentages and high posterior probabilities. Recent classification proposed by Stone (2006a, b, 2014) divided the genus into 13 sections of which he refrained to provide any section for the species from India and Indo-Malayan region. The sectional classification was based on smaller species-groups within each of the larger, geographically based groups. The current sectional classification is supported by our phylogenetic study including Indian representatives. The phylogeny reveals that the Indian members are nested with African members, namely *M. laterifolium*, *M. afflateriflorum*, *M. occultum* and *M. magnifoliatum* and form a strong supported clade (99 BS, 0.99 PP). Also *M. magnifoliatum* belonging to section *Magnifoliata* collected from Tanzania, Africa, is basal to the clades (1 & 2) of the Indian species and is phylogenetically isolated. This points to the fact that the possible origin of the Indian species is in Indo-Malayan or Indian sub-continent with probably only one event of dispersal.

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Author contribution

Plant materials were collected by Sivu, Pradeep and Pandurangan, AKP and MDD analysed molecular data. All authors helped in writing the manuscript.

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Review Article

Atlas of *Bryum* Hedw. Species from India

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ABSTRACT

India is recorded as one of the mega biodiversity countries on the earth. The unique geographical zone and the physical-climatic features of the various biogeographic area resulted in the remarkable floral diversity of India. Bryophytes are small imaged amphibians with three different lineages such as liverworts, hornworts and moss. The category moss represents the largest group with more number of species. The present study aims to compile *Bryum* species of India based on all the available literature and information from herbaria of various organizations. *Bryum* is one of the largest genus among the moss species with morpho-plasticity of characters. Leaves form the unique character of the species, but a high discrepancy in leaves is recorded among the various species of the genus therefore it is wise to select other features unless it is established on specimens of diverse ecology. Sporophytic characters are ideal, but in most species, they remained unexplored as compared to the gametophytic datay. Similarly, the sporophytic capsules are highly diverse in size and their configuration is often irregular with abnormal peristomial characters. Further, the spores are diverse in size and shape. More than 45 species were recorded by various bryologists from India. Many species are similar in look with confusing characters. Therefore, revision of *Bryum* is warranted to eliminate the overlapping and complex allied clusters among the reported species.

Keywords: Bryophytes, *Bryum*, Characters, Distribution, India, Species diversity.

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INTRODUCTION

Bryophytes are specialized species that represent the second highest lineage among terrestrial plants after the Angiosperms.[1] Most of the species possess high surviving capacity under a wide variety of environmental conditions and also form an inherent part of the ecosystem where they form the pioneer group. They are common in different forest types, damped areas, dry areas and other habitats. Though fundamentally terrestrial, few are aquatic like *Riccia fluitans, Ricciocarpus natans* and *Riella* spp. Species of *Cryptothallus* and *Buxbaumia* are saprophytic liverworts contrary to the autotrophic bryophytes.

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Bryum Hedw., an acrocarpous species of Bryaceae. 21 species from seven northeastern states of the Himalayas such as Arunachal Pradesh, Assam, Manipur, Meghalaya, Nagaland, Sikkim and West Bengal were documented.[2] Out of the 21 species, *B. argenteum* var. griffithii (Muell. Hal.) Gangulee, *B. billardieri* Schwaegr., *B. pallescens* Schleich. ex Schwaegr., *B. pseudotriquetrum* (Hedw.) P. Gaertn., B. Meyer and Scherb., *B. pseudotriquetrum* var. subrotundum (Brid.) Gangulee and *B. reflexifolium* (Ochi) Ochi were recently reported from Meghalaya; *B. billardieri* Schwaegr. from Manipur, *B. apiculatum* Schwaegr., *B. caespiticium* Hedw. and *B. pseudotriquetrum* var. subrotundum (Brid.) Gangulee were new reports from West Bengal.

Bryum species are small to robust, with variable size and coloration, forming tufts, terrestrial or often epiphytic. The stem was a few millimetres to centimetres in size, mostly reddish brown, usually with many rhizoids. Cross Section reveals firm-walled cortical cells and developed or poor central strands of smaller thinner-walled cells. Leaves evenly spaced on stem or clustered and enlarged

at stem apex (comose), erect or - escalate under damp environmental condition, rounded, elliptic, ovate or lanceolated, acute, acuminated, or rarely rounded at apex, ± concave, not complanate, often with secondary pigments, toothed or entire, bordered, recurved or less often plane, sometimes decurrent; upper laminal cells hexagonal or rhombic-hexagonal, thin- or firm-walled, porose or not, becoming more oblong in lower leaf; marginal cells differentiated, linear, usually forming a strong or weak border. Costa strong, excurrent, percurrent or occasionally shorter, with a single abaxial stereid band. Brood bodies (gemmae, tubers, or bulbils) are recorded.

Bryum species are dioicous or monoicous. Perichaetia is apical on the main trunk or on mini lateral branches originating from the stem base, very often overtopped by subperichaetial innovations (seems lateral); perichaetial leaves are mostly moderately differentiated. Perigonia with multiple filiform paraphyses and antheridia. Setae elongate, flexuose to cygneous, one per perichaetium; capsules cernuous, pendent or rarely suberect, variable in form, mostly pyriform, clavate, cylindric, or rarely globose, well-developed neck, straight or curved; stomata numerous, superficial, and restricted to the neck; annulus well-formed and revolvable; operculum conic, sometimes apiculate. Peristome is double and often regular; exostome teeth yellowish-brown or pale, finely papillose below and mostly hyaline and baculate above, bordered, densely trabeculate on adaxial surface; endostome with thick basal sheath, well-developed, perforated or fenestrated segments, and with cilia in groups of 1–3, appendiculate, nodose, or occasionally reduced or absent. Calyptra cucullate, is smooth and the spores are spherical and nearly < 30 µm in size.

Bryum is one of the mega genus with multiple taxonomic issues among the moss category with a range of plasticity in morphological characters. Some estimates revealed 800 species [3] or even 1050 species.[4] Ochi estimated 180 or more species distributed globally,[5] while only 24 species were accepted in New Zealand. Ochi provided an ideal abstract for classification of the Bryaceae.[5]

Spenc attempted radical changes in the classification of *Bryum*.[6] Spence and Ramsay reassigned Australian species traditionally placed in *Bryum* into five genera while retaining five Australian species within a narrowly circumscribed *Bryum*.[7]

Generally, a highly-developed peristome in *Bryum* is referred to as a perfect category i.e., a double peristome with the following specialities such as 1. exostome teeth with a distinct median zig-zag abaxial visual line, finely papillose on the lower abaxial surface, mostly hyaline and baculate above, bordered, and densely trabeculate adaxially; and 2. endostome arising from a thick basal sheath, with well-developed, keeled, and perforate segments, and appendiculate cilia in groups of 1–3. Thus, the perfect peristome (which is similar to that occurring in certain *Hypnum* spp. and their allied species) provides a reference point linked with the study of moss morphology. Characters of the peristome have historically been used in the construction of classifications of moss and recently it assumed a less significant, with the development of classifications based primarily on molecular features.

The variability of many *Bryum* species makes identification difficult especially if sterile. Vegetative features are used the possible way in key preparation of the species. Many of the species have distinct characters which facilitate their easy recognition. However, some of these features are difficult to incorporate into a conventional identification key. Thus, some *Bryum* collections were difficult to identify practically.

Many *Bryum* spp. possess rhizoidal tubers in the populations and these can often facilitate species recognition. Tuber morphology is of taxonomic significance in the differentiation of species included in the *B. erythrocarpum* complex. Tubers can be sparse, even in species reputed to bear them consistently. *B. erythrocarpum* complex *sensu* Crundwell and Nyholm is given under the discussion of *B. duriusculum*, which is the most widespread member of the complex.[8] Six species of the *B. erythrocarpum* complex are accepted which includes *B. duriusculum, B. radiculosum, B. ruderale, B. sauteri, B. rubens* and *B. tenuisetum*.

Although sharing features with other genera in Bryaceae or the Mniaceae (notably *Brachymenium* and *Pohlia*), the genus *Bryum* usually is easily distinguished by its rhombic-hexagonal laminal cells, mostly percurrent or excurrent costae, usually bordered and recurved leaf margins, and often cernuous or pendent capsules. Plants belonging to *Pohlia* generally have longer and narrower laminal cells and lack leaf borders, whereas *Brachymenium* is predominantly epiphytic and more robust and has erect capsules with highly reduced endostomes. Mostly, the key to *Bryum* species and its allied genera is based on the length of the largest stem leaves (including perichaetial leaves but excluding the excurrent portion of the costa) as follows: robust, leaves >4.0 mm; large, leaves 3.0–4.0 mm; medium-sized, leaves 1.5–3.0; and small, leaves <1.5 mm.

Bryum affine Lindb. and Arn. and *B. bimum* Scherb. have been used as a "dumping ground" for several disputed species from New Zealand. The correct application of these and other names associated with them has been the source of taxonomic and nomenclatural confusion

for some time.[4,9-11] The resolution of this taxonomic and nomenclatural tangle (also involving *B. creberrimum*, q.v.) is beyond the scope of the present review.

The name is *Bryum chrysoneuron* Mull. Hal. was applied by several New Zealand workers (including Dixon, Sainsbury, Allison, and Linzey) to at least three tuber-bearing species (*B. duriusculum, B. sauteri, and B. clavatum*). Ochi attempted to refine the application of the name *B. chrysoneuron* but was unable to locate the type material (collected by S. Mossman "ad flumen Wairoa-river prope portum Kaipara").[12] The holotype was probably destroyed in the WWII burning of the Berlin herbarium. Efforts to locate potential type material for this name in other herbaria have failed. Given the lack of identifiable type material, and uncertainty surrounding the application of Müller's name, *B. chrysoneuron* is considered a nom. dub. and it is not applied in this work. A large proportion of the collections previously named *B. chrysoneuron* are referable to *B. duriusculum*.

The highly variable *Bryum microerythrocarpum* Mull. Hal. and Kindb. is a Canadian type, common in the northern parts of the hemisphere, and is also recorded from New Zealand regions.[8] It is likely a later name for *B. duriusculum* Hook. f. and Wilson, which has a New Zealand type. The relationship between these two species is best examined in a monographic context and *B. microerythrocarpum* is not discussed further in this part.

The name is *Bryum obconicum* Hornsch. was applied to New Zealand material by Hooker and Wilson.[13] That name has been applied to numerous collections in New Zealand herbaria that are referred to as *Rosulabryum capillare*. Syed considered much material named as *B. obconicum* Hornsch. to belong to *B. torquescens* Bruch.[14] In this treatment, *Bryum obconicum* is not accepted as a member of the New Zealand flora. In this scenario, an attempt was made in the *Bryum* species recorded from India (Table 1) and was compiled in the present study.

MATERIALS AND METHODS

The method used for the study was a combination of field, herbarium record analysis and literature review related to the species.

Primary Data Collection

Data about *Bryum* species was obtained from a field study in various districts of Kerala and Tamil Nadu.

Secondary Data Collection

Survey of available literature from online and offline modes about *Bryum* species. Also referred to various resources such as ENVIS Hub: Kerala, India Biodiversity Portal, British Bryological Society etc. Similarly, the herbarium collections available across Southern parts of India were also checked to validate the species name recorded.

RESULTS AND DISCUSSION

'Hortus Indicus Malabaricus' by Henricus van Rheede was the first report of bryophyte resources from the Western Ghats. He described the moss as 'poem-peda', the commonest species of mosses from South India, later renamed as *Bryum coronatum* Schwagr., by Robinson.[2] Gangulee[43] made valuable contributions to the genus *Bryum*. He described twenty-two species of *Bryum* from Eastern and adjacent regions of India. In his report, Sikkim has high diversity which is 12 taxa followed by 9 species from Darjeeling. The lowest number of species was from Arunachal Pradesh and Assam i.e., with 2 taxa each. Dandotiya *et al.*,[33] contributed data about Indian *Bryum* species in his 'A checklist of the bryophytes of India'. Which included 45 *Bryum* species from various Indian states. Among which highest number of taxa was listed from eastern Himalayas (26 numbers). Barukial reported 4 species from Assam.[45] First report of *B. argenteum* from Nagaland was done by Bansal and Nath.[46] They also reported *B. bessonii* from Eastern Himalayas and *B. coronatum* from Meghalaya for the first time.[46]

Pradhan and Joshi[47] recorded 39 ***Bryum*** species from Nepal. Rawat *et al.*, surveyed Mosses (Bryophyta) of Gangetic Plains, India[48] and revealed only 3 species of ***Bryum*** only. Sameer Ahmad Thoker and Sapan Patel reported 5 species from Jammu and Kashmir,[49] Afroz Alam *et al.*, documented 15 species of *Bryum* from Central India.[17] *Bryum* occurs even in the cold desert of Leh Ladakh.[50] 4 species were reported by Anshul *et al.,* from Ladakh. The checklist of the mosses of Karnataka by Frahm *et al.,* reported 10 species.[18] 26 taxa of the genus were documented from the 4 states of Peninsular India[15] (Karnataka, Kerala, Maharashtra, Tamil Nadu) and Goa of Western Ghats, whereas 8 species were reported from Andhra Pradesh, parts of Odisha and Tamil Nadu of Eastern Ghats by Bansal and Virendra Nath (2014).[15] Only two species were recorded such as *B. argenteum* and *B. wightii* from Aralam Wildlife Sanctuary of the Western Ghats by Manju *et al.*,[51] In Kerala, more species were reported from Idukki by Suman,[52], Joshi[35] (reported 8 species), and Wayanad by Manju *et al.*,.[53]

CONCLUSION

Bryophtes represent ecologically unique amphibians with high diversity in various ecological habitats. The

Table 1: *Bryum* species in India.

Sl. No	Binomial	Specimens examined	Location
1	*Bryum alpinum* Huds. *ex* With. Syst. Arr. Brit. Pl. (ed. 4) 3: 824. 1801.[15-16,20,30-31,33] Habitat: Grows on wet soil and rock	Western Ghats: Kerala: Vattakkayam, Kakkayam, Kozhikode, alt. 1050 m, on rocky patch, Coll.: Manju and K.P. Rajesh 120180 (CAL)[15]	Western Ghats: Kerala-Kozhikode; Maharashtra-Kasara (Thal Ghat), Khandala, Mahabaleshwar; Tamil Nadu-Nilgiri hills, Palni hills
2	*Bryum ambiguum* Duby. Die Musci der Flora von Buitenzorg 2: 544. 1904.[17]		South India
3	*Bryum apalodictyoides* Mull. Hal., Bot. Zeitung (Berlin) 11: 21. 1853. [15,18-19,33,42]	Western Ghats: Karnataka: Herb. Walker, near Hatur, Coorg, India, on dry exposed rocks in bamboo jungle, Coll.: T.L. Walker 189, Det.: *V.F. Brotherus* (FH); Herb. Walker, near Nalknad Palace, Coorg, India, on tree trunks, Mar. 1898, Coll.: *T.L. Walker* 326, Det.: *V.F. Brotherus* (FH); Bryophytes of Western India, Union of India, Bombay State, Satara district, Mahabaleshwar, near the summit of the Western Ghats, altitude about 4500 feet, 17°55' N, 73°40' E, stone wall, Coll.: Hale H. Cook, Det.: H.A. Gleason, Jr. (FH 15, 16).	Western Ghats: Karnataka-Kodagu (Hatur, Nalknad Palace); Kerala-Palakkad (Silent Valley); Maharashtra-Mahabaleshwar; Tamil Nadu-Kodaikanal (Tiger Chola), Nilgiri hills, Palni hills Eastern Himalayas
4	*Bryum apiculatum* Schwaegr., Sp. Musc. Frond., Suppl. 1(2): 102. f. 72. 1816.[15,31,33,42] Habitat, Terrestrial	Western Ghats: Kerala: Muthanga range, Wayanad WLS, alt. 878 m, Coll.: Manju 84510 (CAL); Tamil Nadu: Sea field, Kanyakumari, 820 m, Coll.: *A.E.D.* Daniels and J.L. Mabel (AEDD 450); Natchur, Palni hills, Coll.: *Foreau* 553a Det.: *H.N. Dixon* (FH). Deccan Plateau and Eastern Ghats: Andhra Pradesh: University of Toronto Herbarium, Flora of India-Herb. Walker, Jeypore Taluq, Vizagapatam, Coll.: *T.L. Walker* 535, 554 Det.: *H.N. Dixon* (FH).	Western Ghats: Karnataka-Agumbe (Hulical Ranges); Kerala-Wayanad; Maharashtra-Khandala, Lonavala, Mahabaleshwar, Purandar Fort; Tamil Nadu-Kanyakumari, Nilgiri hills hills (Udhagamandalam-Naduvattam), Palni hills; Deccan Plateau and Eastern Ghats: Andhra Pradesh-Guntur, Vishakapatnam; Odisha-Koraput, Puri; Tamil Nadu-Shervaroy hills, Himalayas, African countries
5	*Bryum argenteum* Hedw., Sp. Musc. Frond. 181. 1801.[15,20-21,30,33,42] Characterized by the smaller size, the leaf tips curved outside and the occurrence in natural habitats, such as soil in open grassland. In contrast, the much 'fatter' *B. argenteum* var. argenteum with straight leaf apices is a nitrophilous species from urban habitats.	Western Ghats: Karnataka: Herb. Walker, Hatur, Coorg, Coll.: *T.L. Walker* 193, Det.: *V.F. Brotherus* (FH); Kerela: Idukki district, Marthoma Campus, Munnar, Leg.: *V. Nath* 247681, 247682B (LWG); Marthoma Campus, Munnar, grows on bricks, Leg.: *V. Nath* 247683A (LWG); Thirunelli Reserve Forest, Wayanad, alt. 1180 m, grows on land cuttings, Coll.: *Manju* (CAL 99625); Tamil Nadu: Narakkad, Tirunelveli, alt. 1000 m, saxicolous, Coll.: *A.E.D. Daniels* (AEDD 76); Herbarium of Edwin B. Bartram, Herbier Charrier, Indes Owglaises, Kodaikanal, 8 mai 1912, Leg.: *R.P. Foreau* (FH); Perumal, May 1923, Coll.: *G.F. Foreau* (FH); Herb. Edwin B. Bartram, Flora of South India, Nilgiri hills, Coll.: *C. Srinivasan* 143, Det.: *E.B. Bartram* (FH); St. Xavier's College, Palamcottah, Palney hills, alt. 6000 ft, Coll.: *G.F. Foreau* (FH); Beschi College Herb., Shembaganur, Palni hills, Kodaikanal, alt. 7000 ft, Coll.: *G.F. Foreau* 16 (FH). Sp. Musc. Frond. 181, 1801.Central India (without any locality as *B.argenteum* var. lanatum) Gujarat: Girnar hill, Pavagarh, Sabarkantha forest, Saputara.[26] Madhya Pradesh: Bhopal Pachmarhi.[29] Rajasthan: Mount Abu[25,27-28] Kumbhalgarh, Udaipur.[23,25]	Western Ghats: Karnataka-Agumbe (Hulical Ranges), Kodagu; Kerala-Chinnar Wildlife Sanctuary, Eravikulam National Park, Idukki, Wayanad; Maharashtra-Kasara (Thal Ghat), Khandala, Mahabaleshwar, Panchgani; Tamil Nadu-Anamalais, Kodaikanal, Nilgiri hills (Udhagamandalam), Palni hills; Deccan Plateau and Eastern Ghats: Odisha-Koraput; Tamil Nadu-Shervaroy hills, China, Japan, Malaysia, Papua New Guinea, Philippines, Taiwan, Thailand, Vietnam, Madagascar, America, Africa and Europe
5a	*B. argenteum* var. argenteum[33]	Nilgiri hills	Nilgiri hills

continued...

Table 1: Cont'd.

Sl. No	Binomial	Specimens examined	Location
5b	*Bryum argenteum* var. griffithii (C.Muell.) Gangulee.[31,33] Habitat: cement wall/ rock	INDIA, Meghalaya: Shillong: Lum Nehru Park, Umiam, alt. c. 1014 m., grows on stony wall, Leg.: V. Sahu and V. Awasthi, 251557 (LWG)	Assam, Manipur , Meghalaya.
5c	*Bryum argenteum* var. lanatum (P.Beauv.) Hamp.[33] Habitat: cement, brick wall,soil	Sikkim, Darjeeling, Arunachal Pradesh, Khasia hills, Orissa hills, W. Himalaya, Kashmir, Manipur, W. Ghats, Nilgiri, Palni	Sikkim, Darjeeling, Arunachal Pradesh, Khasia hills, Orissa hills, W. Himalaya, Kashmir, Manipur, W. Ghats, Nilgiri, Palni
6	*Bryum atrovirens* Brid., Muscol. Recent. 2(3): 48 1803.[31,33] Habitat: Terricolous; on soil	On way to Hemkund, alt. ca 3343 m, Leg.: S. Chandra 200872G, 200893C (LWG).	Assam, Manipur, Sikkim, Kumaon, Mussoorie
7	*Bryum auratum* Mitt. J. Proc. Linn. Soc., Bot., Suppl., 1: 67, 67, 1859[35] Habitat:Wet rocks	Munnar	Idukki
8	*Bryum badhwari* Ochi.[33,37-38] Habitat: soil	Kedarnath Wildlife Sanctuary (KWLS), Garhwal Himalaya,[38]	Western Himalaya, Manipur and Eastern Himalayas
9	*Bryum bessonii* Ren. and Card., Suppl. Prodr. Fl. Bryol. Madag. 59. 1909.[15,31] Rupicolous; on stony wall	Dehra Dun district, Mussoorie, Company Garden, alt. ca 1945 m, Leg.: V. Nath and party 228205C (LWG).	Western Ghats: Goa-Rivona and Zambaulim; Tamil Nadu-Kodaikanal (Shenbaganur), Palni hills. Uttarakhand: Garhwal hills - Mussoorie; Kumaun hills - Nainital, Pithoragarh
10	*Bryum bicolcor* Dicks. Fasciculus Plantarum Cryptogamicarum Britanniae 4: 16. 1801.[33]		Sikkim, Darjeeling, W. Himalaya, Kumaon, Nainital
11	*Bryum billardieri* Schwaegr., Sp. Musc. Frond. Suppl. 1(2): 115. 1816.[15,31,33] Habitat:Common on humic soil and earth covered rocks in forests at all elevations	Western Ghats: Karnataka: *B. ramosum* (Hook.) Mitt., Herb. Walker, near Verajpet, Coorg, dry clay banks, Coll.: *T.L. Walker* 290, Det.: *V.F. Brotherus* (FH); KERALA: near Eravikulam Hut, Eravikulam NP, Munnar, Idukki, alt. 1975 m, epiphytic on *Cupressus* associated with Lichen and *Drymoglossum*, Coll.: *Manju* 76053a (CAL); Shendurney Wildlife Sanctuary, Kollam W. Ghats, 560 m, rupicolous, 04.11.2008, Coll.: *R. Felix* (AEDD 245). Tamil Nadu: Himalayan Mosses, Ootacamund, 7500 ft, on soil, Coll.: *H. Gangulee*, Det.: *E.B. Bartram* (FH 3156); Ex Rijksherbarium, Leiden, Nilgiris, Naduvattam, along road from Utacamund to Gudalur, on tree trunk, *ca* 2000 m, Leg.: *A.J.G.H. Kostermans* 4 (FH); Herbier Charrier, Indes Owglaises, Kodaikanal, Leg.: *R.P. Foreau* (FH); Perumal, Leg.: *G.F. Foreau* (FH); St. Xavier's College, Palamcottah, Palney hills, 5600 ft., 1929, Coll.: *G.F. Foreau* (FH); Mosses of Southern India, Madras State, Madura district, Palni hills, Kodaikanal and surrounding region, Shembaganur, Tiger Shola, alt. *ca* 5600 ft, Leg.: *G. Foreau* 184, Residue of "Musci Madurenses Indiae Meridionalis Exsiccati", issued by Georges Foreau, S.J. distributed by The New York Botanical Garden (FH); Herb. Of Edwin B. Bartram, Herbier Charrier, Indes Owglaises, Tiger Shola, Gubey hills, Leg.: *R.P. Foreau* (FH).	Western Ghats: Karnataka-Kodagu (Verajpet, Ponnapet); Kerala-Eravikulam National Park, Idukki, Shendurney Wildlife Sanctuary; Tamil Nadu-Kodaikanal (Law's Ghat road, Shenbaganur and Tiger Chola), Madurai, Nilgiri hills (Udhagamandalam-Naduvattam), Palni hills, Perumal

continued...

Table 1: Cont'd.

Sl. No	Binomial	Specimens examined	Location
12	*Bryum bornholmense* Wink. and R. Ruthe Hedwigia, 38 (Beibl. 3): 120, 120, 1899[36]	Bikaner[25]	Rajasthan
13	*Bryum bryoides* (R. Br.) Angstrom[17]		Western Himalayas
14	*Bryum caespiticium* Hedw., Sp. Musc. Frond. 180. 1801.[15,21,31] Habitat: brick wall	Madhya Pradesh: Raisen - Bhimbetka.[22] Mandla- Kanha National Park.[19] *Bryum cappi*lare Hedw., Sp. Musc. Frond. 182, Ptychostomum cappilare(Hedw.) D.T. Holyoak and N.Pederson	Western Ghats: Tamil Nadu-Kanyakumari, Tirunelveli Madhya Pradesh
15	*Bryum capillare* Hedw., Sp. Musc. Frond., 182. 1801.[15,20,31,33-34,42] Habitat: On damp soil or on small rocks in semi shaded areas of semi-evergreen forests	Western Ghats: Kerala: Idukki district, Mesthirishola, Eravikulam NP, Munnar, alt. 2000 m, grows on rocky patch, Coll.: *Manju* 80218 (CAL); TAMIL NADU: Kanyakumari, Sea field, 820 m, terricolous, Coll.: *A.E.D. Daniels* and *J.L. Mabel* (AEDD 416)[39] p; GOA: Keri Surfa (Border of Goa-Karnataka), corticolous, Coll.: *Sulabha Phatak* (LWG 552, 558).	Western Ghats: Goa-Keri Surfa; Kerala-Eravikulum National Park, Idukki, Munnar, Wayanad; Tamil Nadu-Kanyakumari, Palni hills, Nilgiri hills (Udhagamandalam-Naduvattam), Tirunelveli; Deccan Plateau and Eastern Ghats: Andhra Pradesh-Guntur; Tamil Nadu-Shervaroy hills. Gujarath China, Thailand, Vietnam, Taiwan, Korea, Japan, Siberia, Central Asia, Europe, North and Central Africa, North and South America, Australia and New Zealand
16	*Bryum cellulare* Hook. *in* Schwaegr. Sp. Musc. Frond., Suppl. 3(1): 214. 1827.[15,20,31,33-34,42] Habitat: On soil cuttings along with other mosses in semi-evergreen forests	Western Ghats: Kerala: Palakkad district, Parambikulam WLS, alt. 1100 m, grows on rocky patch, Coll.: Manju 106823 (CAL). Gujarat: Pavgarh, Saputara, Waghai Botanical Garden[26] Rajasthan: Mount Abu.[25]	Western Ghats: Kerala-Kakkavayal Reserve Forest, Parambikulam Tiger Reserve, Wayanad; Tamil Nadu-Nilgiri hills (Doddabetta), Palni hills (Gundar Shola); Deccan Plateau and Eastern Ghats: Andhra Pradesh-Guntur Western Himalayas, Gujarath Myanmar, China, Japan, Sumatra, Java, Philippines, Taiwan, Europe, North and Central Africa and Australia
17	*Bryum clavatum* (Schimp.) Mull. Hal., Sp. Musc. Frond., 1: 292. 1848[31]	Garhwal hills in Uttarakhand	Uttarakhand: Garhwal hills - Arnigadh, near Mussoorie
18	*Bryum constricta*[33]		Kumaon, Shimla, Mussoorie, Nainital, Punjab, Darjeeling, Sikkim, Rajasthan, Gujarat
19	*Bryum coronatum* Schwaegr., Sp. Musc. Frond., Suppl. 1(2): 103. 71. 1816.[20,31,32-34] Habitat: On calcareous soils or walls and also on rocks along with *Funaria hygrometrica* and *Hyophila involuta* in homesteads and in semi-evergreen forests. Distribution: It is common throughout the study area, mostly in the mid altitudinal range from 500-800 m	Western Ghats: Karnataka: Shimoga, Agumbe, alt. *ca* 600 m, grows on soil, Leg.: S. Chandra and V. Nath 204124 (LWG); Bryotheca Elevier, S.W. Brit. India, Mangalur (South Canara), Aug. 1906, Leg.: *Rev. J. Pfleiderer* 6821, Det.: *V.F. Brotherus* (FH); Herb. Walker, dry clay ground at Pollebetta, South Coorg, India, Coll.: *T.L. Walker* 215, Det.: *V.F. Brotherus* (FH); Herb. Walker, logs in Bamboo jungle-Ponnapet in South Coorg, India, Coll.: *T.L. Walker* 238, Det.: *V.F. Brotherus*(FH); Kerala: MG University campus, Kottayam, alt. 40 m, grows on brick wall, Coll.: K.P. Rajesh 120380 (CAL); GOA: Margao, Lithophyte, on laterite walls, Coll.: Mini N. Vijayan (LWG 8); Tamil Nadu: Sea field, Kanyakumari, 820 m, saxicolous, Coll.: A.E.D. Daniels and J.L. Mabel (AEDD 472). Deccan Plateau and Eastern Ghats: Andhra Pradesh: University of Toronto Herbarium, Flora of India-Herb. Walker, Jeypore Taluq, Vizagapatam, 2000-4500 ft, Coll.: T.L. Walker 525, 541, 563, 575, Det.: *H.N. Dixon* (FH); Himalayan mosses, near Cuttack, 29.X.58, Coll.: *H.C. Gangulee* 3115, Det. *E.B. Bartram* (FH). Gujarat Pavagarh, Saputara,Waghai Botanical Garden[26] Madhya Pradesh: Bhopal Pachmarhi[29] Mandla: Kanha National Park[18] Rajasthan: Kumbhalgarh.[23,25]	Western Ghats: Goa-Margao, Rivona, Zambaulim; Karnataka-Kodagu, Mangalur (South Canara), Agumbe (Hulical Ranges, Kanagalgudda); Kerala-Eravikulum National Park, Idukki, Wayanad; Maharashtra-Kasara (Thal Ghat) Khandala, Mahabaleshwar, Pune; Tamil Nadu-Kanyakumari, Maramalmalai, Mundanthurai, Tirunelveli; Deccan Plateau and Eastern Ghats: Andhra Pradesh-Vishakhapatnam; Odisha-Cuttack, Koraput, Puri. Gujarth China, Borneo, Philippines, Thailand, Brazil, Bolivia, Peru and Mexico

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Table 1: Cont'd.

Sl. No	Binomial	Specimens examined	Location
20	*Bryum dichotomum* Hedw., Sp. Musc. Frond. 183. 1801.[15,31,42] Habitat: On land cuttings	Mussoorie, alt. ca 2136 m, × 86-119 µm, Leg.: V. Sahu 251452 (LWG)	Western Ghats: Kerala. Uttarakhand: Garhwal hills Mussoorie; Kumaun hills - Nainital, Pithoragarh
21	*Bryum dunense* A.J.E. Sm. and H. Whitehouse, J. Bryol. 10:41, 1978.[21]	Kumbhalgarh,[23-24] Mount Abu[25]	Rajasthan
22	*Bryum euryphyllum* Dix. and P. Vard., Archives de Botanique, Bulletin Mensuel 1(8-9): 170. 1927.[15,33]		Western Ghats: Karnataka, Kerala.
23	*Bryum flaccum* Wilson ex Mitt. J. Proc. Linn. Soc., Bot., Suppl., 1: 72, 72, 1859[33]		Sikkim Eastern Himalayas
24	*Bryum ghatense* Broth. et Dix[20] Habitat: Grows on moist wall	Lonavala and Mahabaleshwar Sedgwick and Dabhade	Maharashtra Sahyadri Hills)
25	*Bryum haematoneurum* Müll. Hal., Nuovo Giorn. Bot. Ital. 4: 17. 17. 1872.[15]		Maharashtra-Purandhar Fort
26	*Bryum intermedium* (Brid.) Bland.[37] Habitat: grows on cement wall	Keishampat	Manipur
27	*Bryum kashmirense* Broth., Acta Soc. Sci. Fenn. 24(2): 24 24 1899.[15]		Western Ghats: Kerala.
28	*Bryum klinggraeffii* Schimp., Hoh. Crypt. Preuss. 81,1858.[21,33]		Rajasthan: Udaipur Gangetic plains
29	*Bryum lamprostegum* Müll. Hal. Bot. Zeitung (Berlin) 11: 22. 1853.[15,33]		Western Ghats: Tamil Nadu-Nilgiri hills.
30	*Bryum laxelimbatum* Hampe ex Ochi J. Jap. Bot., 43: 112, 112, 1968[33]		Kumaon
31	*Bryum madurense* (Dix. and P. Vard.) Ochi, J. Hattori Bot. Lab. 35: 67. 1972.[15]		Western Ghats: Tamil Nadu-Madurai, Upper Palni hills
32	*Bryum medianum* Mitt J. Proc. Linn. Soc., Bot., Suppl., 1: 74, 1859[43,54] Habitat: Moist soil	Coorg: Ponnapet. Nepal and South India	Karnataka, Nepal
33	*Bryum mildeanum* Jur. Verh. *Bryum mildeanum* Jur., Verh. Zool.-Bot. Ges. Wien 12: 967.1862. *Bryum apiculatum* Schwaegr., Sp. Musc. Frond., suppl. 1, 2: 102.1816.[21]	Zool.-Bot. Ges. Wien Gangetic plains	Rajasthan:Kumbhalgarh wildlife sanctuary,Mount Abu (Bansal and Nath represent as *Bryum apiculatum*).[25]

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Table 1: Cont'd.

Sl. No	Binomial	Specimens examined	Location
34	*Bryum neelgheriense* Mont. Syn. Musc. Frond., 1: 255, 255, 1848[33]	This species is related to *B. billardieri* but has filamentous gemmae in the leaf axils. It was collected once in Honey Valley. Walker collected the species in Coorg on dry clay banks near Virajpet [as *B. ramosum* (Harv.) Mitt.]. The species is treated in the *B. billardieri* complex[40] as well in the B. wightii complex,[41] but seems to be related to *B. billarderi* in the same way as *Bryum moravicum* Podp. and *B. capillare* Hedw. in Europe.	Karnataka
35	*Bryum pachycladum* Cardot ex Potier de la Varde, 1925 Rev. Bryol., 52: 38, 38, 1925[33]		Kodaikanal
36	*Bryum pachytheca* Müll. Hal., Syn. Musc. Frond. 1: 307. 1848.[15]	Western Ghats: kerala: Malappuram Dist., Calicut University Campus, alt. *ca* 40 m, grows on rocky wall, Coll.: *Manju* 87001 (CAL).	Western Ghats: Kerala-Calicut University Campus Kodaikanal
37	*Bryum pallescens* Schleich. ex Schwaegr., Sp. Musc. Frond., Suppl. 1(2): 107. 75. 1816.[31] Habitat: Terricolous; on soil in association with other moss species	Dehra Dun, Chakrata, Janglat Chowki-Deoban, alt. ca 2865 m, Leg.: S. 12. Chandra 202852 (LWG).	Uttarakhand: Garhwal hills - Chakrata, Dehra Dun, Mussoorie, Deoban; Kumaun hills - Nainital.
38	*Bryum paradoxum* Schwaegr., Sp. Musc. Frond., Suppl. 3, 1(1): 224a. 1827.[15,20-21,31,33,44] Habitat: Terricolous.	Western Ghats: Kerala: Kattumala, Eravikulam NP, Munnar, Idukki, alt. 2100 m, grows on rocky patch where water drips regularly, Coll.: *Manju* 80224 (CAL); TAMIL NADU: Herbarium of Edwin B. Bartram, Herbier Charrier, Indes Owglaises, Kodaikanal, 1912, Leg.: *R.P. Foreau* (FH); St. Xavier's College, Palamcottah, Palney hills, alt. 7000 ft, Coll.: *G.F. Foreau* (FH); Perumal, Leg.: *G.F. Foreau* (FH); Mosses of Southern India, India, Madras State, Madura district, Palni hills, Kodaikanal and surrounding region, Shembaganur, Leg.: G. Foreau, Residue of "Musci Madurenses Indiae Meridionalis Exsiccati", issued by Georges Foreau, S.J. distributed by The New York Botanical Garden (FH); Madras State, Madura district, Palni hills, Kodaikanal and surrounding region, Lower Palni hills, Perumalmalai Shola, Residue of "Musci Madurenses Indiae Meridionalis Exsiccati", issued by Georges Foreau, S.J., Distributed by the New York Botanical Garden, Leg.: *G.* Foreau (TNS 051340). Gujarat: Saputara.[26] Madhya Pradesh: Mandla: Kanha National Park[19] Rajasthan: Mount Abu[15,26-27]	Western Ghats: Karnataka-Mysore, Nandi hills; Kerala-Agasthyamalai Biosphere Reserve, Eravikulum National Park; Maharashtra-Purandhar Fort; Tamil Nadu-Agasthyamalai Biosphere Reserve, Kodaikanal (Law's Ghat road, Shenbaganur), Madurai, Nilgiri hills, Palni hills. Assam, Meghalaya. Gujarat[34]
39	*Bryum plumosum* Dozy. and Molk., Ann. Sci. Nat. Bot. Ser. 3, 3(2): 301. 1844.[33,42] Habitat: On earth cuttings in moist deciduous forests. New Caledonia		Recorded from India (Kerala, Assam, Calcutta, Orissa, Western Himalaya), Sri Lanka, China, Japan, Sumatra, Java, Celebes, Borneo, Philippines, Taiwan, Australia
40	*Bryum porphyroneuron* var. erythrinum (Mitt.) M.Fleisch. Die Natürlichen Pflanzenfamilien I (3): 590. 1904.[21,33]		Madhya Pradesh: Raisen: Bhimbetka, Pachmarhi
41	*Bryum pseudotriquetrum* (Hedw.) P. Gaertn., B. Mey. *et* Scherb., Oekon. Fl. Wetterau 3(2): 102. 1802[15,21,31,33] Habitat: Rupicolous;	On way to Taluka from Sankri regions, Uttarkashi, alt. ca 1998 m, Leg.: A.K. Asthana 252429B (LWG).	Western Ghats: Kerala-Eravikulam National Park, Wayanad. Rajasthan:Mount Abu[15]

continued...

Table 1: Cont'd.

Sl. No	Binomial	Specimens examined	Location
42	*Bryum pseudotriquetrum* var. *subrotundum* (Brid.) Gangulee, Mosses E. India, 4: 994. 1974.[15,31,33] Habitat: Rupicolous	Dehra Dun, Mussoorie, Lal Tibba route, alt. ca 2370 m, Leg.: V. Nath	Western Ghats: Tamil Nadu-Nilgiri hills (Doddabetta). Uttarakhand: Mussoorie. Garhwal hills –
43	*Bryum recurvulum* Mitt., J. Proc. Linn. Soc., Bot., Supp;.1:74, 1859.[20-21,31,33]	Herbarium of Edwin B. Bartram, Herbier Charrier, Himalaya, Indes Owglaises, N.W.: Himalaya, Mussoorie (FH).	Gujarat: border area with Rajasthan without specific locality.[26]
44	*Bryum reflexifolium* (Ochi) Ochi in Ohashi, Bull. Univ. Museum, Univ. Tokyo N. 8: 261. 1975.Habitat: Saxicolous[31]	INDIA, Meghalaya: East Khasi Hills: Shillong, on way to Jowai, alt. c. 1287 m, grows on rock, Leg.: V. Sahu and V. Awasthi, 251689B (LWG); West Bengal: Darjeeling, Tiger hill, alt. c. 2545 m, grows on soil covered rock, Leg.: A.K. Asthana and V. Sahu, 224073E (LWG); on way to Tonglu, alt. c. 2576 m, grows on rock, Leg.: A.K. Asthana and V. Sahu, 224354 (LWG).	Meghalaya, Sikkim, West Bengal.
45	*Bryum retusifolium* Card. and Varde, Rev. Bryol. 50: 20. 1923. *Foreau* (FH 1835).[15,31,33] Habitat: Rupicolous; on rocks	Specimens examined: WESTERN GHATS: TAMILNADU: St. Xavier's College, Palamcottah, Palney hills, 7000 ft, Coll.: *G.F.* (FH 1929); Herbarium of Edwin B. Bartram, Herbier Charrier, Indes Owglaises, Perumal, Leg.*: R.P.* Uttarkashi district, on way to Taluka from Sankri, alt. ca 1998 m, Leg.: diameter. A.K. Asthana 252429D (LWG).	Western Ghats: Tamil Nadu-Kodaikanal, Madurai, Palni hills. Uttarakhand: Garhwal hills - Uttarkashi.
46	*Bryum rubens* Mitt., In Hooker's J. Bot. Kew Gard. Misc.8: 232, 1856.[21,31]	Rajasthan: Mount Abu (Bansal and Nath,2014;[25]	Rajasthan
47	*Bryum salakense* Card., Annuaire Conserv. Jard. Bot. Genève, 15-16: 166. 1912.[15] Habitat: Epiphytic	WESTERN GHATS: KERALA: Wayanad, Pakshipadalam, alt. *ca* 1100 m, Coll.: *K.P. Rajesh* 99750 (CAL).	Western Ghats: Kerala-Wayanad; Deccan Plateau and Eastern Ghats: Tamil Nadu-Shervaroy hills
48	*Bryum srilankenese* Mohamed J. Bryol., 12: 25. f. 2, 25, 1982[18]	Coorg: damp earth near Nalknad Palace, T.L. Walker 329 (H)	Karnataka
49	*Bryum teretiusculum* Hook. ex Harv. Icones Plantarum 1: pl. 20, f. 1. 1836.[33]		Uttar Pradesh (Tehri), Mussoorie, Assam, Khasia hills
50	*Bryum truncorum* (Brid.) Brid.[33]		Kerala
51	*Bryum tuberosum* Mohamed and Damanhuri, Bryologist 93(3): 288. 1990.[42] Habitat: On rocky patches		Kerala, Karnataka, Malaysia
52	*Bryum thomsonii* Mitt., Jour. Proc. Linn. Soc., Bot., Suppl. 1: 73. 1859.[15,21,31] Habitat: Terricolous.	Uttarakhand: Garhwal hills - Vishnuprayag; Kumaun hills - Nainital. Rajasthan: Mount Abu	Western Ghats: Karnataka-Kodagu; Tamil Nadu-Nilgiri hills; Deccan Plateau and Eastern Ghats: Andhra Pradesh-Guntur, Visakhapatnam
53	*Bryum tuberosum* Mohamed and Damanhuri, Bryologist 93(3): 288. 1990.[15] On rocky patch	Western Ghats: Karnataka: Shimoga Dist., Agumbe, alt. *ca* 600 m, grows on walls and rocks, Leg.: *S.* Chandra and V. Nath 204116B (LWG); Kerala: Wayanad, Hairpin area, alt. 750 m, on rocky patch, Coll.: *Manju* 80093 (CAL).	Western Ghats: Karnataka-Agumbe, Uduppi; Kerala-Wayanad Karnataka, Malaysia
54	*Bryum turbinatum* (Hedw.) Turn. Muscol. Hibern. Spic. 127. 1804[31] Habitat: Rupicolous	Uttarakhand: Garhwal hills - Mussoorie, Tehri	Western Himalayas Uttarakhand: Garhwal hills - Tehri.

continued...

Table 1: Cont'd.

Sl. No	Binomial	Specimens examined	Location
55	*Bryum uliginosum* (Brid.) Bruch, Schimper and W. Gümbel *in* Bryol. Eur. 4: 88. 1839[20-21,31,33] Habitat: Corticolous, Terricolous;	Chamoli Dist., Valley of Flowers, alt. ca 3510 m, Leg.: S. Chandra 200812C (LWG); on way to Hemk .Leg.: S. Chandra 200922B (LWG)und, alt. ca 3343 m, RAJASTHAN: Mount Abu [25,27]	Western Ghats: Kerala; Tamil Nadu-Nilgiri hills (Udhagamandalam-Naduvattam).
56	*Bryum weigelii* Spreng. Mant. Prim. Fl. Hals. 55. 1807[31] Habitat: Terricolous	Uttarakhand: Garhwal hills - Satopanth glacial bed.	Western Himalayas
57	*Bryum wightii* Mitt., J. Proc. Linn. Soc., Bot., Suppl. 1: 74. 1859. [15,20-21,33,42,44] Grows moderately at high altitude regions, near wet areas such as waterfalls, often on moist rocky substratum, mostly associated with *Utricularia* sp. and *Campylopus* sp. in semi-evergreen, evergreen, shola forests and in grasslands	Western Ghats: Goa: Keri Surfa (Border of Goa-Karnataka), Terricolous, Coll.: *Sulabha* Phatak (LWG 564); Karnataka: Herb. Walker, by small spring at the foot of a cliff of gneiss, Mercara, Coorg, India, Coll.: T.L. Walker 280, Det.: *V.F.* Brotherus (FH); Herb. Walker, damp earth near Nalknad Palace, Coorg, India, Coll.: *T.L. Walker* 329, Det.: *V.F. Brotherus* (FH); Kerela: Idukki, near Devikolam, alt. *ca* 1800 m, grows on bark of tree, Leg.: *D.K. Upreti* 204009 (LWG); Munnar, Devikolam, alt. *ca* 1590 m, on water logged rocks, Leg.: V. Nath 248401 (LWG); Wayanad Dist., Manikkunnumala, near MSSRF, alt. *ca* 970 m, on rocky patch, Coll.: *Manju* 120297 (CAL); Maharashtra: Bryophytes of Western India, Union of India, Bombay state, Satara district, near the summit of the Western Ghats, Mahabaleshwar, 17°55' N, 73°40' E, altitude about 4500 feet, on stone, semi-sheltered, early Distr.: *H.A.* Gleason, Jr., Coll.: Hale H. Cook 46, 50 Det.: *E.B. Bartram* (FH); Tamil Nadu: Herbier Charrier, Indes Owglaises, Kodaikanal, Leg.: R.P. Foreau (FH); Beschi College Herb., Shembaganur, Palni hills, Kodaikanal, Leringe Path, about 6700 ft, Coll.: *G.F.* 17 (FH); Herbarium of Edwin B. Bartram, Herbier Charrier, Indes Owglaises, Pombarai, Leg.: R.P. Foreau (FH); Mosses of Southern India, Madras State, Madura, Palni hills, Kodaikanal and surrounding region, Kodaikanal, Residue of "Musci Madurenses Indiae Meridionalis Exsiccati", issued by Georges Foreau, S.J. distributed by The New York Botanical Garden, Leg.: *G. Foreau* 98; (FH, TNS 051214). Madhya Pradesh: Pachmarhi[29] *Campylodontium flavescens* (Hook.) Bosch and SandeLac. Bryol. Jav. 2: 128, 1865. Jharkhand:Chhota Nagpur: Netarhat (Gangulee, 1978-80)[43] *Campylopus ericoides* (Griff.) A. Jaeger, Ber. Thatigk.St. Gallischen Naturwiss. Ges. Madhya Pradesh: Pachmarhi	Western Ghats: Goa; Karnataka-Agumbe (Hulical Ranges, Kanalgudda), Kodagu (Nalkad Palace, Mercara); Kerala-Agasthyamalai Biosphere Reserve, Idukki, Kannur, Munnar, Parambikulam Tiger Reserve, Vellarimala, Wayanad; Maharashtra-Mahabaleshwar; Tamil Nadu-Agasthyamalai Biosphere Reserve, Kodaikanal (Perumal Malai), Madurai, Nilgiri hills (Udhagamandalam-Levinge Path, Naduvattam, Thodabetta), Palni hills; Deccan Plateau and Eastern Ghats: Tamil Nadu-Namakkal (Kolli hills). Maharashtra

genus *Bryum* is recorded from most parts of the country with wide variations of characters. 45 species were documented by various taxonomists from India. But, many species were seems to be overlapping. Future studies using the molecular technique to differentiate the species are warranted.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

ABBREVIATIONS

B: Bryum.

SUMMARY

Bryophytes occupy various ecological regimes including adverse conditions. Most species showed morpho plasticity in characters. The genus *Bryum* is one of the largest genus, distributed throughout India and is an ideal example of this. Many species showed morphological similarities, but placed in different species. Thorough revision is warranted to discriminate the allied species of the genus using molecular or other modern approaches.

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Advances in Bioresearch

ORIGINAL ARTICLE

Herbals as natural immunity boosters: some observations from native people of Kerala

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ABSTRACT
Formulation of new effective anti-coronaviral drugs and therapies is important and currently, there is no established pharmacological strategy for the prevention and/or treatment of the coronavirus infection. The present study deals with the survey on the immunity enhancing plant species practiced by the local people, which improve the health and immune system. They believe that strengthen the immunity naturally with the help of medicinal plants/herbs. Herbals contain a pool of secondary metabolites which can enhance the immunity. Immunity refers body's ability to identify and resist large numbers of infectious and potentially harmful pathogens enabling the body to prevent or resist diseases and inhibit organ and tissue damage via multiple mechanisms. For overcoming viral issues, the different plant parts such as root, stem, leaf, flower, seeds, fruits and their crude extracts that have been used in the Indian traditional system of medicine and have clinical proven activity. In the present investigation, a survey was conducted to collect information about the use of traditional medicinal plants for immunity boosting. The survey has reported 132 plants belonging to diverse families and 42 species were validated scientifically connected with immunity. Major tribal communities interviewed were Kurumba, Muduga, Irula, Kattu Naiken & the local crude drug practicing people of the area. Mode of usage of the different species was also reported. Fabaceae species was found to be of high frequency in terms of its use, followed by Lamiaceae. It is high time to provide awareness and training to conserve the herbals from extinction from the wild habitats through the local gram panchayath.
Key words: Tribal, Immunity, COVID-19, ethno-botanical survey, herbals, plant parts

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INTRODUCTION

World Health Organization (WHO) recorded that approximately 67% of the global population depends upon local herbal remedies for the health care of its people. In fact, medicinal plants are the aboriginal healers of mankind. They not only provided food and shelter but also crude drugs to cure many ailments. Ethnic medicine or traditional medicine, has always existed in diverse forms in different civilizations like Ayurveda & siddha (India), Egyptian, Western, Chinese, Kampo (Japan) and Greco-Arab or Unani-Tibb (South Asia). Globally, herbal drugs are currently being resurveyed through extensive search on different zones and their medicinal features [1].

Diseases of pandemic class are of global issue in the present century, to cause substantial morbidity regardless of extensive medical innovations. Anti-viral treatments have been distraught because of mutant nature of virus enough to reduce the drugs targeting viral components [2]. Globalization, climate change and fast urbanization has led to contagious outbreak by rising or re-emergence of viruses, posing disaster menace towards communal health and safety, specifically in such unprecedented times where there are no potential vaccines available. For the last few centuries, the earth has ventured the incidence of catastrophic viral disorders like Severe Acute Respiratory Syndrome, Middle East Respiratory Syndrome, dengue and chikungunya within human beings [3]. Stringari *et al*., [1] reported that COVID-19 was the third potent disease of animal origin, which is prevailing in almost four corners of the world by

getting initiated from a single place. Nearly, 213 countries of the entire earth have been affected in less than 90 days by this pernicious virus.

Clinically, plants as immunomodulators is categorized into immunoadjuvants i.e., enhance the vaccine efficacy - immune stimulants (modulators of the immune response). It has been recorded that they are exploited as selectors between cellular and humoral helper T1 (Th1) and helper T2 cells (Th2), immunoprotective, immunodestructive, and reagenic (immunoglobulin E (IgE)) versus IgG type immune responses—posing a real challenge to vaccine designers [4]. Immunostimulants are non-specific enhancer of body's resistance to infection. They function via innate and adaptive immune responses. In healthy people, they serve as prophylactic and promoter agents, i.e., as immunopotentiators, by enhancing the basic level of immune response. In the individual with impairment of immune response, they are expected to act as immunotherapeutic molecules [5]. Immunosuppressants are structurally and functionally heterogeneous drugs, which are often concomitantly administered in combination regimens to treat different organ transplant rejection and autoimmune diseases [6].

Ayurveda is the vital tradition practiced from time immemorial in India, Sri Lanka and other countries. It has a sound. Atharvaveda (1200 bc), Charak Samhita and Sushrut Samhita (1000–500 bc) are the philosophical and experimental basis that give narration of over 700 herbals. Many herbals used in the Indian traditional system devoted to enhancement of the body's resistance have attracted the attention of biologists globally. Diverse medicinal plants exhibit not only immunomodulatory potentialities but also with antioxidant, antiasthmatic, antiarrhythmic, antiinflammatory, hepatoprotective, antidiabetic, hypocholesterolemic, antimicrobial, cardiotonic, diuretic, and anticancer powers.

Saba Farooq and Zainab Ngain [7] reviewed that plants based natural products as alleged remedies for viral infection. Phytochemicals from many plant extract have been documented for antiviral features. *Stephania tetrandra* of Menispermaceae showed the presence of bis-benzylisoquinoline alkaloids such as fangchinoline, tetrandrine and cepharanthine reported to inhibit protein expression, repress infectivity, and inhibit the replication of coronavirus in human and virus-induced host reappearance. In India, traditional practices based on garlic, cardamom, pennyroyal, liquorice, pepper, turmeric, tragacanth and hedge nettle have been alleged for an effective cure against COVID-19. Curcumin, derived from turmeric, is widely used for potential COVID-19 treatment due to stronger interaction with protease enzyme as compared to other phytochemicals like pepper, pennyroyal and tragacanth. In this juncture, the present survey was undertaken to document the immune-modulating potential plants used by the native practicing people and tribals of the remote areas of Palakkad.

MATERIAL AND METHODS

Sampling area, informants and data gathering

Silent valley is located in the Nilgiri hills, between 11°03' to 11°13' N (latitude) and 76°21' to 76°35' E (longitude), has a core area of 89.52 km² (34.56 sq mi), which is surrounded by a buffer zone of 148 km² (57 sq mi). The climate is tropical with summer rains constituting the bulk of the precipitation. Average minimum temperature varies from 8º to 14ºC and average maximum temperature varies from 23ºto 29ºC. The hottest months are April and May when the mean temperature is 23 °C and the coolest months are January and February when the mean temperature is 18o C. Annual average rainfall is 2717 to 4543 mm.

The ethnobotanical survey was conducted from November 2020 to February 2021. It was planned to trace immune modulating plants used by the native crude drug practicing people and tribals such as Kurumba (Thudukki), Muduga (Karuvara), Irula (Mukkali) and Kattu Naiken (Mundakulam) who have adequate knowledge in ethnic therapeutic practices. The native experts in traditional medicine in the outer skirts of Silent valley hamlets were interviewed and discussed. 16 tribal and 34 native people were included in the survey. Aged and experienced people on use of traditional medicinal plants were prioritized for consideration.

Oral interviews and discussions by interviewer from each informant were recorded. Data were also collected using questionnaires in their local dialect. Traditional medicines used for promoting immunity were gathered from the tribal and native practicing indigenous medicines. Most interviews were arranged by native people familiar with tribal and who could communicate with the tribal communities. Questionnaires were used to collect information from the informants. The questionnaires used included mainly plant name, parts of the plants used, mode of preparation and application. Each such information was validated thrice with different people from different localities. The common names of plants and dosage or mode of administration were documented from the field.

RESULTS AND DISCUSSION

The study focused mainly on herbals for immunity booster uses reported by the tribal/native people from the outer skirts of Silent valley, Palakkad. The present investigation enlisted 132 plants were used for immunity booster (Table 1). Maximum medicinal species were reported from Fabaceae followed by Lamiaceae (Table 2). Among the species, 42 of them were validated scientifically (Table 3). *Andrographis paniculata, Azadirachta indica, Moringa oleifera, Psidium guajava, Ocimum sanctum*, *Piper nigrum, Zingiber officinale, Curcuma longa* were commonly used by the people for multiple of treatments. The secondary metabolites present in the plants may be the possible reason for their therapeutic efficacies.

Leaves (75) were the most frequently used plant parts, followed by roots (30) and fruits (23) (Fig. 1). The major mode of preparation is infusion (42) followed by boiled singly (35) and others (59) (Fig.2.). Preparations were made with water, honey, alcohol, lime water, and milk as solvent. The mode of administration was mostly oral. Most of the reported species were herb which was followed by tree and climber. Most of the plants are wild and some are cultivated, whereas others are both cultivated and wild (Table 1). The species like *Allium cepa*, *A. sativum*, *Costus speciosus*, *Emblica officinalis*, *Curcuma longa, Zingiber officinale*, *Artemisia annua* and *Vitex negundo* were the most frequently cited in study area.

The present study reports the usage of these ethnomedicinal plants, but needs to be validated by pharmacological studies. Some proven immune boosting plants may exert their action through their polyphenols/alkaloids/flavonoids/anthocyanins etc. The study highlighted the pivotal role of traditional herbal medicine for the treatment of viral issues in the local areas of Silent valley. Ethnobotanical survey is useful for researchers and pharmaceutical companies for further studies on isolation, purification and identification of the lead compounds, which can be formulated into immune boosting drugs. The purified drugs can be subjected to preclinical and clinical trials for further validations.

The coronavirus disease is highly transmittable with no effective antiviral therapy to combat the infection [1]. However, in the present survey, the obtained data highlighted the role of cultivated spices and wild herbs in the treatment of COVID-19. The survey has been conducted to identify the various home remedies used during COVID-19, which include many such spices and herbs.

As per the survey data, most people using ginger, clove, cinnamon, black pepper, and tulsi as main ingredients in drug preparation. It was noticed that cinnamon, ginger extracts, black pepper, tulsi, and turmeric play vital role against SARSCoV- 2 (COVID-19) and other such pathogenic infections, which was also validated by recent studies mentioned in the Table 3. The obtained knowledge was authenticated by Vaghasiya et al., [8], for example the usage of *Ocimum sanctum* for immunomodulatory activity. Firoj et al., [9] recoded the use of nearly 12 herbals species increased the level of helper T cells as well as natural killer cells, which helps fight against viral infection. *O. sanctum* is recorded in the Ayurveda for curing pain, pneumonia, diarrhea, cough, and fever which are the common symptoms of COVID-19. *Piper nigrum* infusion provides relaxation from sinusitis and nasal congestion, which were also the common syndromes of COVID-19 [2]. Ashish Singh et al., [10] reviewed that flavonoids in pepper, induces the body's immunity constantly due to its antiviral mode of action. Rajagopal et al., [11] also recommended the intake of black pepper and ginger in a daily diet as it may resist the coronavirus replication. According to the tribal data, intake of Amla/wild lemon as the source of vitamin C for enhancing immunity is ideal.

Flower et al., [12] documented that the clinical trial in the USA among 167 patients with sepsis-related ARDS indicated that uptake of 15 g/day of vitamin C for 4 days may reduce the mortality in these patients. The three hospitals in Hubei, China clinical trial on patients with confirmed SARS-CoV-2 infection in the ICU validated the same i.e., high-dose intravenous vitamin C (12 g of vitamin C/50 mL every 12 h for 7 days) provided defensive effect without any side effects in critically COVID-19 patients [13].

According to the Indian spices export data, 23% of spice exports was enhanced during the COVID-19 pandemic compared with 2019. The Indian spices includes pepper, ginger, turmeric, coriander, cumin, fennel, fenugreek, nutmeg, spice oils cardamom, and mint products to USA, UK, Germany, France, Italy, Canada, Australia, UAE, Iran, Singapore, China, and Bangladesh, which confirms the potential medicinal role of spices of India globally. do Rosário and de Siqueira[3] also accounted the importance of Indian medicinal species as drug. Saba Farooq and Zainab Ngain [7] recorded that the natural drugs were potential for treatment for Coronavirus diseases. Babich *et al.,* [14] reviewed that medicinal plants Strengthen Immunity during a Pandemic outbreaks. Cohen [15] reviewed *Ocimum sanctum* as magical herb for all reasons. Kalikar *et al*., [16] recorded the immunomodulatory effect of *Tinospora cordifolia* extract in human immunodeficiency virus positive patients.

Table 1. Checklist of immunity booster plants used by the tribals & local people

Sl.No.	Binomial	Family	Parts used
1	*Andrographis macrobotrys* Nees	Acanthaceae	Leaves and Stem
2	*Rungia pectinata* (L.) Nees	Acanthaceae	Leaves and Roots
3	*Hemigraphis crossandra* (Steud.) Bremek.	Acanthaceae	Leaves
4	*Thunbergia fragrans* Roxb.	Acanthaceae	Leaves
5	*Justicia procumbens* L.	Acanthaceae	Leaves and Roots
6	*Andrographis paniculata* Burm.f) Nees	Acanthaceae	Whole plant
7	*Adhatoda vasica* Nees	Acanthaceae	Leaves
8	*Desmos lawii* (Hook.f. & Thomson) Saff.	Annonaceae	Leaves
9	*Miliusa tomentosa* (Roxb.) Finet & Gagnep.	Annonaceae	Fruits
10	*Amaranthus dubius* Mart. ex Thell.	Amaranthaceae	Leaves
11	*Amaranthus tricolor* L.	Amaranthaceae	Leaves
12	*Amaranthus hypochondriacus* L.	Amaranthaceae	Leaves and Seeds
13	*Aerva lanata* (L.) Juss.	Amaranthaceae	Whole plant
14	*Achyranthes aspera* L.	Amaranthaceae	Whole plant
15	*Allium sativum* L.	Amaryllidaceae	Bulbs
16	*Allium cepa* L.	Amaryllidaceae	Bulbs and Leaves
17	*Mangifera indica* L.	Anacardiaceae	Leaves and Fruits
18	*Spondias indica* (Wight & Arn.) Airy Shaw & Forman	Anacardiaceae	Fruits
19	*Centella asiatica* (L.) Urb.	Apiaceae	Leaves
20	*Cuminum cyminum* L.	Apiaceae	Seeds
21	*Trigonella foenum graecum* L.	Apiaceae	Leaves and Seeds
22	*Pimpinella anisum* L.	Apiaceae	Seeds
23	*Carum carvi* L.	Apiaceae	Seeds
24	*Alstonia venenata* R. Br.	Apocynaeae	Roots and Fruits
25	*Cryptolepis buchananii* R.Br. ex Roem. & Schult.	Apocynaeae	Roots and Stem
26	***Dracaena*** *terniflora* Roxb.	Asparagaceae	Roots
27	*Artemisia annua* L.	Asteraceae	Leaves
28	*Conyza bonariensis* (L.) Cronq.	Asteraceae	Leaves and Flowers
29	*Echinacea angustifolia* DC.	Asteraceae	Leaves, Stem and Roots
30	***Senecio*** *scandens* Buch.-Ham. ex D.Don	Asteraceae	Whole plant
31	*Vernonia amygdalina* Delile.	Asteraceae	Leaves
32	***Impatiens balsamina*** L.	Balsaminaceae	Leaves and Flowers
33	*Basella alba* L.	Basellaceae	Leaves
34	*Stereospermum kunthianum* Cham.	Bignoniaceae	Leaves, Bark and Roots
35	*Capparis tomentosa* Lam.	Capparidaceae	Roots
36	*Cannabis sativa* L.	Cannabaceae	Leaves and Seeds
37	*Carica papaya* L.	Caricaceae	Leaves and Fruits
38	*Combretum collinum* sub sp. elgonense (Exell) Okafora	Combretaceae	Leaves
39	*Terminalia chebula* Retz	Combretaceae	Fruits
40	*Kalanchoe densiflora* Rolfe.	Crassulaceae	Leaves
41	*Cucurbita maxima* Duchesne.	Cucurbitaceae	Flowers, Fruits and Seeds
42	***Momordica*** *charantia* L	Cucurbitaceae	Fruits and Roots
43	***Momordica dioica*** Roxb. ex Willd.	Cucurbitaceae	Fruits, Leaves and Roots
44	*Momordica sahyadrica* subsp.anamalayana K.J.John.,K. Pradheep et Krishnaraj subsp. nov.	Cucurbitaceae	Fruits and Leaves
45	*Cyperus rotundus* L	Cyperaceae	Rhizome
46	*Jatropha curcas* L.	Euphorbiaceae	Whole plant
47	*Manihot esculenta* Crantz.	Euphorbiaceae	Leaves, Seeds and Roots
48	*Acacia torta* (Roxb.) Craib	Fabaceae	Leaves, Roots and Stem
49	*Cassia occidentalis* L	Fabaceae	Leaves and Seeds
50	*Mimosa diplotricha* C.Wright	Fabaceae	Leaves and Roots
51	*Albizia odoratissima* (L.f) Benth.	Fabaceae	Bark
52	*Xylia xylocarpa* (Roxb.) W.Theob.	Fabaceae	Leaves and Seeds
53	*Crotalaria heyneana* Graham ex Wight & Arn.	Fabaceae	Leaves
54	*Alysicarpus vaginalis* Linn. DC.	Fabaceae	Roots
55	*Crotalana humifusa* Benth.	Fabaceae	Leaves
56	*Pongamia pinnata* (L.) Pierre.	Fabaceae	Roots

57	*Pterocarpus marsupium* Roxb.	Fabaceae	Leaves, Bark, Stem and Flowers
58	*Crotalaria mysorensis* Roth.	Fabaceae	Leaves and Flowers
59	*Spatholobus roxburghii* Benth.	Fabaceae	Leaves and Stem
60	*Crotalaria retusa* L.	Fabaceae	Whole plant
61	*Tephrosia pulcherrima* (Baker) Gamble.	Fabaceae	Leaves
62	*Desmodium heterocarpon* (L.) DC	Fabaceae	Roots
63	*Teramnus labialis* (L.f) Sperng.	Fabaceae	Leaves
64	*Desmodium heterophyllum* (Willd.) DC	Fabaceae	Roots
65	*Uraria rufescens* (DC.) Schindl.	Fabaceae	Leaves
66	*Desmodium pulchellum* (L.) Benth.	Fabaceae	Leaves, Roots and Flowers
67	*Desmodium triquetrum* (L.) DC	Fabaceae	Leaves
68	*Desmodium triangulare* (Retz.) Merr.	Fabaceae	Leaves
69	*Vigna pilosa* (Willd.) Baker.	Fabaceae	Leaves and Roots
70	*Vigna trilobata* (L.) Verdc.	Fabaceae	Whole plant
71	*Vigna wightii* Bedd.	Fabaceae	Leaves
72	*Erythrina indica* Lam.	Fabaceae	Leaves
73	*Entada rheedei* Spreng.	Fabaceae	Seeds
74	*Mucuna pruriens* (L.) DC.	Fabaceae	Seeds
75	*Tamarindus indica* L.	Fabaceae	Leaves, Fruits and Seeds
76	*Glycyrrhiza glabra* L.	Fabaceae	Root and Rhizome
77	*Caesalpinia sappan* L.	Fabaceae	Stem
78	***Ocimum sanctum* L.**	Lamiaceae	Whole plant
79	*Leucas zeylanica* (L.) W.T.Aiton	Lamiaceae	Whole plant
80	*Acrocephalus hispidus* (L.) Nicolson & Sivad.	Lamiaceae	Leaves
81	*Leucas hirta* (B.Heyne ex Roth) Spreng.	Lamiaceae	Whole plant
82	*Leucas indica* (L.) R.Br. ex Sm.	Lamiaceae	Leaves
83	*Anisochilus carnosus* (L.f) Wall	Lamiaceae	Leaves
84	*Gomphostemma heyneanum* Wall ex.Benth.	Lamiaceae	Leaves
85	*Ocimum basilicum* L.	Lamiaceae	Leaves
86	*Callicarpa tomentosa* (L.) L.	Lamiaceae	Leaves
87	*Vitex altissima* (L.)f.	Lamiaceae	Leaves
88	*Vitex negundo* L.	Lamiaceae	Leaves, Seeds and Roots
89	*Cinnamomum verum* J. Presl.	Lauraceae	Bark
90	*Aloe vera* (L.) Burm.f.	Liliaeae	Leaves
91	*Abutilon indicum (*L.) Sweet	Malvaceae	Leaves and Flowers
92	*Sida cordifolia* L.	Malvaceae	Whole plant
93	*Azadirachta indica* A. Juss.	Meliaceae	Leaves and Seeds
94	*Tinospora cordifolia* (Willd.) Miers	Minispermaceae	Root, Stem and Leaves
95	*Morus alba* L.	Moraceae	Fruits, Roots and Leaves
96	*Ficus arnottiana* (Miq.) Miq.	Moraceae	Bark, Seeds and Fruits
97	*Ficus nervosa* B.Heyne ex Roth	Moraceae	Leaves
98	*Ficus drupacea* Thunb.	Moraceae	Fruits and Roots
99	*Moringa oleifera* Lam.	Moringaceae	Leaves, Roots, Seed, Bark, Fruit, Flowers and Immature Pods
100	*Psidium guajava* L.	Myrtaceae	Fruits and Leaves
101	*Syzygium cumini* (l.) Skeels	Myrtaceae	Bark
102	*Syzygium aromaticum* (L.) Merr. & L.M.Perry	Myrtaceae	Flower buds and Leaves
103	*Osbeckia malabarica* (Hook. f.) Cogn.	Melostomaceae	Flowers
104	*Nyctanthes arbor-tristis* L.	Oleaceae	Flowers
105	*Passiflora edulis* Sims	Passifloraceae	Leaves and Fruits
106	*Sesamum indicum* L.	Pedaliaceae	Seeds
107	*Bridelia micrantha* (Hochst.) Baill	Phyllanthaceae	Bark, Leaves and Roots
108	*Flueggea virosa* (Roxb. ex Willd.) Royle	Phyllanthaceae	Roota and Fruits
109	*Phyllanthus emblica* L.	Phyllanthaceae	Fruits
110	*Plantago major* L.	Plantaginaceae	Leaves
111	*Piper nigrum* L.	Piperaceae	Fruits and Leaves
112	*Cynodon dactylon* (L.) Pers.	Poaceae	Whole plant
113	*Salomonia ciliata* (L.) DC.	Polygalaceae	Roots
114	*Portulaca oleracea* L.	Portulacaceae	Whole plant
115	*Rubia cordifolia* L.	Rubiaceae	Roots
116	*Geophila repens* (L.) I.M.Johnst.	Rubiaceae	Leaves and Fruits

117	*Ophiorrhiza mungos* L.	Rubiaceae	Roots
118	*Naringi crenulata* (Roxb.) Nicolson	Rutaceae	Whole plant
119	*Aegle marmelos* (L.) Corrêa	Rutaceae	Leaves and Fruits
120	*Withania somnifera* (L.) Dunal.	Solanceae	Roots and Fruits
121	*Solanum nigrum* L.	Solanceae	Fruits
122	*Santalum album* L.	Santalaceae	Stem
123	*Urtica dioica* L.	Urticaceae	Leaves and Roots
124	*Lantana camara* L.	Verbenaceae	Leaves and Flowers
125	***Zygophyllum*** *fabago* L.	Zygophyllaceae	Leaves
126	*Curcuma longa* L.	Zingiberaceae	Rhizome
127	*Boesenbergia pulcherrima* (Wall.) Kuntze	Zingiberaceae	Leaves and Rhizome
128	*Globba ophioglossa* Wight.	Zingiberaceae	Rhizome
129	*Costus speciosus* (J.König) Sm.	Zingiberaceae	Leaves and Rhizome
130	*Zingiber neesanum* (J.Graham) Ramamoorthy	Zingiberaceae	Rhizome
131	*Zingiber officinale* Roscoe	Zingiberaceae	Rhizome
132	*Curcuma zedoaria* (Christm.) Roscoe	Zingiberaceae	Rhizome

Table 2. List of plants under various Families used

Family	Number of species
Acanthaceae	7
Annonaceae	2
Amaranthaceae	5
Amaryllidaceae	2
Anacardiaceae	2
Apiaceae	5
Apocynaceae	2
Asparagaceae	1
Asteraceae	5
Balsaminaceae	1
Basellaceae	1
Bignoniaceae	1
Capparidaceae	1
Cannabaceae	1
Caricaceae	1
Combretaceae	2
Crassulaceae	1
Cucurbitaceae	4
Cyperaceae	1
Euphorbiaceae	2
Fabaceae	30
Lamiaceae	11
Lauraceae	1
Liliaeae	1
Malvaceae	2
Meliaceae	1
Minispermaceae	1
Moraceae	4
Moringaceae	1
Myrtaceae	3
Melostomaceae	1
Oleaceae	1
Passifloraceae	1
Pedaliaceae	1
Phyllanthaceae	3
Plantaginaceae	1
Piperaceae	1
Poaceae	1
Polygalaceae	1
Portulacaceae	1
Rubiaceae	3
Rutaceae	2

Solanceae	2
Santalaceae	1
Urticaceae	1
Verbenaceae	1
Zygophyllaceae	1
Zingiberaceae	7

Sl.No	Name of the Plant	Family	Parts used	Mode of usage	Used by the Tribe/Native people	Validated scientifically
1.	*Psidium guajava*	Myrtaceae	Whole plant	Aqueous extract	Kattu Naiken & locals	Antiviral (IF H5N1), antimicrobial activity
2.	*Glycyrrhiza glabra*	Fabaceae	roots & rhizomes	Aqueous extract	Kurumba, Muduga, & locals	Antiviral, antimicrobial, antioxidant, antitumor activity
3.	*Curcuma longa*	Zingiberaceae	Roots	Aqueous extract	Kurumba, Muduga, Irula, Kattu Naiken & locals	Antiviral activity (IF H5N1), prevention
4.	*Artemisia annua*	Asteraceae	Whole plant	Aqueous extract	locals	Antiviral activity (SARS-CoV)
5.	*Syzygium aromaticum*	Myrtaceae	Flower buds	Aqueous extract	Muduga, Irula, Kattu Naiken & locals	antimicrobial, anti-fungal, anti-viral, an-ti-inflammatory, cytotoxic, analgesic, anesthetic activities, antioxidants
6.	*Withania somnifera*	Solanaceae	root and the leaves	Aqueous extract	Kurumba, Muduga, Irula, Kattu Naiken & locals	cell-mediated immunity
7.	*Cuminum cyminum*	Apiaceae	seeds	Aqueous extract	Kurumba, Muduga, Irula, Kattu Naiken & locals	immunomodulator
8.	*Piper nigrum*	Piperaceae	fruits	Aqueous extract	Kurumba, Muduga, Irula, Kattu Naiken & locals	anti-inflammatory, antioxidant, anti-bacterial & fever reducing actions but immune system
9.	*Trigonella foenum graecum* L.	Apiaceae	seeds	Aqueous extract	Kurumba, Muduga, Irula,	hypocholesterolaemic, effects, Anti-inflammatory
10.	*Cinnamomum verum*	Lauraceae	bark	Aqueous extract	Kurumba, Irula, Kattu Naiken & locals	Antioxidant & antiviral
11.	*Allium cepa*	Amarydillaceae	Bulb	Aqueous extract	Irula, Kattu Naiken & locals	Antiviral activity IFA H1N1)
12.	*Allium sativum*	Amarydillaceae	Roots	Aqueous extract	Kurumba, Muduga, & locals	Roots Antiviral activity (IFA—H1N1)
13.	*Caesalpinia sappan*	Fabceae	wood	Aqueous extract	Kurumba, Muduga, & locals	Antiviral activity (IFA—H1N1, H3N2, H9N2)
14.	*Andrographis paniculata*	Acathaceae	Leaves	Aqueous extract	Kurumba, Muduga, Irula,	Antiviral activity (IF H5N1)
15.	*Tinospora cordifolia*	Menispermaceae	Whole plant	Aqueous extract	Kurumba, Muduga, Irula,	Anti-viral
16.	*Ocimum sanctum*	Lamiaceae	Whole plant	Aqueous extract	Kurumba, Muduga, Irula, Kattu Naiken & locals	Antioxidant Anti-viral
17.	*Zingiber officinale*	Zingiberaceae	Rhizome	Aqueous extract	Kattu Naiken & locals	NF-kB Suppressor
18.	*Pimpinella anisum*	Apiaceae	leaves	Aqueous extract	Kurumba, Muduga, Irula, Kattu Naiken & locals	antiviral and immune-stimulating
19.	*Carum carvi*	Apiaceae	seeds	Aqueous extract	Kattu Naiken & locals	antiviral and immune-stimulating
20.	*Ocimum basilicum*	Lamiaceae	Whole plant	Aqueous extract	Kurumba, Muduga & locals	antiviral and immune-stimulating

21.	*Emblica officinalis*	Phyllanthaceae	fruits	Aqueous extract	Kurumba, Muduga, Irula, & locals	vitamin c, calcium antiviral
22.	*Azadirachta indica*	Meliaceae	leaves	Aqueous extract	Irula, Kattu Naiken & locals	Immunomodulators
23.	*Aloe vera*	Asphodelaceae	leaves	Aqueous extract	Irula, Kattu Naiken & locals	immune and cardiovascular system
24.	*Adhatoda vasica*	Acanthaceae	leaves	Aqueous extract	Kurumba, Muduga,	inhibit DTH reactiveness, increased the percentage neutrophil adhesion, promoting increased phagocytic activity
25.	*Aegle marmelos*	Rutaceae	bark	Aqueous extract	Kurumba, Irula, Kattu Naiken	stimulates immune system
26.	*Carica papaya* L.	Carricaceae	Fruits	Aqueous extract	Kurumba, Muduga, Irula & locals	down regulates IL-4, IL-5, eotaxin, TNF-α, NF-κB, and iNOS levels thus exhibits anti-inflammatory effect
27.	*Cassia occidentalis* L.	Fabaceae	leaves	Aqueous extract	Irula, Kattu Naiken & locals	anti-asthmatic potential by decreasing mRNA expression of Th1/Th2 cytokine in lung tissue
28.	*Cynodon dactylon*	Poaceae	Whole plant	Aqueous extract	Kurumba, Muduga, & locals	significant increase in antibody
29.	*Jatropha curcas* L.	Euphorbiaceae	Leaves, roots	Aqueous extract	Irula, Kattu Naiken & locals	ameliorated both cellular and humoral antibody response
30.	*Solanum nigrum* L.	Solanaceae	seeds	Aqueous extract	Kurumba, Muduga & locals	increment in the percentage of CD4+ T lymphocyte and a decrease in the percentage of CD8+ T lymphocyte of tumor
31.	*Vitex negundo* L.	Verbanaceae	leaves	Aqueous extract	Kurumba, Muduga, locals	inhibits HIV-1 reverse transcriptase activity
32.	*Abutilon indicum* L.	Malvaceae	Aerial parts	Aqueous extract	Kattu Naiken & locals	stimulatory effect on T lymphocytes.
33.	*Achyranthes aspera* L.	Amaranthaceae	Root	Aqueous extract	Kurumba, Muduga, locals	cytokine based immunomodulatory
34.	*Cyperus rotundus* L.	.Cyperaceae	Rhizome	Aqueous extract	Kattu Naiken & locals	humoral-mediated immunity by stimulating B and T cell proliferation
35.	*Nyctanthes arbor-tristis*	Oleaceae	Leaves, flowers and seeds	Aqueous extract	locals	splenocytes proliferation and increased production of cytokines, especially IL-2 and IL-6
36.	*Momordica charantia*	Cucurbitaceae	Leaves	Aqueous extract	Muduga, Irula, Kattu Naiken	neutrophils and macrophages stimulates
37.	*Pongamia pinnata* L.	Faboideae	seeds	Aqueous extract	Kurumba, Muduga,	immune cell signaling events needed for continued recruitment of neutrophils
38.	*Plantago major*	Plantaginaceae	Whole plants, seeds	Aqueous extract	Kurumba, Muduga, Irula, Kattu Naiken & locals	anti-HSV-1, anti-HSV-2 and anti-ADV-3 activities.
39.	*Santalum album*	Santalaceae	Stem	Aqueous extract	, Kattu Naiken & locals	inhibited cell proliferation, nitric oxide production and CD14 monocyte
40.	*Terminalia chebula* Retz.	Combretaceae	Fruits	Aqueous extract	Irula, Kattu Naiken & locals	increase in humoral antibody titer and delayed-type hypersensitivity
41.	*Sida cordifolia* L.	Malvaceae	Seeds	Aqueous extract	Kurumba, Irula, Kattu Naiken	roduction of T-cell precursor
42.	*Sesamum indicum* L.	Pedaliaceae	Seed	Aqueous extract	Muduga, Irula & locals	suppress cellular immunity with the domination of Th2 responses

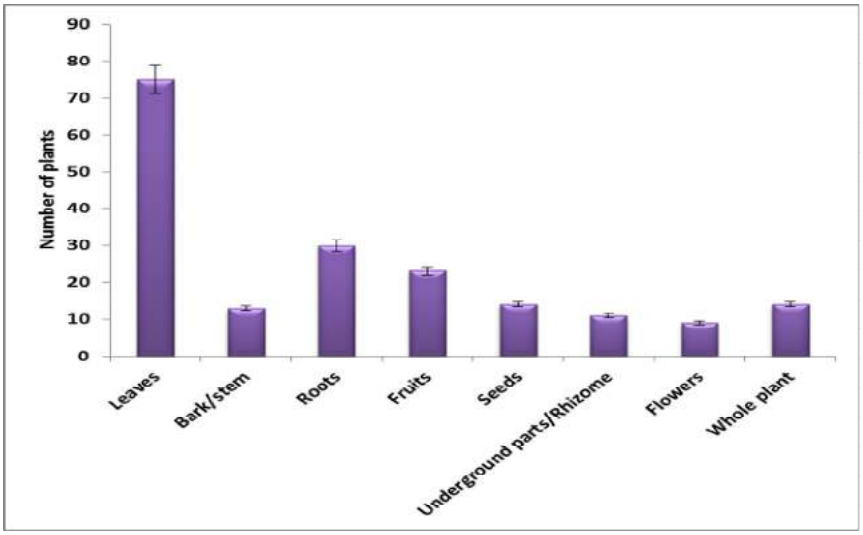

Figure 1. The various plant parts used by the practicing people

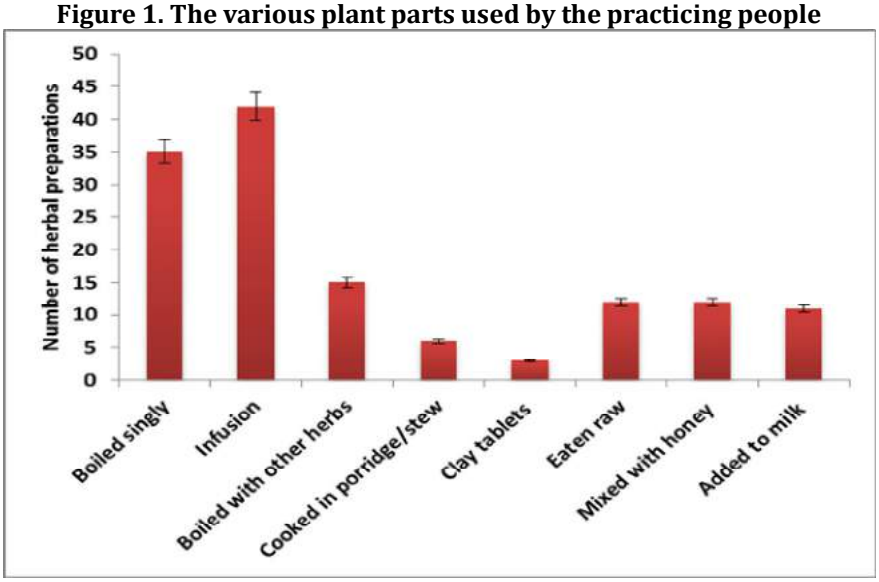

Figure 2. The preparation of herbal medicines by the practicing people

CONCLUSION

In the present ethno-botanical survey revealed the relationship of humans with the nature in terms of medicinal plants especially for their health care. Tribals and native people in this region use these traditionally available plants for health and believe that these are easily available, less expensive and have no side effects. The present situation of ethnic knowledge regarding to immune boosting plants is gradually disappearing from the country side due to deforestation, tourism impact on natural vegetation of these region, population growth and heavily construction and also due to global warming. Scientific policies have to be implemented to conserve the local wild plants. Farmers and local communities should be addressed in the cultivation of herbals at least on their barren land. During the present survey of plant species related with the medicinal value provides comprehensive information of the immune alleviation properties of the species. Based on the data it can be ascertained that the Silent valley outer skirts area has high potential of herbal species. Therefore there is an urgent need to educate and bring awareness in the local communities, through workshops and training programs about the need of medicinal plants and their conservation.

ACKNOWLEDGEMENT

The authors are grateful to the native people and tribal communities for their kind support provided to carry out the present survey successfully.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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INVESTIGATIONS ON THE EFFECT OF SYNTHETIC FEED ON BROILER CHICKEN

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Abstract
Progressive genetics and management has allowed the broiler industry to produce heavier chicken in a more efficient manner. Consequently the age to market from farm in broiler chicken has been gradually reduced. This is due to the use of synthetic feed as broiler diet. Carbohydrates produced by several grains and protein supplements are the two main components of broiler feed. In addition to these, aminoacids like methionine,lysine etc., are also added to increase the weight. In the present study the effects of synthetic feed on weight gain, feed conversion ratio, cholesterol level and morphological and anatomical variations on broiler chicks (Cobb 500) were studied. The experimental period was 21 days. This study was led to the conclusion that synthetic feed induces significant weight gain in broilers. In addition to it synthetic diet also results higher cholesterol level and cardiac deformities.

Key words: Broiler, feed conversion ratio,methionine, lysine, cholesterol, cardiac deformities

Introduction

Poultry meat is an important source of proteins, minerals and vitamins to balance the human diet. Specially developed varieties of chicken are now available with quick growth and high feed conversion efficiency. Depending on the farm size, broiler farming can be a main source of income. Poultry farming includes raising of various types of domestic birds commercially for the purpose of meat, eggs and feather production. The most common and widely raised poultry in the world are chicken. Again, these may be broilers or layers. Commercial chicken farming is most successful business in Asia and other parts of the world. Proper care of birds and farm management practices will result in decent profits in short period of time. Basically broilers are raised for meat purpose whereas layers for egg production (Iji, P. A., A. A. Saki, and D. R. Tivey. 2001). Farmers can even go for back yard chicken farming or country chicken rising at home. Apart from meat and egg production, manure that produced in the farm has good market value. This manure can be used as organic compost in various field crops. Poultry meat production in the country has increased 18 fold from 81,000 tons in 1971 to 1440,000 tons in 2004 (Adeola O,1994).

Materials and Methods

Animal selection

Broiler chickens, *Gallus gallus domesticus* (Cobb 500) are, bred and raised specifically for meat production. Commercial broilers generally reach slaughter weight in between five to seven weeks of age. One day old broilers which are healthy and active were purchased from a commercial hatchery in Thiruvananthapuram. Broilers of bodyweight of almost 50g were used for the experiment. They were kept in pens with raised wire floors in an environmentally controlled room.

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Experimental design

The birds were divided into two groups consisting of six in each pen. The dimension of the pen was 2mx8m . The group I (Normal Feed-NF) was kept as control which was given normal feed. Normal feed was formulated with millets and rice. Group II (Synthetic Feed-SF) was fed with synthetic diet. The experimental period was 21 days. The feed and water were supplied *ad libitum* throughout the experimental period. The feeders and drinker were fixed in such a way that the birds were able to eat and drink conveniently. Feed and fresh drinking water were supplied to the experimental birds daily once in the morning and again in the afternoon. The birds were always exposed to continuous lighting of 24 hours. The brooder temperature was maintained at about 34^0C up to seven days of age, gradually decreased to 26^0C by 21st day of age. Body weight gain, feed intake, and feed conversion ratio were calculated. Feed conversion ratio can be calculated by the formula,

Feed Conversion Ratio (FCR)

= Feed intake (g) / Live weight (g)

Cholesterol estimation

At the end of third week, one bird of average weight from each pen was selected and blood was collected from the wing vein. Blood samples were taken in test tubes without anticoagulant and labelled according to each pen and the serum was collected. Cholesterol was determined according to CHOD-PAP [cholesterol oxidase (CHOD) - phenol + aminophenazone (PAP)]method (Ellefson, RD and Garaway, WT).

Anatomical studies

At the end of third week, one bird of average weight from each pen was selected and the heart from the birds were dissected out and was cross sectioned.

Statistical analysis

Student's t test was done for finding the significance.

Results

1. Body weight gain

Weight gain of birds fed with normal and synthetic feed show marked differences. The weight gain at the end of three week experiment was 405 g and 725 g respectively. Weight gained by broilers is given in table 1, 2 and 3.

Table 1 Weight gain during the first week

DAYS	CONTROL (g)	SYNTHETIC FEED (g)
1	50	50
2	55	55
3	59	65
4	65	85
5	75	105
6	85	125
7	105	150

Table 2 Weight gain during the second week

DAYS	CONTROL (g)	SYNTHETIC FEED (g)
1	115	175
2	130	205
3	150	230
4	170	275
5	190	305
6	215	350
7	250	400

Table 3 Weight gain during the third week

DAYS	CONTROL (g)	SYNTHETIC FEED (g)
1	275	455
2	300	485
3	325	535
4	330	595
5	350	640
6	380	685
7	405	725

2. Feed intake

The feed intake at the end of three week experiment was 70g and 69g for normal and synthetic chicks respectively. There was no significant difference in feed consumption. The feed intake of broilers is given in the table 4, 5 and 6.

Table 4 Feed intake during the first week

DAYS	CONTROL (g)	SYNTHETIC FEED(g)
1	10	10
2	13	12
3	15	14
4	15	16
5	20	20
6	25	27
7	27	32

Table 5 Feed intake during the second week

DAYS	CONTROL (g)	SYNTHETIC FEED(g)
1	30	38
2	33	40
3	35	43
4	40	50
5	45	52
6	50	55
7	52	56

Table 6 Feed intake during the third week

DAYS	CONTROL (g)	SYNTHETIC FEED (g)
1	55	58
2	58	60
3	60	63
4	62	65
5	63	66
6	66	68
7	69	70

3. Feed Conversion Ratio (FCR)

Feed conversion ratio of broilers fed with normal and synthetic food show no significant difference in the first week. But in second and third week FCR shows a marked difference. The feed conversion ratio at the end of three week experiment was 0.170g and 0.096g respectively. The feed converting efficiency of chicks fed with synthetic feed is very high in comparison with the control one. The feed conversion ratio of broilers is given in table 7, 8 and 9.

Table 7 Feed conversion ratio during the first week

DAYS	CONTROL (g)	SYNTHETIC FEED (g)
1	0.2	0.2
2	0.236	0.218
3	0.254	0.215
4	0.230	0.188
5	0.266	0.190
6	0.294	0.216
7	0.257	0.213

Table 8 Feed conversion ratio during the second week

DAYS	CONTROL (g)	SYNTHETIC FEED (g)
1	0.260	0.217
2	0.253	0.195
3	0.233	0.186
4	0.235	0.181
5	0.236	0.170
6	0.232	0.157
7	0.20	0.14

Table 9 Feed conversion ratio during the third week

DAYS	CONTROL (g)	SYNTHETIC FEED (g)
1	0.20	0.127
2	0.193	0.123
3	0.184	0.117
4	0.187	0.109
5	0.18	0.103
6	0.173	0.099
7	0.170	0.096

4. Average weight gain, feed intake and feed conversion ratio (FCR)

Average body weight gain, feed intake and food conversion ratio of broilers is given in table 10.

Table 10 Average weight gain, feed intake and FCR

Experiment	Weight gain	Feed intake	Feed conversion ratio (FCR)
Control	253.33	49.33	0.209
Synthetic feed	425	52.66	0.149

5. Cholesterol level in serum (mg/dl)

The results of serum cholesterol level were presented in table 11.The cholesterol level of control group is lower than that of broilers given synthetic feed.

Table 11. The cholesterol level

Experiment	Cholesterol level (mg/dl)
Control	176.27
Synthetic feed	186.44

Figure 1.Heart of normal diet fed chick (left) and synthetic diet fed chick (right)

Figure 2.Cross section of a normal chicken heart (left) and heart from a chicken fed with synthetic diet (right).

Discussion

From the study it was found that poultry fed with synthetic diet showed marked increase in body weight. Maximum carcass yield is an important objective in the modern poultry industry, which demands an optimum protein supply. Methionine is an important amino acid in protein synthesis in broilers. The presence of methionine and lysine in synthetic feed play a major role in increasing the body weight of chicks. The -

increasing weight gain with increasing methionine levels in the diet was also been reported by Dilger RN, Baker DH (2008).The synthetic diet fed chicks show a lower FCR than control. Lower FCR indicates high feed converting efficiency and increased body weight gain. Gadzirayi , E. Mutandwa (2006) reported that pellet diets gave greater feed intake than did normal forms.

In the present study significantly higher level of serum cholesterol was observed in poultry fed with synthetic diet. Hypercholesterolemia (higher level of cholesterol) may be due to higher dietary intake of fatty food or due to higher cholesterol synthesis in the body. The observed result may be due to the combined effect of both these mechanisms(Kwiterovich, P.O., 1997).

In our study, synthetic diet fed chicks showed difficulty in locomotion .It was observed that these chicks often lie on the floor of the cage. Lesions were also observed on the legs of these chicks.Skeletal problems in broilers affect predominantly the locomotor system and are often referred to under the general term leg weakness. Similar results were reported by **Chehraghi *et al* (2013)**

In our study it was found that the heart of broilers fed with synthetic feed showed enlargement (Figure 1). Marked dilation of both ventricular chambers and considerably thinner left ventricular wall were observed (Figure 2).

Broilers suffer from two forms of heart failure: ascites and sudden death syndrome (SDS). Ascites and SDS are relatively common and are likely to be due to the fact that the broilers' fast growth requires high levels of oxygen to support metabolic demands (Blair, 1990). All their energy is spent on growth and efficient feed conversion, leaving them short of oxygen for their other bodily needs so that their hearts have to work much harder. Ascites affects fast growing chickens when the right side of their hearts becomes enlarged in response to increased workload during the bird's rapid growth (Olkowski *et al* 1995). The bird has to breathe more rapidly and its lungs become congested. SDS is an acute heart failure disease that affects mainly male fast-growing chickens which seem to be in good condition (Bin *et al* 2007).

Conclusion

From the study it was found that broiler chicken fed with synthetic diet showed significant weight gain than that of control. Synthetic diet fed poultry exhibited lower FCR.This indicates their high ability to convert food into meat. Poultry fed with synthetic diet showed some morphological and anatomical deformities. It includes leg lesions and overgrown right ventricle of the heart. Regarding serum cholesterol level, synthetic diet induced higher level of cholesterol than normal.

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A STUDY ON THE EFFECT OF ANTIBIOTIC DOXYCYCLINE ON BROILER

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Abstract

The use of sub therapeutic dose of antibiotic doxycycline on broilers on weight gain and feed conversion ratio was studied. Doxycycline was administered to broilers once in seven days of the experimental period (Total 3 doses / chick).The dosage was 20 mg/kg body weight. The antibiotic was dissolved in water and was orally administered. Experimental period was 21 days. Weight gain in broilers which were treated with doxycyclin was high when compared to control group. There was no significant difference in feed intake in both the groups. Feed conversion ratio in antibiotic administered group was low when compared to control group

Key words: Digestion, Absorption, Prophylactic

Introduction

The Indian poultry market, consisting of broilers and eggs was worth INR 1,750 Billion in 2018. The market is further projected to reach INR 4,340 Billion by 2024. Poultry is one of the fastest growing segments of the agricultural sector in India today. While the production of agricultural crops has been rising at a rate of 1.5 to 2 percent per annum, that of eggs and broilers has been rising at a rate of 8 to 10 percent per annum. As a result, India is now the world's fifth largest egg producer and the eighteenth largest producer of broilers.(Agricultural and Processed Food Products Export Development Authority)

Antibiotics have been used for more than five decades in commercial poultry enterprises. In addition to control diseases, antibiotics help to enhance intestinal digestion and absorption of nutrients and thereby improve growth (Miles and Harms, 1984). Although sub-therapeutic antibiotics have been used successfully for years, there is a growing concern about their continued use as performance enhancers with regard to build-up of antibiotic resistance in the human population. Several approaches are now being considered as alternatives to antibiotic growth promoters. About 90% of the antibiotics used in agriculture are for growth promotion and prophylactic purposes rather than treating disease infections (Chadwick and Goode, 1997). It is estimated that more than 8 million kg of antibiotics (about one third of all antibiotics) are used sub-therapeutically for growth promotion in the United States.

Doxycycline is one of the antibiotics commonly used in poultry farming. It is considered as the 'second generation' tetracycline mainly active against Gram-positive and Gram-negative aerobic and anaerobic bacteria. (Riond and Riviere, 1988).

Doxycycline is a semi synthetic tetracycline derivative. Doxycycline is used in poultry, turkeys, and cattle’s for the treatment of infections due to bacteria at doses of 10-20 mg/kg for 3-5 days.

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Materials and Methods

Animal selection

Broiler chickens (*Gallus gallus domesticus*) of the breed White cobb were selected for the study. Healthy and active birds were purchased from a commercial hatchery. Almost same sized broilers of body weight 50g were used for the experiment. One day old broiler chickens were kept in pens with raised wire floors in an environmentally controlled room. The birds were divided into two groups consisting of six in each pen. They were kept in pens having a dimension of 2m x 8m. First group was control and was not treated with antibiotic. While the second group was administered with antibiotic doxycycline.Both the groups were fed with same synthetic feed.

Doxycycline was purchased from the market. Experimental period was 21 days and the broilers were administered 3 doses of doxycyclin in seven days duration. The dosage was 20 mg/kg body weight. The antibiotic was dissolved in water and was orally administered..

The data regarding the body weight gain, amount of feed intake and the feed conversion ratio were collected. The feed conversion ratio can be calculated using the following equation.

Feed Conversion Ratio (FCR) =

Feed intake (g) / Live weight (g)

Statistical analysis

Student's t test was done for finding the significance.

Results and Discussion

1. Body weight gain: The use of sub therapeutic doses of doxycycline antibiotic on broilers promotes growth. Weight gain of broilers with and without antibiotics show remarkable differences. Weight gain at the end of three week experiment was 600g in control and 800g in doxycycline treated ones. The results are graphically represented in figure 1, 2 and 3.

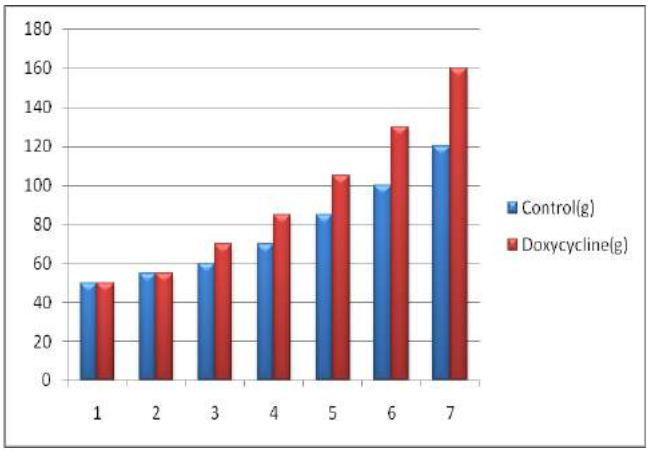

Figure 1. Weight gain during the first week

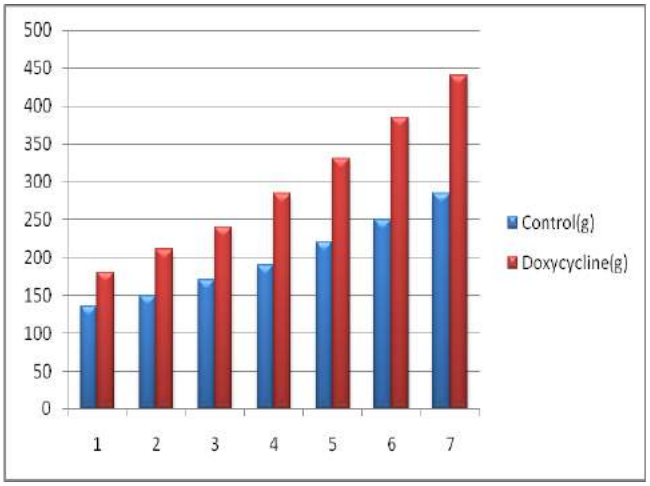

Figure 2. Weight gain during the second week

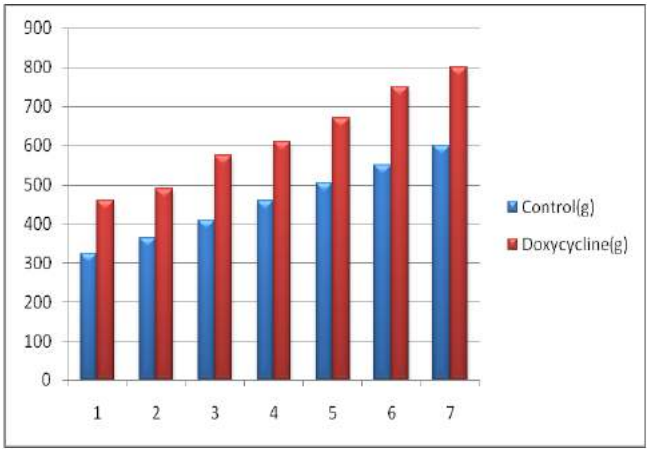

Figure 3. Weight gain during the third week

2. Feed intake

Feed intake of broilers at the end of three week experiment was 69g for control and 73g for doxycycline treated ones. There was no significant difference in feed intake in both the groups. The results are graphically represented in figure 4, 5 and 6.

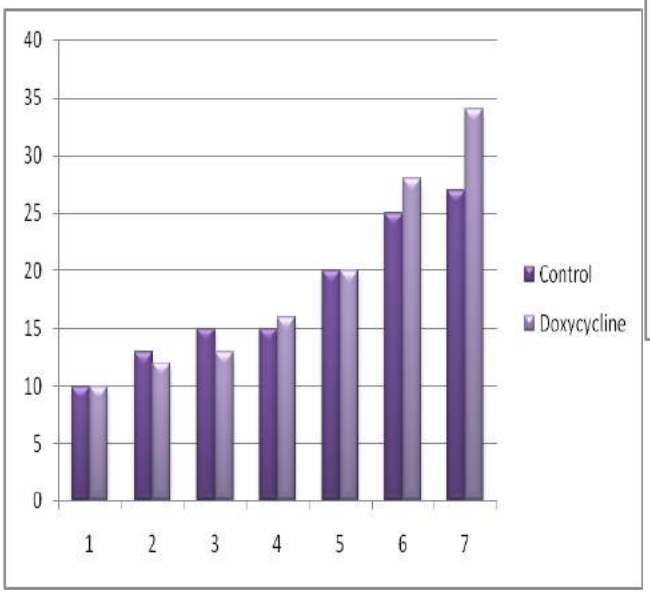

Figure 4. Feed intake during the first week

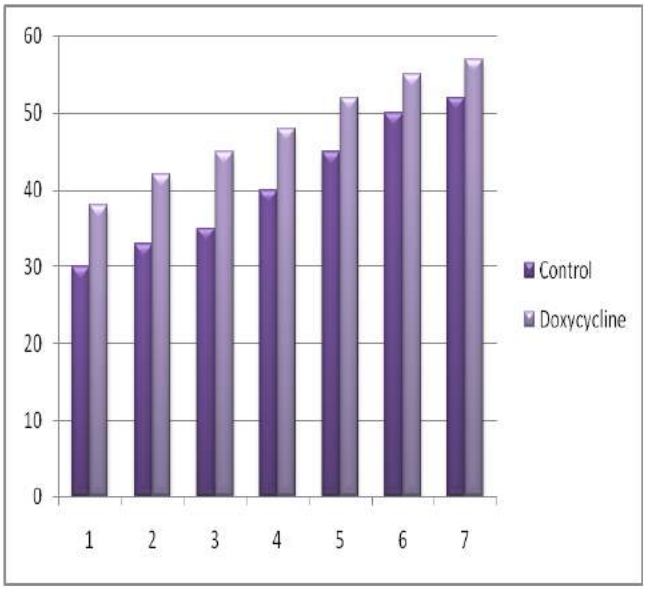

Figure 5. Feed intake during the second week

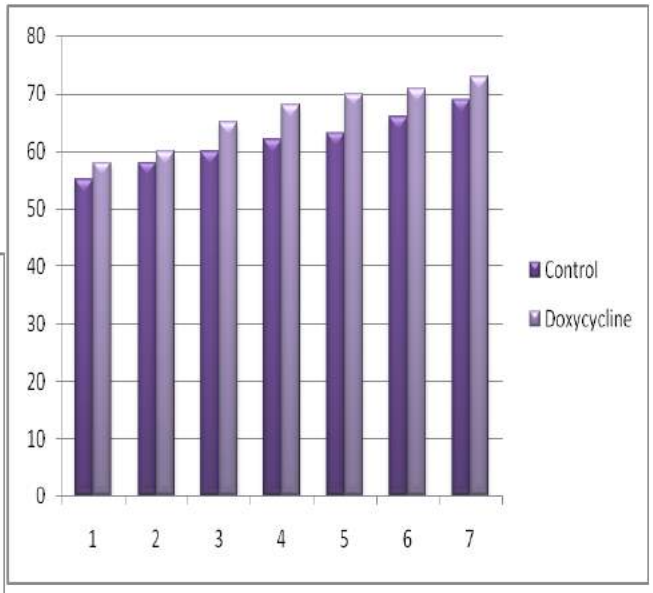

Figure 6. Feed intake during the third week

3. Feed Conversion Ratio (FCR)

Feed conversion ratio shows a remarkable difference during the second and third week. Feed conversion ratio of broilers at the end of third week experiment was 0.11g for control and0.091g for doxycycline treated ones. The results are graphically represented in figure 7, 8 and 9.

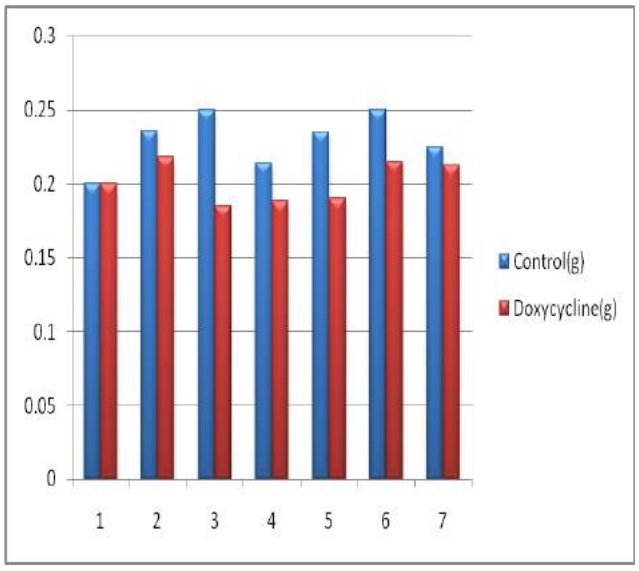

Figure 7. Feed conversion ratio during the first week

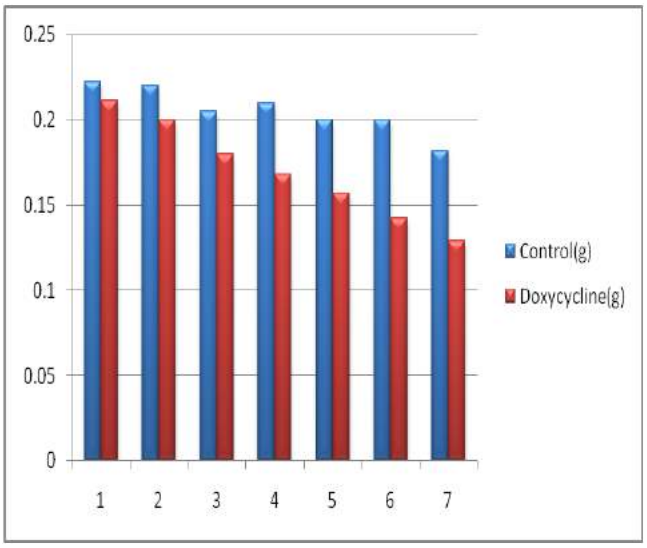

Figure 8. Feed conversion ratio during the second week

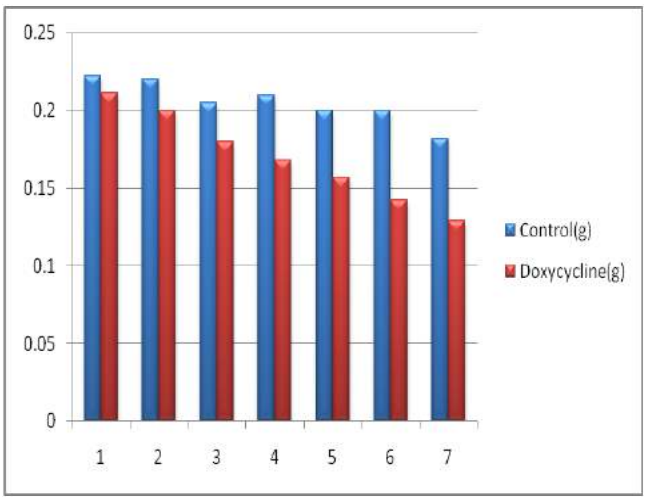

Figure 9. Feed conversion ratio during the third week

4. Average weight gain, feed intake and feed conversion ratio (FCR)

Average body weight gain, feed intake and food conversion ratio of broilers is given in Table 1.

Table 1. Average weight gain, feed intake and FCR

Experiment	Weight gain	Feed intake	Feed conversion ratio (FCR)
Control	245.47	40.14286	0.190
Doxycycline	337.1429	44.52381	0.15981

Diet supplemented with doxycycline resulted increased body weight. Doxycycline acts as growth promoter and thereby increasing the growth of broilers. The modes of action of antibiotics is their ability to alter gut microbial balance thereby reducing the population of pathogenic microbes and improving feed efficiency and growth. Many reports indicate the weight enhancing effect of antibiotics. These results are in agreement with that given by Alloui *et.al.* (2001), Mehdi *et.al.*(2011) with Panda *et.al.*, (2005).

Antibiotics promote improved growth response because of an effect on the microflora in the gastrointestinal tract. The continuous use of antibiotics at sub therapeutic levels in animal feeds to promote improved weight gain and feed conversion in broilers has become a controversial issue because of concerns over development of antibiotic resistance. The mode of action of the antibiotics used as feed additives to promote improved weight gain and feed conversion in broilers was reported by Feighner and Dashkevicz, (1987).Similar results had also reported by Bedford, (2000) and Choudhari et.al. (2008) where a more balanced micro population in gut is expected to lead a greater efficiency in digestibility and utilization of food, which consequently results in an enhanced growth and improved feed conversion ratio. The significant benefits of antibiotic supplementation observed on chick growth and feed conversion study were in agreement with many reviewers Mehdi, (2011).The possible mechanism of this phenomenon can be explained as follows. Antibiotic growth promoters are known to suppress the gut bacteria, leaving more nutrients for chick to be absorbed for greater weight gain.

The Feed Conversion Ratio (FCR) was significantly lower in chicks which had received the doxycycline antibiotic up to the end of experiment. Feed conversion ratio in the control group was slightly higher than that of the group of chicks that were subjected to antibiotic treatment. Lower FCR indicates high feed efficiency and increased weight gain. The results were in accordance with Yeo and Kim, (1997) who

reported that the use of antibiotics in broiler chicks significantly improved the daily body weight gain and feed efficiency. From obtained results it can be concluded that administration of antibiotics in broilers led to significantly better feed conversion to body mass compared to basal diet.

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Review

One-pot synthesis and characterization of Schiff base macrocyclic complexes as a potential bioactive core – a review

J. P. Remiya, T. S. Sikha & B. Shyni

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Abstract

Schiff base macrocycles play a remarkable role in the advancement of modern coordination chemistry in light of their importance to various multidisciplinary research fields. Bioinorganic chemistry has grown tremendously and provides opportunities to use macrocyclic Schiff base metal complexes as therapeutic agents. Macrocyclic Schiff base complexes have been studied on account of their ability to coordinate a variety of metal ions, preparative accessibility and growing applicability in numerous fields. In view of their pharmacological or biological properties, metal complexes of Schiff base macrocycles opened up a new vista of prospects in synthetic organic chemistry. Various methods were embraced to develop macrocyclic Schiff base metal complexes, along with their pharmacological properties. One of the simplest and effective methods for macrocyclic synthesis is an *in-situ* approach where the appearance of a metal ion in the cyclization reaction increases the yield of the macrocyclic product. This review focuses on the one-pot synthesis of biologically significant Schiff base macrocyclic metal complexes reported from 2005-2021.

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Synthesis, spectral characterization and biological evaluations with DFT analysis on molecular geometry and NLO of 1,4,7,10-tetraazacyclotetradecane-11,14-dione

J.P. Remiya [a], T.S. Sikha [a], B. Shyni [a], L. Anitha [a], C.S. Nair Lakshmi [a], E.G. Jayasree [b]

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Highlights

- Synthesis and spectral characterization of diamide macrocyclic ligand.

- Simulated IR and Raman frequencies data correlated well with the experimental spectral results.
- TD-DFT calculation explains the excitation properties of the compound.
- MESP and NBO analysis were performed.
- NLO activity of the compound was determined experimentally.

Abstract

A novel 14-membered tetradentate N_4 macrocyclic ligand, STETA (1,4,7,10-tetraazacyclotetradecane-11,14-dione) was synthesized by [1+1] cyclic condensation of succinic acid with triethylenetetramine through reflux method in ethanolic solvent. The synthesized macrocyclic ligand was experimentally characterized by C H N analysis, FT-IR, FT-Raman, electronic, ^{1}H NMR, ^{13}C NMR and ESI MS. Optimization of molecular geometry and spectral (FT-IR, FT-Raman, ^{1}H/^{13}C NMR) analysis of STETA were performed by employing DFT with B3LYP/6-311+G(d) basis set and computational results were correlated with experimental (NMR, IR, Raman) spectral values. Electronic absorption properties of STETA were monitored using TD-DFT approach and also theoretical UV–vis results were experimentally compared. FMO analysis, MEP plot, global reactivity descriptors, first-order hyperpolarizability and NBO analysis were rationalized on the ground of DFT computation. NLO activity of title molecule was confirmed by both molecular hyperpolarizability calculations and SHG measurements. *In vitro* antibacterial activity and DPPH radical scavenging effects of STETA were screened.

Graphical abstract

Tetraaza macrocyclic compound was synthesized and characterized by spectral techniques. Molecular geometry optimization was performed by employing DFT/B3LYP/6-311+G(d) method. Computational results were comparable with experimental spectral values.

Journal of Physical Organic Chemistry

RESEARCH ARTICLE

Exploring the oxidation chemistry of hydroxy naphthoic acid: An experimental and theoretical study

Shibin B. Naduvilpurakkal, Sunil Paul M. Menacherry, Sreekanth R. Nair, Thao P. Nguyen, Pramod G. Nair, Usha K. Aravind, Charuvila T. Aravindakumar

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Abstract

Elimination of polycyclic aromatic hydrocarbons (PAHs) from aquatic environment is extremely important, as they are identified pollutants. The oxidative degradation of two model PAHs, namely 3-hydroxy-2-naphthoic acid (3HNA) and 6-hydroxy-2-naphthoic acid (6HNA), collectively represented as HNAs in this report, were investigated by utilizing a combined approach of pulse radiolysis, theoretical studies and high-resolution mass spectrometry (HRMS). Hydroxylated adduct radicals of HNAs (3HNA–λ_{max}; 340 nm; $k_2 = [1.09 \pm 0.07] \times 10^{10}$ dm^3 mol^{-1} s^{-1}, 6HNA–λ_{max}; 350 nm; $k_2 = [9.43 \pm 0.05] \times 10^9$ dm^3 mol^{-1} s^{-1}) were recognized as the immediate intermediates upon their reaction with hydroxyl radical ($^{\bullet}OH$). While theoretical calculations revealed the contributions from C1 and C4 adducts into the experimentally observed spectrum of 3HNA, the C5 adduct accounted as the major contributor for 6HNA. Investigations using specific oxidants, such as sulfate ($SO_4^{\bullet-}$) and oxide ($O^{\bullet-}$) radicals, helped to exclude the contributions from other minor pathways (e.g., one-electron oxidation

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Synthesis of oxydiacetate functionalized strontium coordination polymer through gel diffusion technique: A new dual luminescent chemosensor for the detection of Copper(II) ions and Cr(VI) oxyanions in aqueous medium

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ABSTRACT

The current scenario shows the wide applicability of coordination polymers (CPs) in various fields due to their structural topology and tunable properties. The development of these molecules with potential application can be obtained by incorporating active metals with highly functionalized ligands under different synthetic conditions. Here in we report a newly synthesized dual luminescent chemosensor based on oxydiacetate functionalized strontium $[Sr(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ by one of the simplest gel diffusion technique at room temperature. The grown crystal was characterized by elemental analysis, FTIR, UV–Visible Spectroscopy, Single Crystal X-ray Diffraction and TG/DTA measurements. Single Crystal X-ray diffraction studies of the synthesized CP revealed a monoclinic crystal system with space group *P*21/*c*. The luminescent properties of the synthesized analyte were analyzed from photoluminescence (PL) spectrum. The coordination polymer displayed an emission of 371 nm upon excitation of 313 nm. The luminescence titration experiments showed that the synthesized coordination polymer dispersed in water, can selectively sense Cu(II) metal ions as well as the Cr(VI) oxyanions $[CrO_4^{2-}/Cr_2O_7^{2-}]$ from the aqueous media with a detection limit of 0.2536 μM and 0.1060 μM respectively. The grown strontium based CP can thus be used as an effective dual luminescent chemosensor for the detection and probing of both Cu^{2+} and Cr(VI) oxyanions $(CrO_4^{2-}/Cr_2O_7^{2-})$ in aqueous medium. The study further suggests the possibility of fabrication of strontium based luminescent chemosensors for the detection of Cu(II) cations and $CrO_4^{2-}/Cr_2O_7^{2-}$ anions in aqueous medium with high selectivity and sensitivity.

1. Introduction

According to United States Environmental Protection Agency (USEPA), Cr(VI) is considered as a hazardous pollutant in environmental samples [1]. These are mutagenic and carcinogenic in nature and the excess intake may lead to the damage of DNA and even disruption of enzyme activities in living systems [2,3]. Chromium is widely used for printing, tanning of leather, polishing of metals, electroplating etc [4]. Cr(VI) ions are present in aqueous medium either in the form of elemental state or in the form of complexes such as $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$. Detection of Cr(VI) in environmental samples and biological systems at a very low concentration is inevitable for the sustainable development of society and human welfare. The ultrasensitive probing as well as selective detection of Cr(VI) in aqueous medium is important due to its high solubility, bioaccumulation effect, environmental mobility etc. [5,6].

Copper is an abundant element in human body showing different oxidation states either in the elemental state or in the complexes. The recommended intake of Cu is limited to a maximum amount of 0.8–0.9 mg/day [7]. The higher intake may lead to the improper functioning of kidney, liver and even death of the person. The other essential metals can be displaced by the high concentration of Cu^{2+} ions in vivo which can lead to the disruption of cellular homeostasis [8].

Now a days lot of research has been going on for the development of new luminescent probes for the detection of Cu(II) and Cr(VI) ions. Out of these probes, coordination polymers are used for the effective detection of both of these ions [9]. Coordination polymers(CPs) or Metal organic frameworks(MOFs) are a variety of molecules with potential

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applications that consists of both organic and inorganic units [10]. These are generally formed by the coordination of the active sites of the ligand to the metal center and repeating these coordination entities which extends in one, two or three dimensions [11]. By incorporating varieties of active metal centers with highly functionalized ligands under different synthetic conditions lead to the formation of CPs with wide structural diversity [12]. Novel CPs or MOFs are formed through the molecular aggregation due to the presence of non covalent interactions like hydrogen bonding, π-π interactions, dipole–dipole interactions etc. [13]. The symmetry and rigidity of the ligands play an important role in the properties of the resulting CPs or MOFs. Introduction of these active molecules opened a new era in the field of catalysis, gas storage, separation of gases, electronic and optoelectronic device applications, photochemical sensing, biosensing, luminescent sensing and antimicrobial applications etc. [14–18]. Most commonly used ligands are polycarboxylates because of their structural rigidity and strong binding interaction towards the metal centers. Oxydiacetic acid is a simple, aliphatic and water soluble dicarboxylic acid that acts as a good ligand with wide application. Oxydiacetic acid functionalized materials are used for the recovery of rare earths [19], adsorption of Ce^{3+} and Nd^{3+} ions from aqueous solution [20], magnetic extraction of Pb(II) and Cr(VI) ions [21], selective and sensitive detection of Cr(VI) ions in aqueous medium [22] etc. Due to the large electronegativity difference between the s block elements and the oxygen atoms, the bonding interaction between them is found to be ionic in nature that controls the coordination geometry [23–26]. Strontium organic frameworks are found to have good luminescent properties [27], semiconducting nature [28], dual emission behaviour [29] etc. Chemical sensing of a molecule towards various analytes can be studied by monitoring the changes in the electrical conductivity, fluorescence behaviour, redox properties, absorption etc. These properties can be studied with the help of UV–visible spectroscopy, electrochemical methods, fluorescence spectroscopy etc. [30].

In the present work, oxydiacetic acid functionalized strontium coordination polymer was developed through gel diffusion technique which is one of the simplest methods for the growth of pure and good quality crystals at room temperature. Comparatively high charge density and ionic nature of alkaline earth metal ions results in the strong bonding interaction with the oxygen atoms present in the carboxylate group of the ligand. These grown crystals are found to be one dimensional coordination polymer and are characterized with the help of elemental analysis, FTIR, UV–Vis, Single crystal XRD, TG-DTA and photoluminescence spectroscopy. Sensing ability of the grown crystal towards Cu^{2+} and Cr(VI) oxyanions ($CrO_4^{2-}/Cr_2O_7^{2-}$) ions were extensively studied. The results showed that the grown crystal is an efficient sensor for the Cu^{2+} and $CrO_4^{2-}/Cr_2O_7^{2-}$ anions in aqueous medium.

2. Experimental section

2.1. Materials

Oxydiacetic acid and strontium nitrate of AR grade (99%) were purchased from Sigma Aldrich. Sodium metasilicate, glacial acetic acid and other metal salts were purchased from CDH, which were used directly without further purification.

2.2. Characterization

The percentage composition of carbon and hydrogen of the crystal was obtained by CHN analysis using Perkin Elmer 2400 series II CHNS organic elemental analyzer. Single crystal X-Ray Diffraction studies were carried out using a Bruker Kappa APEXII CCD diffractometer with graphite monochromator Mo Kα (λ = 0.71073 Å) radiation. FT-IR spectrum was recorded on a Thermoscientific Nicolet iS50 using KBr pellets in the range 4000–400 cm^{-1}. UV–Visible absorption measurements were taken from Agilent Technologies Carry 5000 Ultra Violet-Visible Spectrophotometer. The thermal stability of the grown crystal was analyzed using PerkinElmer STA 8000 with a heating rate of 10 °C per minute in nitrogen atmosphere. Photoluminescence spectral analysis was carried out by Perkin Elmer FL 6500 fluorescence spectrophotometer. Molecular graphics employed were done using MERCURY Version 3.1f.

2.3. Crystal growth of $Sr[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$

The good quality crystals were grown through gel diffusion technique [31–33]. It is one of the simplest methods for the growth of crystals at room temperature. The gel was prepared by mixing an aqueous solution of sodium metasilicate of density (1.02–1.06 g/cm^3) and ligand of desired molarity (0.2–1.5 M) was transferred to several test tubes of length 20 cm and diameter 2.5 cm. The pH of the gel was adjusted using dilute glacial acetic acid with constant stirring for getting a homogeneous mixture. The gel was allowed to set; once gelled, strontium nitrate solution of desired molarity (0.1–1.5 M) was carefully added along the walls of the test tubes without disturbing the gel. In order to prevent the evaporation of solution and to avoid the contamination, the mouth of the test tube was covered with parafilm tape. The grown crystals were separated, washed with distilled water and dried.

$$\mathbf{Sr(NO_3)_{2(aq)} + C_4H_6O_{5(aq)} \xrightarrow{pH-6.5} \left[Sr(C_4H_4O_5){\cdot}(H_2O)_3\right]_n{\cdot}nH_2O}$$

Compound: Colourless crystals. Yield (72%). FT-IR(cm^{-1}): 3300 υ(OH)str, 1568 υ(OCO)*asym* str, 1415 υ(OCO)*sym* str, 538 υ(Sr-O). Elemental analysis: Calculated(%): C, 16.9; H, 4.12. Experimental (%): C, 15.78; H, 4.22.

2.4. Preparation of analyte solution for sensing

A solution of $Sr[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ was prepared in distilled water. Different micro molar concentrations (0.2 μM, 0.4 μM, 0.6 μM, 0.8 μM and 1.0 μM) of both metal and anion solutions were prepared separately using distilled water. Mixture of both the solutions was allowed to vortex for 30 min at room temperature. 3 ml of the supernatant solution was collected and the sensing ability of the coordination polymer towards cations and anions were done using fluorescence spectroscopy [34]. The spectrum was recorded on excitation at a wavelength of 313 nm.

2.5. Reusability of the analyte for sensing Cu^{2+} and Cr(VI) oxyanions

$Sr[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ was dispersed in distilled water. 0.5 μM solutions of both Cu^{2+} and Cr(VI) oxyanion were prepared separately. 0.5 μM solution of Cu^{2+}/Cr(VI) was added to the CP solution and the mixture was vortexed for 30 min and record the emission spectrum of the supernatant solution. After the first quenching experiment the CP was then collected, washed thoroughly with distilled water. The recovered CP was further used for the successive quenching experiments [35].

3. Results and discussion

3.1. Crystal growth and structural characterization

Small colourless crystals of $Sr[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ were obtained in quantitative yield at the interface of the gel solution within 10 days and are found to be air stable. Normally the crystals were grown at room temperature, that minimizes the chances of defects in them. The chemically inert nature of the gel provides a three dimensional matrix for the reaction and it controls the kinetics of reaction between the ligand and the metal salt. The transparent nature of the gel helps to monitor the nucleation and growth of crystals regularly [36]. The gel density, pH and concentration of both ligand and the metal play an

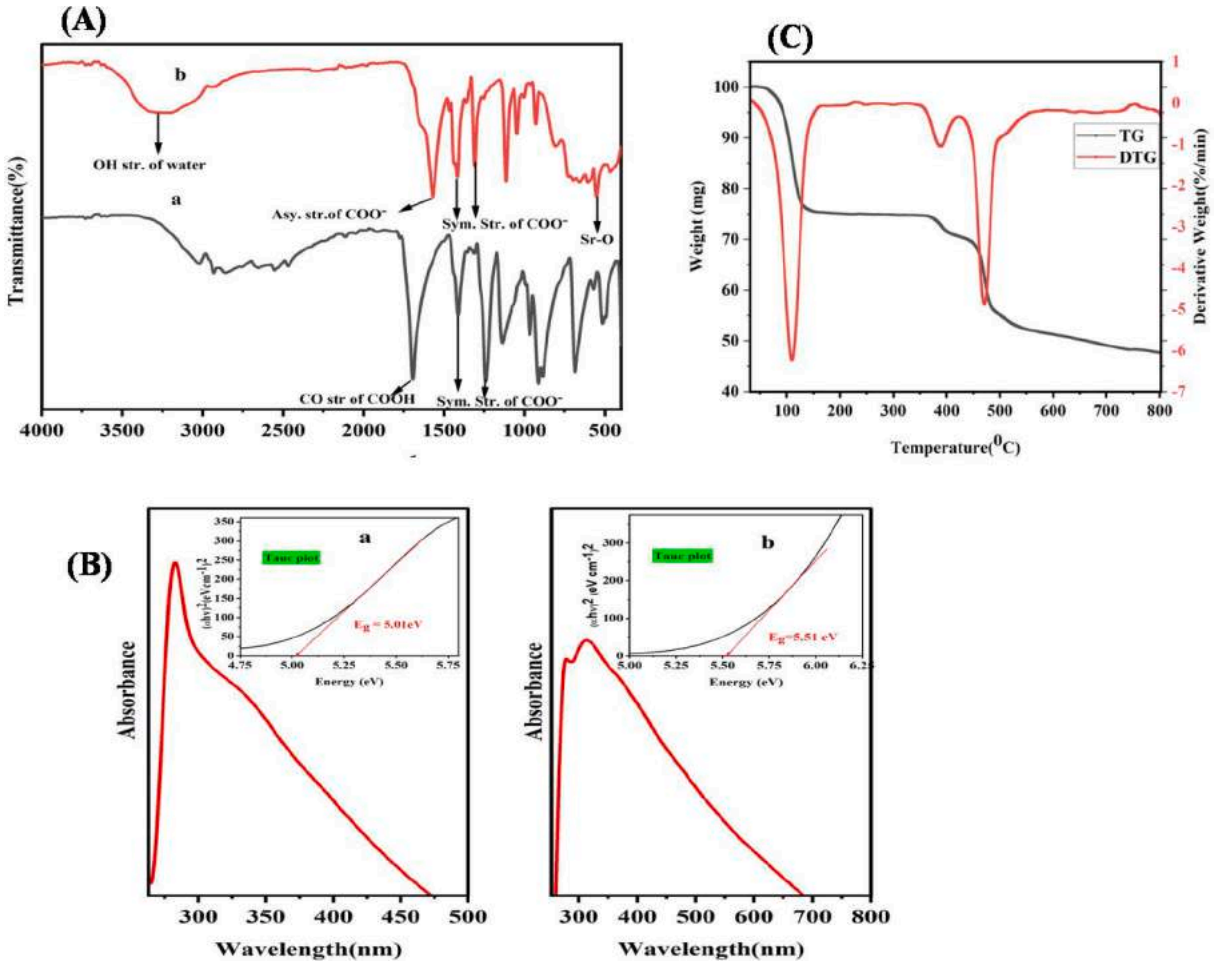

Fig. 1. (A) IR spectra of (a) oxydiacetic acid and (b) $[Sr(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ (B)UV–Visible spectra of (a) oxydiacetic acid and (b) $[Sr(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ and (C) TG/DTG curve of $[Sr(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$.

important role in the development of good quality crystals. The optimum conditions for the good quality crystals was 1:1 concentration of oxydiacetic acid and strontium nitrate (0.5 M) at a pH of 6.5 with a gel density of 1.03 g/cm^3.

The elemental analysis data is in good agreement with the theoretical molecular formula i.e, $Sr[(C_4H_4O_5)(H_2O)_3].H_2O$, shown in Table S1 in the Supplementary Materials section.

Inorder to identify the mode of coordination and the nature of the functional groups IR spectra of both ligand and crystal were recorded and shown in Fig. 1**(A).** The solid state absorption spectra of oxydiacetic acid and the crystal were recorded and shown in Fig. 1**(B).** Based on these data, band gaps were calculated using Tauc plot. The ligand and the crystal showed an absorption maximum at 282 and 313 nm respectively which is due to n to π* transitions. It is clear from the UV visible spectrum that the coordination results in a red shift of 31 nm. From the Tauc plot, the band gaps obtained are 5.01 eV and 5.51 eV respectively. Increasing the magnitude of band gap shown by the crystal structure attributes the unavailability of the free electron for the rapid conduction. As per the thermogravimetric analysis, shown in Fig. 1**(C),** the grown crystal undergoes three stage decomposition. First decomposition at 109 °C with a weight loss of 24.11% (24.51%, theoretical), corresponds to the loss of both lattice and coordinated water molecules. The second stage decomposition started at 387.2 °C indicating the pyrolysis of the ligand and after the third stage decomposition, the percentage of weight obtained (51.4%) is in good agreement with theoretical calculations (50.26%) that corresponds to the presence of the residual strontium carbonate.

Table 1
Crystal data and structure refinement for $[Sr(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$.

Empirical formula	$C_4\ H_{12}\ O_9\ Sr$
Formula weight	291.76
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 11.3790(17) Å, α = 90°. b = 7.1273(10) Å, β = 114.474(3)°. c = 13.089(2) Å, γ = 90°.
Volume	966.1(2) Å^3
Z, Density (calculated)	4, 2.006 Mg/m^3
Absorption coefficient	5.608 mm^{-1}
F(000)	584
Crystal size	0.200 × 0.180 × 0.150 mm^3
Theta range for data collection	1.966 to 28.916°.
Index ranges	$-15\le h\le 15$, $-9\le k\le 9$, $-17\le l\le 17$
Reflections collected	15,547
Independent reflections	2553 [R(int) = 0.0864]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.3094
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2553/12/152
Goodness-of-fit on F^2	1.010
Final R indices [I > 2 sigma(I)]	R1 = 0.0398, w$R2$ = 0.0849
R indices (all data)	R1 = 0.0660, w$R2$ = 0.0961
Extinction coefficient	0.0288(16)
Largest diff. peak and hole	1.498 and −0.920 e.Å^{-3}

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2\text{-}F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

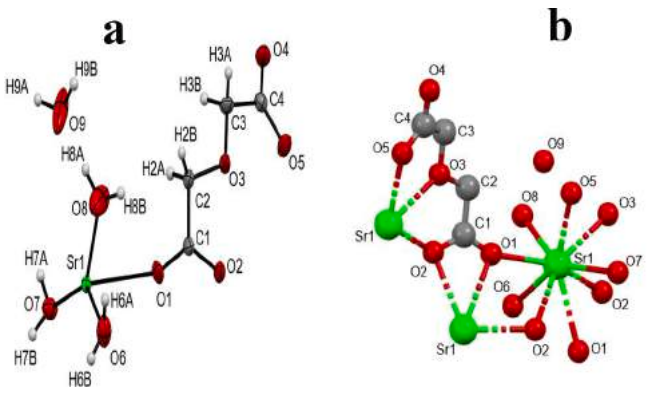

Fig. 2. (a) ORTEP diagram of strontium oxydiacetate and (b) coordination environment of $[Sr(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$.

The single crystal X-Ray diffraction studies showed that the grown crystal is a one dimensional co-ordination polymer that crystallizes in monoclinic crystal system with space group *P*21/*c*. The details of the crystal data and structure refinement is given in Table.1.

The crystal structure of $[Sr(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ formed from oxydiacetic acid and strontium carbonate, has already been reported via slow evaporation from oxydiacetate and strontium carbonate[37]. One strontium ion coordinated to four oxygen atoms constitutes the asymmetric unit and possess a distorted tetrahedral geometry. One of the oxygen atoms is from the carboxylate group (O_1) of oxydiacetic acid, that behaved as a monodentate ligand and the remaining from three water molecules (O_6, O_7 & O_8). A lattice water molecule is also present in the asymmetric unit. The coordination environment shows that the strontium metal is nine coordinated to oxygen atoms, of which three from water molecules and the remaining six from the two oxydiacetate units. Each oxydiacetate unit acts as a tridentate ligand and one of the carboxylate oxygen behave as a bridge between the two strontium atoms. The asymmetric unit of the crystal along with atom numbering scheme and the coordination environment of the strontium metal are shown in Fig. 2**(a)** and **(b)** respectively.

The selected bond lengths and bond angles are shown in Table S2 **in the Supplementary Materials section.** The packing of the molecule when viewed along the axis 'a' is shown in Fig. 3**(a).** When viewed along 'a' axis showed the one dimensional polymeric structure of the molecule in a zig-zag manner with water molecules on the surface, indicating the hydrophilic nature of the complex. When viewed along axis 'c', it is found that two adjacent Sr atoms are connected by the oxygen atoms from the ligand that forms diamond shaped Sr_2O_2 rings, which extends along one direction. This gives a ladder like structure to the polymer.

Hydrogen bonding interactions found in the crystal structure makes it a stable polymer. The coordinated water molecule forms hydrogen bonds with the ligand and the lattice water. Similarly, the lattice water also forms hydrogen bonds with the ligand and the coordinate water. O(9)-H(9B)…O(5) and O(9)-H(9A)…O(4) represent the hydrogen bonding between the carboxylate oxygen atoms (O(5) and O(4)) of the ligand. O(6)-H(6A)…O(2),O(6)-H(6A)…O(8), O(6)-H(6B)…O(8) and O(6)-H(6B)…O(9) indicates the hydrogen bonding between the coordinated water molecules. O(7)-H(7A)…O(4) and O(7)-H(7B)…O(6) shows the hydrogen bonding between the coordinated water molecule and the nearby carboxylate oxygen. O(8)-H(8A)…O(9) and O(8)-H(8B)…O(7) indicates the hydrogen bonds of coordinated water with lattice water and another coordinated water respectively. The hydrogen bonding interactions in the strontium based CP are shown in Fig. 3**(b)** and the selected hydrogen bonds [Å and ^{0}] are given in Table S3 **in the Supplementary Materials section.**

3.2. Luminescent characteristics

One dimensional coordination polymer containing dicarboxylic acid as ligands and alkaline earth metals as luminescent centers find immense emission characteristics. The fluorescence spectra of both the ligand and the coordination polymer (CP) is shown in Fig. 4. Ligand shows a sharp intense emission at 365 nm at an excitation of 282 nm. The emission is

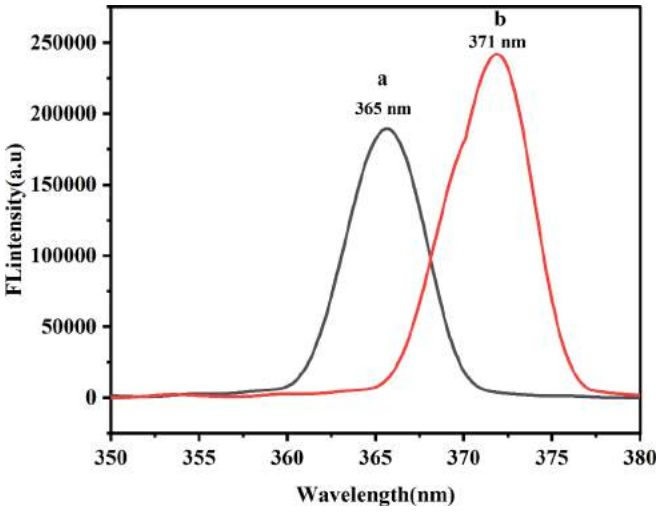

Fig. 4. Fluorescence Spectra of a) oxydiacetic acid b) Sr $[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$.

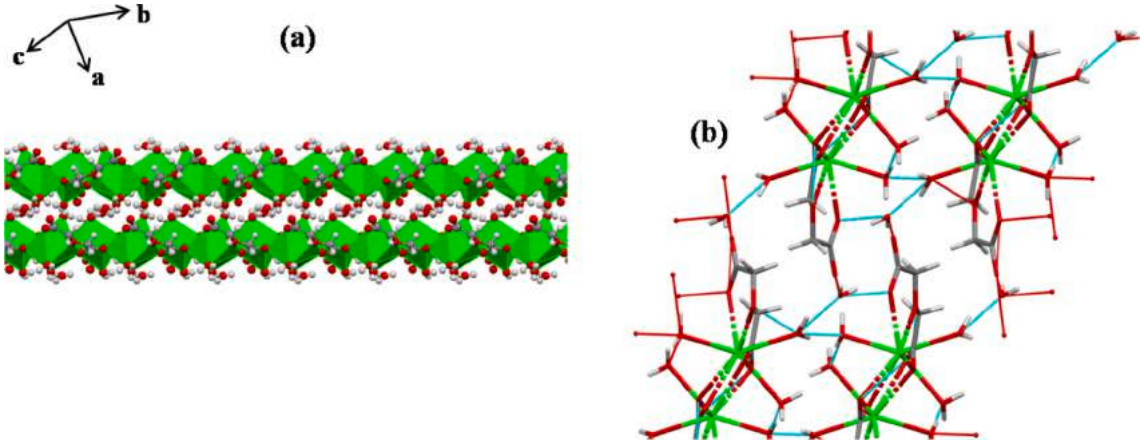

Fig. 3. (a) Packing diagram viewed along 'a' axis and (b) hydrogen bonding interactions in the $[Sr(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$.

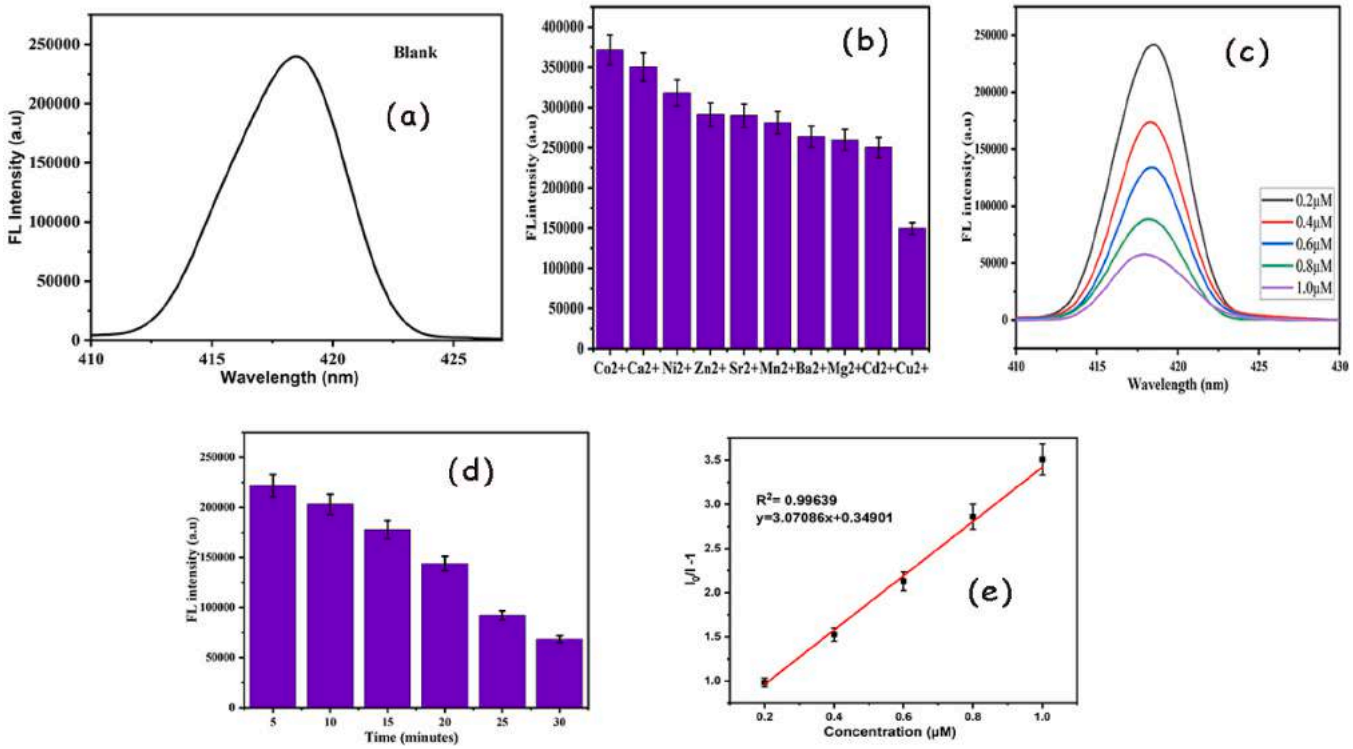

Fig. 5. (a) Fluorescence intensitiey of CP in water (b) Fluorescence intensities of CP during the sensing experiments conducted in presence of various divalent cations (c) Variations in the fluorescence emission of CP by successive addition of Cu^{2+} solution (d) Variation of fluorescence intensity of CP with respect to time (e) Stern Volmer Plot (S-V) for the sensing of Cu^{2+} ions.

due to n to π* transitions and interligand fluorescence [38]. Complex on excitation at 313 nm gives an emission at 371 nm. On comparing with the fluorescence spectra of ligand, a red shift in emission occurred when it was converted into CP which may be due to the Ligand to Metal Charge Transfer process (LMCT) [39].

3.3. *Selective sensing of divalent cations by* $Sr[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$

Coordination polymers with luminescent centers can act as a chemo sensing platform for the detection of the various inorganic metal ions present in biological as well as environmental samples. Particularly the coordination polymers showing emission below 600 nm can be used for the bioimaging of internal organelle [40]. In order to understand whether the synthesized coordination polymer can sense or probe the environmental contaminants, several luminescent experiments for selective sensing of both cations and anions were carried out. For understanding the sensing of CP towards the various metal ions, equimolar concentrated solutions of nitrate salts of different divalent metal ions were used.

Divalent cations selected for the sensing studies were Co^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Sr^{2+}, Mn^{2+}, Ba^{2+}, Mg^{2+}, Cd^{2+} and Cu^{2+}. CP was dispersed in distilled water. Equal quantities (10 ml of 0.5 μM) of different divalent cations were added slowly. The resulting mixture was vortexed continuously for 30 min at room temperature. Supernatant clear solution was decanted and fluorescence spectra of the same were recorded manually. The CP shows significant changes in the emission characteristics in the presence of various divalent cations. The fluorescene intensity of CP in water and the variation of fluorescence intensities in the presence of divalent cations are shown in Fig. 5**(a)** and **(b)** respectively. The fluorescence intensity of CP is increased by 53.08%, 44.52%, 30.58%, 19.50%, 19.16%, 15.80%, 8.7%, 6.4%, 3% for Co^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Sr^{2+}, Mn^{2+}, Ba^{2+}, Mg^{2+} and Cd^{2+}respectively. From the graph, it is clear that the FL intensity of the CP showed a large decrease in presence of Cu^{2+} ions, i.e, CP detects Cu^{2+} ions by means of fluorescence quenching and it further suggests a fluorescence turn off mechanism.

The sensing ability of CP towards the presence of Cu^{2+} is further examined by varying concentration of Cu^{2+} ions and time. The variation of fluorescence intensity of CP by the successive addition of Cu^{2+} were studied and shown in Fig. 5**(c)**. The results showed that on increasing the concentration of Cu^{2+} from 0.2 to 1 μM, the intensity of fluorescence emission of CP seems to be decreased. Thus, the quenching of fluorescence increases with increase in concentration of Cu^{2+} solution. Quenching efficiencies of CP towards the quantification of Cu^{2+} were calculated as 0.6%, 28.35%, 44.70%, 63.31% and 76.02% associated with each successive addition of Cu^{2+} solutions of concentrations of 0.2 μM, 0.4 μM, 0.6 μM, 0.8 μM and 1 μM respectively. The variation of fluorescence intensity with time is shown in Fig. 5**(d)**. As the time goes on, a "turn off" mechanism is followed due to the selective time bound detection of Cu^{2+}ions. The fluorescence emission of CP is diminished by 8.8% after 5 min of addition of solution of Cu^{2+} which goes on decreasing and reaches to 71.68% after 30 min of addition of Cu^{2+} solution. As the time of contact of CP with Cu^{2+} ions increases, fluorescence emission of CP decreases exponentially. The Ksv value calculated from Stern-Volmer equation is found to be $3.17 \times 10^6 M^{-1}$ and the value is comparable with the reported values of sensors showing efficient fluorescence quenching ability [41]. The higher Ksv value further suggests the better activity of CP towards the sensing as well as probing of Cu^{2+} ions in aqueous media. Stern Volmer plot for the detection of Cu^{2+} ions is shown as Fig. 5**(e)** and it gives a linear relationship between $I_0/I - 1$ against the concentration of Cu^{2+} solutions added. Standard deviation of intercept is calculated from the equation,

Standard deviation of Intercept=(Standard error of Intercept) $\times n^{1/2}$.

where n is called number of measurements taken. Limit of Detection value (LOD) is calculated from the equation as.

LOD = 3.3×(standard deviation of intercept/slope).

Standard deviation of intercept is found to be 0.2360 and LOD value is calculated as 0.2536 μM. LOD value gives the concentration level up to which sensing of the analyte can be done with 95% accuracy. The

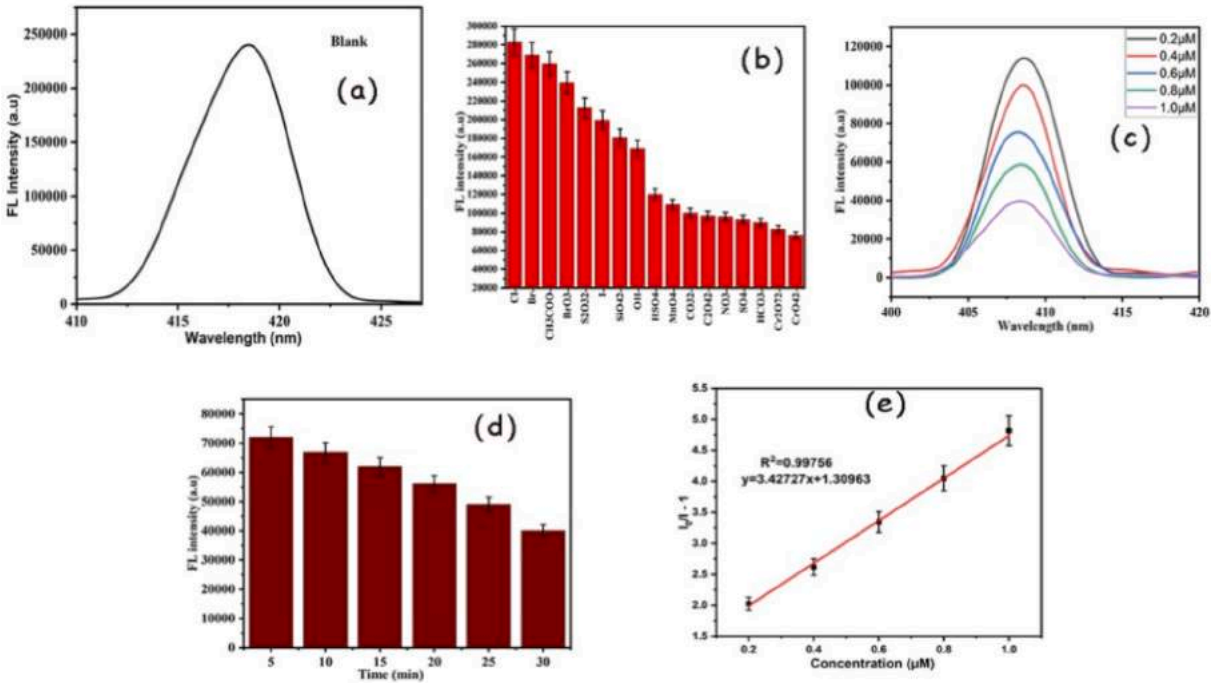

Fig. 6. (a).Fluorescence intensity of CP in water(b) Variation of fluorescence intensity of CP in presence of different anions (c) Fluorescence spectra of CP recorded after each successive addition of chromate (CrO_4^{2-})/$Cr_2O_7^{2-}$solution (d) The variation of fluorescence emission of CP with respect to time (e) Stern Volmer plot(S-V Plot) obtained after the addition of various concentrations of CrO_4^{2-}/$Cr_2O_7^{2-}$.

obtained LOD value when compared with the other sensors reported in the literature, further suggests that the synthesized CP can act as a better candidate for future sensing applications.

3.3.1. *Mechanism of binding Sr[(C4H4O5)(H2O)3]n·nH2O*

Plausible mechanisms for the quenching behavior of CP towards the presence of Cu^{2+} were also suggested. There exist different mechanisms for sensing of Cu^{2+} ions. One among them is the replacement of Sr^{2+} ions of CP by Cu^{2+} ions [42]. The ionic radii of Sr^{2+} and Cu^{2+}ions are 132 pm and 87 pm respectively [43]. Due to the small size of Cu^{2+} ions, it is unable to fit properly on the lattice site of Sr^{2+}. These rules out the possibility of replacement of Sr^{2+} by Cu^{2+} ions. Second type of mechanism suggested in literature is the occlusion of Cu^{2+} ions within the pores present in the lattice structure of the resultant polymer. The current work discussed the synthesis of one dimensional coordination polymer formed from oxydiacetic acid and Sr^{2+} and lacks the presence of open channels or pores in its lattice structure. The same reason rules out the possibility of occlusion of Cu^{2+} ions within the lattice structure. The third plausible and suggested mechanism is due to the electron transfer occurred from the ligand oxydiacetic acid to the Cu^{2+} ions [44]. Copper(II) being a paramagnetic with partially filled d orbital inhibit the electron transfer taking place between the LLCT, thus resulting in the quenching of fluorescence [45] which has to be further confirmed by experimental methods. From the crystal structure it is also clear that there exist uncoordinated oxygen atoms in the lattice structure of the synthesized crystal. These donor oxygen atoms can transfer the electrons to Cu^{2+} ions and getting bonded to each other.

3.4. *Selective sensing of anions by Sr[(C4H4O5)(H2O)3]n·nH2O*

In a typical sensing experiment, equimolar concentrations of 14 salt solutions of univalent and divalent anions such as Cl^-, Br^-, CH_3COO^-, BrO_3^-, $S_2O_3^{2-}$, I^-, SiO_4^{2-}, OH^-, HSO_4^-, MnO_4^-, CO_3^{2-}, $C_2O_4^{2-}$, NO_3^-, SO_4^{2-}, HCO_3^-, $Cr_2O_7^{2-}$ and CrO_4^{2-} were prepared. CP is dispersed in 5 μM concentrated solutions of all these ions separately and the variation in the FL intensity is noted. The results obtained are shown in Fig. 6**(b)**. On analyzing the results, we could observe that in the presence of Cl^-, Br^- and CH_3COO^-, the fluorescence intensity of CP is increased. The CrO_4^{2-} is predominant in alkaline medium where as $Cr_2O_7^{2-}$exists in acidic medium [46]. Both CrO_4^{2-}/$Cr_2O_7^{2-}$ oxyanions are present at equilibrium state at a neutral pH. During all the sensing experiments performed, the pH value of analyte solution was found to be 7. Thus the results suggest the existence of CrO_4^{2-}/$Cr_2O_7^{2-}$ions at equilibrium during all the fluorescence measurements.

The results suggest a "turn-off" mechanism of the CP towards the sensing as well as quantification of anions such as BrO_3^-, $S_2O_3^{2-}$, I^-, SiO_4^{2-}, OH^-, HSO_4^-, MnO_4^-, CO_3^{2-}, $C_2O_4^{2-}$, NO_3^-, SO_4^{2-}, HCO_3^-, $Cr_2O_7^{2-}$ and CrO_4^{2-}. Out of all these anions, CP shows highest turn off fluorescence in presence of micromolar amounts of CrO_4^{2-}/$Cr_2O_7^{2-}$ ions. The efficiency towards the detection of anions such as Cl^-, Br^- and CH_3COO^- were calculated and obtained as 16.60%, 10.67% and 6.8% respectively. The quenching efficiency for the other anions was calculated from Stern-Volmer equation. The quenching efficiency of CP towards the presence of BrO_3^-, $S_2O_3^{2-}$, I^-, SiO_4^{2-}, OH^-, HSO_4^-, MnO_4^-, CO_3^{2-}, $C_2O_4^{2-}$, NO_3^-, SO_4^{2-}, HCO_3^-, $Cr_2O_7^{2-}$ and CrO_4^{2-} are 12.61%, 18.11%, 25.31%, 30.39%, 50.72%, 54.96%, 58.77%, 60.04%, 60.33%, 61.73%, 63%, 65.97%, 68.51% respectively. Thus, selectivity experiments showed that Cr(VI) oxyanions will quench the fluorescence of CP to a greater extend. Sensing ability of CP towards the presence of chromate/dichromate ion was further analysed by means of varying concentration of chromate/dichromate ions from 0.2 μM to 1 μM. The results obtained are shown in Fig. 6**(c)**. The spectra shows that the fluorescence intensity of CP decreases gradually on the successive addition of a mixture of chromate/dichromate ions at equilibrium from 0.2 μM to 1 μM. Quenching efficiency for each incremental addition of chromate/dichromate ions to the CP is calculated by means of Stern-Volmer equation. The calculated values for quenching efficiency were 52.85%, 58.75%, 68.96%, 75.95% and 83.57% for concentrations 0.2 μM, 0.4 μM, 0.6 μM, 0.8 μM and 1 μM respectively. The fluorescence intensity of CP is almost diminished on addition with 1 μM solution of mixture of chromate/dichromate ion solution. The variation in the quenching of fluorescence with increment of time was also studied and shown in Fig. 6**(d)**. Sensing experiments were repeated from a time of 5

Table 2
Comparison of various CP/MOF sensors for the detection of Cr(VI) ions in aqueous solution.

Sensor	Analyte	Ksv (M^{-1})	LOD(M)	Reference
$[Zn(btz)]_n$	CrO_4^{2-}	3.19×10^3	1.0×10^{-5}	[47]
	$Cr_2O_7^{2-}$	4.23×10^3	2.0×10^{-6}	
$[Eu_2(tpbpc)_4{\cdot}CO_3{\cdot}H_2O]{\cdot}$ DMF·solvent	CrO_4^{2-}	4.85×10^3	3.3×10^{-7}	[48]
	$Cr_2O_7^{2-}$	1.04×10^4	1.07×10^{-6}	
$[Zr_6O_4(OH)_8(H_2O)_4(sbtc)_2]$ (BUT-28)	$Cr_2O_7^{2-}$	1.02×10^5	1.2×10^{-7}	[49]
$\{[Zn_2(TPOM)(NH_2\text{-}BDC)_2]{\cdot}4H_2O\}_n$	CrO_4^{2-}	4.45×10^3	4.8×10^{-6}	[50]
	$Cr_2O_7^{2-}$	7.59×10^3	3.9×10^{-6}	
$\{[Cd(4\text{-}BMPD)(BPDC)]{\cdot}2H_2O\}_n$	$Cr_2O_7^{2-}$	6.4×10^3	$3.76 \times 10^{-}$	[51]
$\{[Cd(4\text{-}BMPD)(SDBA)(H_2O)]{\cdot}0{\cdot}5H_2O\}_n$	$Cr_2O_7^{2-}$	4.97×10^3	4.86×10^{-5}	
5,3,4-MOF-Tb	$Cr_2O_7^{2-}$	1.37×10^4	1.4×10^{-4}	[52]
$[Tb(Hbptc)(H_2O)4]{\cdot}H_2O$	CrO_4^{2-}	1.04×10^5	2.88×10^{-7}	[53]
	$Cr_2O_7^{2-}$	1.27×10^4	2.3×10^{-6}	
$[Cu_2(bpp)_2Cl]{\cdot}Hapta{\cdot}H_2O$	CrO_4^{2-}	1.97×10^3	1.52×10^{-5}	[54]
	$Cr_2O_7^{2-}$	5.56×10^3	5.36×10^{-6}	
$[Y(BTC)(H_2O)6]_n$:0.1Eu	CrO_4^{2-}	1.18×10^3	3.0×10^{-8}	[55]
	$Cr_2O_7^{2}$	4.52×10^3	4.0×10^{-8}	
$[Zn(IPA)(L)]_n$	CrO_4^{2-}	1.00×10^3	1.83×10^{-5}	
	$Cr_2O_7^{2-}$	1.37×10^3	1.20×10^{-5}	[56]
$[Zn(ttz)H_2O]_n$	CrO_4^{2-}	2.35×10^3	2.0×10^{-5}	
	$Cr_2O_7^{2-}$	2.19×10^3	2.0×10^{-6}	
$[Cd(IPA)(L)]_n$	CrO_4^{2-}	1.30×10^3	2.52×10^{-6}	
	$Cr_2O_7^{2-}$	2.91×10^3	2.26×10^{-6}	
Ln^{3+}@MIL-121	$Cr_2O_7^{2-}$	4.34×10^3	5.4×10^{-8}	[42]
$Sr[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$	CrO_4^{2-}	5.089×10^6	1.06×10^{-7}	This work

min to 30 min by adopting the same methodology. The fluorescence emission of CP decreases gradually as the time moves on. At 30 min, fluorescence emission of CP is almost diminished with a quenching efficiency of 83.53%. Stern-Volmer plot (S-V Plot) is drawn between relative intensity ($I_0/I - 1$) and concentration of Cr(VI) oxyanions (CrO_4^{2-}/$Cr_2O_7^{2-}$) added and is shown in Fig. 6**(e)**. The same graph gives a good linear relationship between relative intensity and concentration of chromate/dichromate added with R^2 value of 0.99756. Higher R^2 value obtained from the regression analysis further suggest the higher accuracy of the experiment. The LOD value for the sensing of mixture of chromate/dichromate was calculated as 0.1060 μM.

The fluorescent probes for the sensing of Cr(VI) reported in the literature is given in Table 2. The table shows various synthesized crystals, their Ksv and LOD values reported so far in literature for the effective sensing of chromate and dichromate ions in aqueous media. The LOD and Ksv values on comparison with the other reported CP/MOF sensors for Cr(VI) anions is in good agreement or even better than the reported values as given in the Table 2. Limit of detection values suggest the least permissible limit to which the detection of chromate and

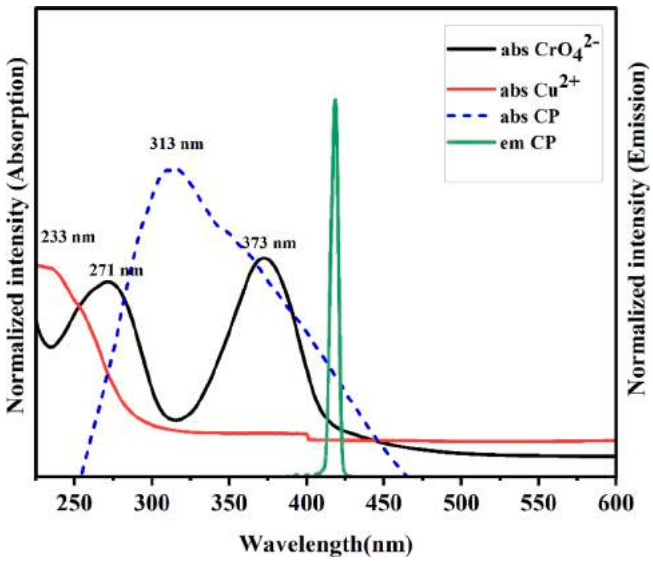

Fig. 7. UV–Visible spectra of CrO_4^{2-}, Cu^{2+}, CP and emission spectra of CP.

dichromate can be done to a maximum of 95% accuracy is in the order of 10^{-7} M. The Ksv value of $5.089 \times 10^6 M^{-1}$ points out the possibility of strontium based coordination polymer can be used as an effective sensor for the detection of Cr(VI) ions. LOD value of $1.06 \times 10^{-7}$is comparable with the reported LOD value of $[Eu_2(tpbpc)_4{\cdot}CO_3{\cdot}H_2O]{\cdot}$DMF·solvent. Even though Sr is an alkaline earth metal, it resemble the co-ordination complex of Eu in its sensing nature towards the detection of metal analytes. The study further suggests the fabrication of chemosensors based on Sr complexes by replacing the complexes of expensive Europium.

3.4.1. *Plausible binding interactions of Cr(VI) oxyanions*

There exist three different plausible mechanisms by which we can explain the sensing of $CrO_4^{2-}/Cr_2O_7^{2-}$by CP. First mechanism suggest that the sensing of $CrO_4^{2-}/Cr_2O_7^{2-}$ may be due to the ground state complexation of CP with the Cr(VI) present in aqueous media due to its hydrophilic nature. The SXRD structure reveals the hydrophilic nature of the prepared analyte which is in good agreement with the suggested mechanism. The second possible mechanism is based on the UV absorption values. The UV absorption value of CrO_4^{2-} and $Cr_2O_7^{2-}$ reported in the literature are coming in the range 230 nm to 500 nm [57]. From the current work, UV absorption value of CP ranges between 262 nm and 685 nm. Data obtained clearly states that the graph of UV absorption spectra of CP overlap with that of absorption spectrum of CrO_4^{2-} and $Cr_2O_7^{2-}$. The competitive absorption of UV will further result in transfer of excitation energy from $Sr[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ to $CrO_4^{2-}/Cr_2O_7^{2-}$ The third mechanism suggests the possibility of weaker non covalent interaction force existing between the hydrophilic O—H groups in the CP with $CrO_4^{2-}/Cr_2O_7^{2-}$ions that may lead to the decrease in electron density in ligand and there by reduces the possibility of electronic transition in ligand.

3.4.2. *Evidences for the fluorescence quenching mechanisms by UV visible spectroscopic studies*

Fluorescence properties of the CP is centered on its versatile architecture and stacking interactions. The entrapped guest molecules are also responsible for the increase or decrease of fluorescence of the prepared analyte. To further confirm the suggested plausible fluorescence quenching mechanism of CP for the sensing of Cu^{2+} cation and Cr(VI) anions, UV–visible spectral studies were carried out. The absorption spectra of K_2CrO_4 and copper chloride were recorded and compared with the absorption and emission spectra of the coordination polymer (CP). The spectra are shown in Fig. 7. From the figure it is evident that

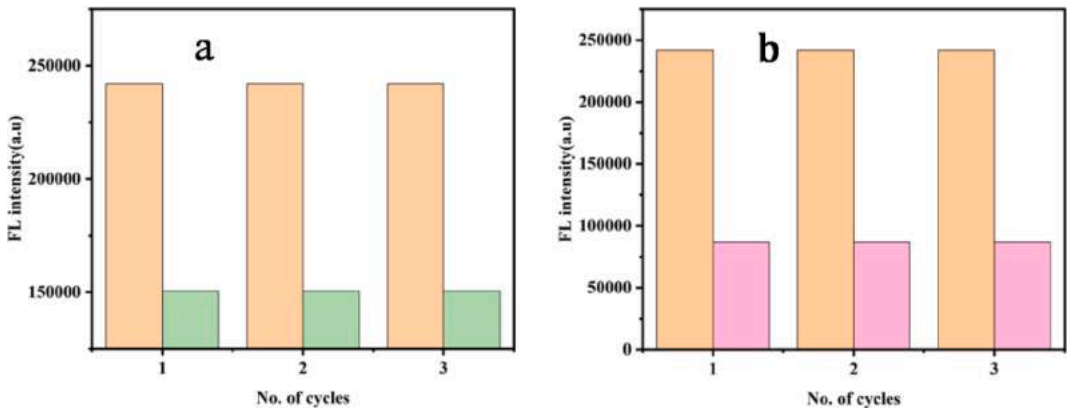

Fig. 8. Reusability test for the sensing of a) Cu^{2+} and b) Cr(VI) oxyanion.

there is a spectral overlap of absorption spectra of both the analytes Cu^{2+} and Cr (VI) ions with the synthesized CP which further suggests a competition of the absorption of exciting light between the analyte and the CP, which can further lead to energy degradation, there by resulting in fluorescence quenching.

The light energy used to excite the CP is completely interfered by the analyte leading to fluorescence quenching. The wavelength of excitation (313 nm) used to trigger the fluorescence of CP is largely overlapped by the UV visible absorption wavelength of the analyte. This large overlap of wavelength between absorption bands of analytes and excitation bands of CP contributes significantly for consuming the energy which is originally deployed to excite for fluorescence emission which can further result in fluorescence quenching [58]. There is another apparent overlap between absorption band of CrO_4^{2-} and emission band of CP. Resonance energy from CP therefore would be more likely to be transferred to both the analytes Cr(VI) and Cu^{2+} ions which can further result in fluorescence quenching of CP.

3.5. Reusability of CP for sensing Cu^{2+} and Cr(VI) oxyanion

The reusability of the coordination polymer for the sensing towards $Cu^{2+}$and Cr(VI) oxyanions was studied and shown in Fig. 8.There is no appreciable change in the fluorescent intensity of CP after three cyles of reusability experiments. This indicates that the CP can act as a smart fluorescent probe for the sensing of both Cu^{2+} and Cr(VI) ions in aqueous medium.

4. Conclusions

Good quality crystals of oxydiacetic acid based strontium Sr $[(C_4H_4O_5)(H_2O)_3]_n{\cdot}nH_2O$ were synthesized through gel diffusion technique at room temperature and its structure is predicted by single crystal X-ray diffraction. The fluorescence spectrum shows a strong and intense emission at 371 nm upon excitation of 313 nm. The probing and selective sensing of Cu^{2+}ions and $CrO_4^{2-}/Cr_2O_7^{2-}$ by grown crystals was examined by fluorescence spectroscopy. Detailed studies showed that the fluorescence intensity of the crystal decreases with increase in the concentration of both Cu^{2+}ions and $CrO_4^{2-}/Cr_2O_7^{2-}$ions and follows a turn off mechanism for the detection of the above mentioned ions. Ksv and LOD values calculated for the selective sensing of Cu^{2+}ions are 3.17 $\times$ 10^6M^{-1}, 2.536 $\times$ $10^{-7}\mu M$ respectively and that of $CrO_4^{2-}/Cr_2O_7^{2-}$ ions are 5.089 $\times$ 10^6M^{-1} and 1.06 $\times$ $10^{-7}M$ respectively. The results shows that the synthesized strontium based coordination polymer can act as a promising candidate for the ultrasensitive detection of inorganic moieties present in trace quantities in aqueous media. A plausible mechanism was suggested for the fluorescence quenching of the coordination polymer towards Cr(VI) and Cu(II) ions. The suggested mechanism was confirmed with the help of absorption spectra of CrO_4^{2-}, Cu^{2+}, CP and emission spectra of CP. The reusability of the analyte in presence of Cu (II) and Cr(VI) ions were studied and found that the material retained its sensing capacity even after the third cycle of sensing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2022.115974.

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Article

ZnO@MOF-5 as a Fluorescence "Turn-Off" Sensor for Ultrasensitive Detection as well as Probing of Copper(II) Ions

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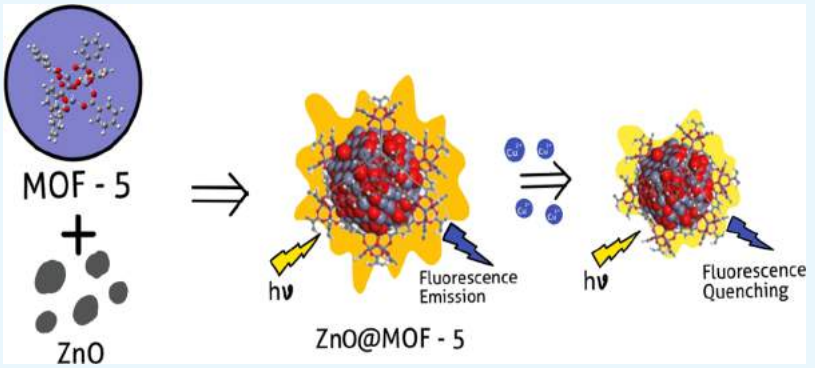

ABSTRACT: Recently, the synthesis, characterization, and structural evaluation of metal−organic framework (MOF) nanocomposites gain more attention due to the versatility in their applications. In the present work, the fluorescent active ZnO@MOF-5 composite was synthesized by encapsulating ZnO nanoparticles into the zinc terephthalate metal−organic framework (MOF-5). ZnO nanoparticles were prepared by a green method using the leaf extract of *Annona muricata*. Incorporation of ZnO nanoparticles onto the framework structure (ZnO@MOF-5) was done by a solvothermal method. The new composite material was characterized by Fourier transform infrared spectroscopy, Powder X-ray diffraction, Ultraviolet−visible spectroscopy, Transmission Electron Microscopy, X-ray photoelectron spectroscopy, Brunauer−Emmett−Teller analysis, Dynamic light scattering, Thermogravimetry-Differential Thermal analysis, and Photoluminescence spectroscopy. The material displayed blue fluorescence with a peak at 402 nm upon excitation at 282.46 nm. ZnO@MOF-5 showed a good fluorescence sensing efficiency toward the detection as well as probing of Cu(II) ions in aqueous solution. Sensing experiments performed revealed that as the concentration of copper ions in the solution increases, the quenching efficiency of the composite also increases. A quenching efficiency of 96.20% was achieved on reaching a concentration of 5 μM. The limit of detection for the sensing of Cu^{2+} ions was calculated to be 0.185 μM.

INTRODUCTION

Metal−organic frameworks are the gateway to the era of molecular engineering and find impeccable significance in different fields like catalysis,[1−3] gas storage,[4] drug delivery systems,[5] gas sensing,[6] energy storage,[7] etc. The tunable porosity and hybrid structure formed by the linkage of organic linkers and inorganic metal nodes make it more feasible for a versatile range of applications. MOFs are promising three-dimensional coordination polymers formed by the linkage of inorganic metal ions joined with organic multitopic ligands. The presence of both acidic as well as basic groups[8] in the framework structures makes it a versatile architecture. Through postsynthetic methodologies, the porosity of MOFs can be tuned,[9] and this makes these coordination polymers a better option than others. The better sensing capacity towards the inorganic metal moieties can be enhanced by tuning the porosity of the frameworks.[9] By preserving structural integrity as well as robustness of metal−organic frameworks, the physicochemical properties can be enhanced by the incorporation of nanoparticles,[10] polymers,[11] perovskites,[11] etc. The nanocomposites find a unique way to tune the porosity to our desired extent for applications such as drug delivery as well as adsorption or encapsulation of microlevel contaminants. Quantification of trace analytes is nevertheless a tedious process due to the lack of sensitivity of probes to a smaller

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extent. Preparation of MOF nanocomposites for environmental remediation purposes is an ongoing research area that needs much attention nowadays. The presence of inbuilt luminescent active sites like organic linkers as well as inorganic metal units makes the MOFs a better luminescent active material among others. The pores with an identical volume further extend the luminescence life by incorporating guest moieties within them. Integration of different moieties like nanoquantum dots, dyes, lanthanides, perovskites, etc. to the metal−organic framework structure will build photoactive sensors for probing chemicals at the nanolevel. Photoactive metallic MOF clusters will act as a better platform for the target-oriented sensing analysis of antibiotics,[12] gases,[13] inorganic metals,[14] pesticides,[15] and chemical explosives.[16] MOFs have inherent luminescence centers, and their luminescence mechanisms[17] include the photoinduced electron transfer (PET) process,[18] ligand-to-metal charge transfer (LMCT), and metal-to-ligand charge transfer (MLCT).

The sensing as well as detection of various inorganic metal ions such as Fe^{3+} ions[19] and Hg^{2+} ions[20] is an emerging area of research. Moreover, sensing of biological molecules such as hemoglobin[21] and lysozymes[22] has dragged more attention since ancient times. The inorganic metal Cu^{2+} ion is one of the abundant species in the human body. The intake of 0.8−0.9 mg of copper per day is needed for the essential growth and development of human beings.[23] However, a higher intake of copper may lead to kidney failure, liver damage, or even death of the person. The same situation gives enormous significance to the development of materials and methods for sensing copper ions. Nowadays, a lot of studies are ongoing for the synthesis of ultrasensitive fluorescent probes for the sensing as well as detection of inorganic metal ions such as copper ions. However, the development of semiconducting nanoparticles@MOF hybrid-based fluorescent ion sensors is an unexplored area of research. Traditional methods adopted for the screening as well as detection of metal ions are Inductively Coupled Plasma Mass Spectroscopy (ICPMS) and Atomic or molecular Absorption Spectroscopy (AAS).[24] These methods are laboratory-based methods and are really helpful for subnanomolar-level analysis. While for analysis of a large number of water samples and real-time monitoring, the development of cheap and cost-effective systems and methods is needed. Thus, importance arises for the synthesis of fluorescent active materials such as MOF−nano hybrid materials that can selectively detect the presence of various inorganic metal ions present in smaller quantities through fluorescence spectroscopy.

Here, we present the synthesis and characterization of a metal−organic framework nanocomposite called ZnO@MOF-5 through a new synthetic strategy using a solvothermal method, and the study further investigates its effect as a better luminescent sensor for sensing of inorganic pollutants such as copper ions in drinking water. PL measurements show that these ZnO-based luminescent MOFs show a unique mechanism for the entrapment of copper ions from water even at a micromolar concentration.

EXPERIMENTAL SECTION

Materials. All the chemicals used for the synthesis were of AR grade. Zinc nitrate hexahydrate (Emplura, Merck Life Science Pvt. Ltd.), terephthalic acid (TCI Chemicals Pvt. Ltd., India), *N*,*N*-dimethyl formamide (Sisco Research Laboratories Pvt. Ltd., Mumbai, India), sodium hydroxide (Central Drug House Pvt. Ltd., New Delhi) were used for the synthesis.

Instruments. Fourier transform measurements were taken by using a Fourier transform infrared spectrophotometer (Thermo Scientific, Nicolet iS50 at CLIF, Kariavattom). Powder X-ray diffraction measurements were taken using an X-ray diffractometer (DST-SAIF Cochin). TEM images were recorded by using a JEOL/JEM 2100 (DST-SAIF Cochin). For understanding the effect of temperature dependence of the synthesized compounds, thermal analysis was carried out by using a thermogravimetric instrument called a simultaneous thermal analyzer (TGA/DTA/DSC) (PerkinElmer, STA8000, CLIF, Kariavattom). UV−visible absorption measurements were taken by a UV−VIS−NIR spectrophotometer (Agilent Technologies, Cary 5000, CLIF, Kariavattom). Photoluminescence spectra were taken by a Fluorolog TCSPC from Horiba Scientific (Dept. of Chemistry, Govt. College for Women, Trivandrum). X-ray photoelectron spectroscopy (XPS) was carried out by an X-ray photoelectron spectrometer (Thermo Scientific, ESCALAB Xi+, CLIF, Kariavattom). Surface area and porosity measurements were done by a BET surface area analyzer (Quantachrome Instruments, Nova Touch lx4 Model, CLIF, Kariavattom). Particle size distribution and zeta potential measurements were done using a Horiba nanoparticle analyzer SZ-100 (Department of Chemistry, University of Kerala, Kariavattom).

Methods. *Synthesis of Zinc Oxide Nanoparticles.* Zinc oxide nanoparticles were synthesized by a green method[25] with slight modifications. $Zn(NO_3)_2{\cdot}6H_2O$ (10 mL, 5 M) was homogeneously mixed with 40 mL of leaf extract of *Annona muricata* for 30 min. The precipitation of zinc hydroxide was done by the gentle addition of 5 M NaOH solution until the pH was 12. The resulting crude precipitate was filtered and washed with distilled water. After calcination at 550 °C for 3 h, the resulting powder of ZnO was collected.

Preparation of MOF-5. Equimolar concentrations (1.5 M) of zinc nitrate hexahydrate and terephthalic acid were dissolved separately in 20 mL of dimethyl formamide and mixed well. The transparent solutions thus obtained were taken in an autoclave and heated at 140 °C for 24 h. The precipitate thus obtained was washed with DMF two to five times, filtered, and dried.

Preparation of ZnO@MOF-5. Synthesized pure ZnO nanoparticles and MOF-5 were mixed in a 1:4 ratio and were dispersed in 40 mL of a dimethyl formamide solvent. The reaction mixture was stirred continuously for 30 min. The whole reaction mixture was taken inside an autoclave, sealed, and heated at 150 °C for 3 h. The remaining mixtures were collected, filtered, and washed with DMF. The resultant was dried under room temperature.

Flourimetric Estimation of Cu^{2+} Ions from $CuCl_2{\cdot}2H_2O$. A solution of ZnO@MOF-5 was prepared by dispersing 0.01 mg of the composite in 10 mL of water. Different micromolar concentrations of cupric chloride solutions were prepared separately in distilled water. A mixture of both solutions was vortexed for 20 min and kept undisturbed. The supernatant solution was decanted, and 3 mL of the same was taken in a cuvette of a fluorimeter. Upon excitation at a wavelength of 282.46 nm, the fluorescence spectrum was recorded. The same procedure was repeated for solutions of concentrations ranging from 0.1 to 5 μM, and FL spectra were recorded. The scheme for the fluorescence quenching of the prepared analyte by copper(II) ions is presented in Scheme 1.

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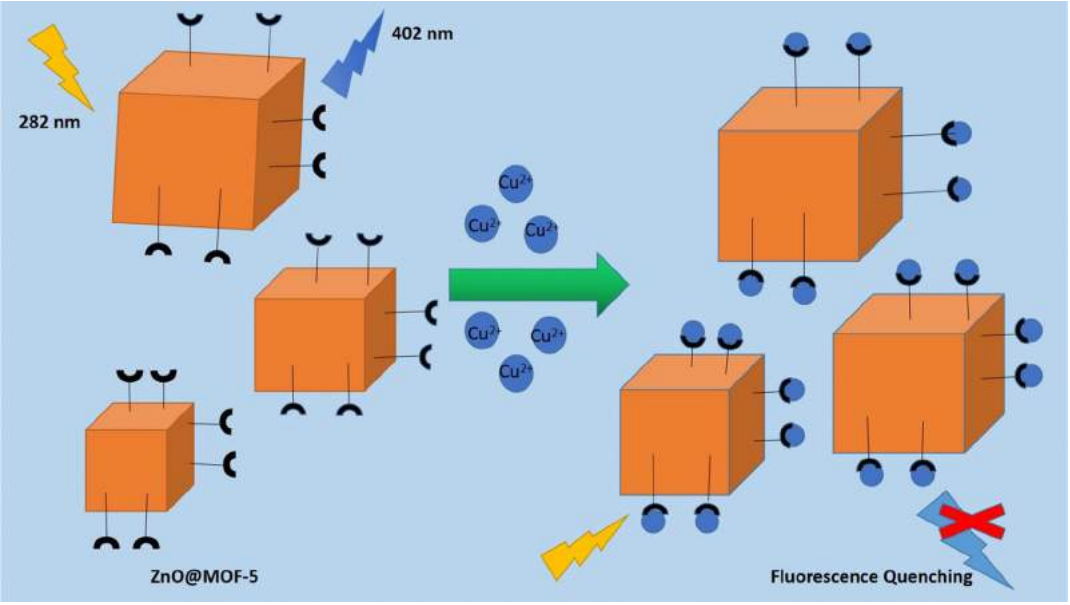
Scheme 1. Diagrammatic Representation for the Fluorescence Quenching of ZnO@MOF-5 by Copper Ions



RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy. FTIR spectra of pure MOF-5 as well as the composite ZnO@MOF-5 were characterized within the wavenumber range of 400−4000 cm^{-1} as shown in Figure 1. The sharp absorption

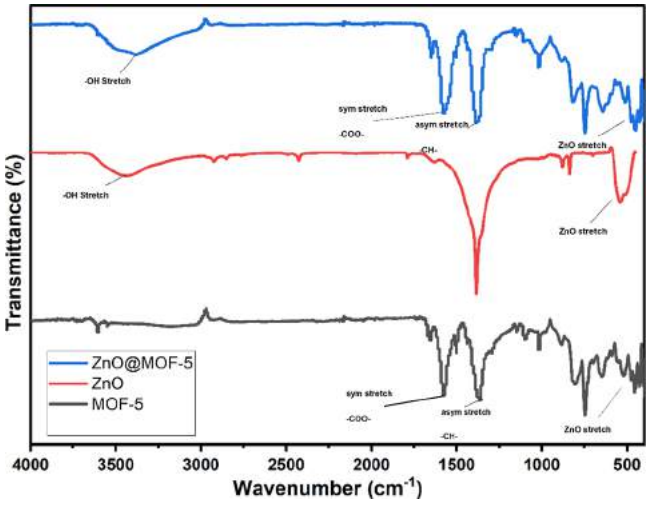


Figure 1. Infrared spectra of MOF-5, ZnO, and ZnO@MOF-5.

band at 1573 cm^{-1} corresponds to the characteristic region of symmetric vibrations of the terephthalic group, which is less than that of the free carboxylic group present on the terephthalic acid group, which indicates the coordination with metal nodes.[2] The absorption bands found between the wavenumbers of 600 and 1200 cm^{-1} are generally ascribed to the fingerprint region of terephthalate-based compounds.

The peaks in the range of 1000−1200 cm^{-1} correspond to the in-plane bending vibration modes of the C−H bond,[10] while the peaks in the range of 600−1000 cm^{-1} correspond to the out-of-plane bending modes[26,27] of C−H bonds, which are present in the benzene (C_6H_6) ring of the 1,4-BDC linker. The absorption peaks found in the range of 1335−1420 cm^{-1} correspond to asymmetric stretching vibrations of CH groups present in the organic linkers. The range of 1680−1715 cm^{-1} shows no characteristic peaks in the spectrum and corresponds to the complete deprotonation of the 1,4-BDC linker. It is in good agreement with that of the work done by Song et al.[28] Multiple peaks below 550 are attributed to the presence of the Zn−O bond of zinc oxide nanoparticles. The broader band at 3376 cm^{-1} is typically assigned to the O−H vibrations of the adsorbed atmospheric moisture. Effective incorporation of ZnO to the MOF was first suggested by the slight shift in the IR stretching frequencies in the composite compared with the pure MOF.

Powder X-ray Diffraction. The crystallinity and phase purity of the synthesized compounds were assessed by means of powder X-ray diffraction and are shown in Figure 2. The X-ray diffractogram reveals an ordered crystalline structure.

The PXRD pattern of zincite is in good agreement with the JCPDS card entry number 96-900-8878 with the space group *P*63*mc*. The XRD pattern of synthesized MOF-5 matches with the JCPDS card entry number 96-432-6738. The Rietveld refined structure shows that the synthesized ZnO sample has unit cell lattice parameters a = 3.25271 and b = 5.21063. The final reduced χ^2 value of 9.8, which is less than 10, suggests good agreement of PXRD patterns with the Crystallography Open Database (COD) file. Refinement also suggests that the synthesized ZnO is in a single phase called zincite.

The presence of the crystal planes (100), (002), (101), (012), (110), (013), (112), (201), (004), and (202) further confirms the formation of ZnO crystal planes corresponding to 2θ values of 31.95, 34.62, 36.45, 47.60, 56.74, 63.11, 68.23, 69.31, 72.7, and 77.04°, respectively. The 2θ values of 6.21, 8.92, 15.76, 17.79, and 18.59° obtained for MOF-5 correspond to the crystal plane indices (200), (220), (420), (333), and (440), respectively. It confirms the formation of the lattice of MOF-5.[29] An additional peak at the peak position of 7.76° may be due to distortions that occurred in the lattice due to environmental exposure of the sample.[30] The ligand-to-metal ratio and the addition of ZnO nanoparticles will greatly influence the XRD patterns of analytes. ZnO@MOF-5 shows slight variations in the peak positions as compared to the

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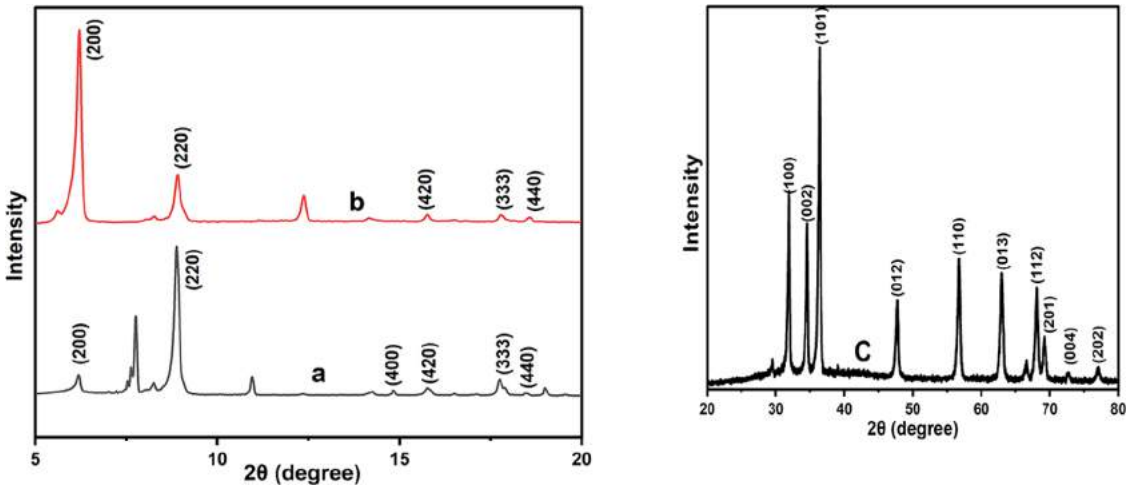

Figure 2. PXRD patterns of (a) MOF-5, (b) ZnO@MOF-5, and (c) ZnO nanoparticles.

MOF-5, which confirms the formation of new lattice planes within the composite. Almost all the peaks in the XRD patterns of ZnO were missing in the composite, which reveals the absence of distinct ZnO and MOF-5 particles. This also suggests the homogeneous distribution of ZnO nanoparticles either in the crystal surface or in the pore channels. The crystallite size of particles was deduced from the Debye–Scherrer equation $D = 0.9\lambda/\beta \cos \theta$ where λ is the wavelength of the X-ray used for the analysis, D is the crystalline size, β is the full width at half-maximum of each peak for calculation, and θ is the Bragg's angle in radians. Measurements done are shown in Table 1.

From Table 1, the crystallite size of ZnO@MOF-5 is 32.23 nm. It is evident that encapsulation of ZnO nanoparticles of 15.22 nm crystallite size to MOF-5 decreases the particle size of MOF-5 from 48.66 to 32.23 nm.

Table 1. Crystallite Size Distribution of Analytes

sample name	peak position (2θ)	FWHM	crystallite size (nm)	average crystallite size (nm)
	7.55525	4.08073	1.942552	
	7.76313	0.07759	102.1532	
MOF-5	8.88005	0.16774	47.2186	48.66
	10.95507	0.09722	81.34142	
	15.78203	0.27073	29.0661	
	17.77364	0.25929	30.27082	
	31.8861	0.34626	22.06063	
	34.5516	3.06×10^{-1}	24.7646	
	36.37493	0.36214	20.8411	
ZnO	47.67027	0.47209	15.39269	15.22
	31.8861	10.51988	0.726122	
	56.7176	0.46212	15.12788	
	62.98221	0.49731	13.62181	
	68.07277	0.52685	12.49557	
	69.19836	0.54498	11.99915	
	6.1903	0.18461	42.97005	
	8.90682	0.22538	35.142	
ZnO@MOF-5	12.35936	0.15591	50.65824	32.23
	18.81938	49.68076	0.157755	

UV–Visible Spectroscopy. UV–visible spectra and Tauc plots of the synthesized compounds are shown in Figure 3.

The MOF-5 and ZnO@MOF-5 show maximum absorption at wavelengths of 288.69 and 282.46 nm with bandgap values of 3.80 and 3.70 eV, respectively. The maximum absorption at 288.69 nm corresponds to the $\pi-\pi^*$ transition exhibited by the π electrons of 1,4-benzene dicarboxylic acid (BDC) and corresponds to $1A_{1g}$ to $1B_{2u}$ excitations.[31] The blueshift towards 282.46 nm is due to the incorporation of ZnO moieties.

Photoluminescence Spectroscopy. Photoluminescence spectra of samples were also recorded and are shown in Figure 4a. For MOF-5, excitation at 288.69 nm gave an emission at 414 nm, and for ZnO@MOF-5, the emission line was obtained at 402 nm at an excitation wavelength of 282.46 nm. The sharp peak at 414 nm corresponds to the ligand-to-metal charge transfer (LMCT) process.[18] The hypsochromic shift in the wavelength occurs due to the incorporation of ZnO nanoparticles to MOF-5. Excitation of ZnO at 350 nm will give two emission peaks at 380 and 602 nm. The emission at 380 nm corresponds to the green emission, and red emission is observed at 602 nm. A higher number of surface oxygen vacancies may be the reason for a stronger PL band, and these defects make it a unique material to be a better photocatalyst among others. The blue emission value of ZnO is less than that of the corresponding MOF as well as the composite, and it may be due to the higher FL emission of ZnO as compared to the ZnO@MOF-5 and MOF-5.

Dynamic Light Scattering Analysis. DLS analysis gives the hydrodynamic diameter as well as the zeta potential of the synthesized samples, and spectra are shown in Figure 4b–e. Size distribution analysis of MOF-5 and ZnO@MOF-5 shows that the particles are polydispersive in nature. Due to this, a wide range of particles with varying sizes are present in the sample. Mean diameters of the metal–organic framework as well as composites of the same are 773.6 and 1036.9 nm, respectively. The diameters obtained are far larger than the size obtained from XRD as well as TEM analysis. This may be due to the reason that the DLS instrument only detects the larger particles with higher diameters.[32] The increase in the diameter when the MOF changes to the composite may be due to the agglomeration of particles or due to the adhesive nature of solvent molecules of water during analysis. The diameters obtained from the DLS analysis are not at all reliable due to the

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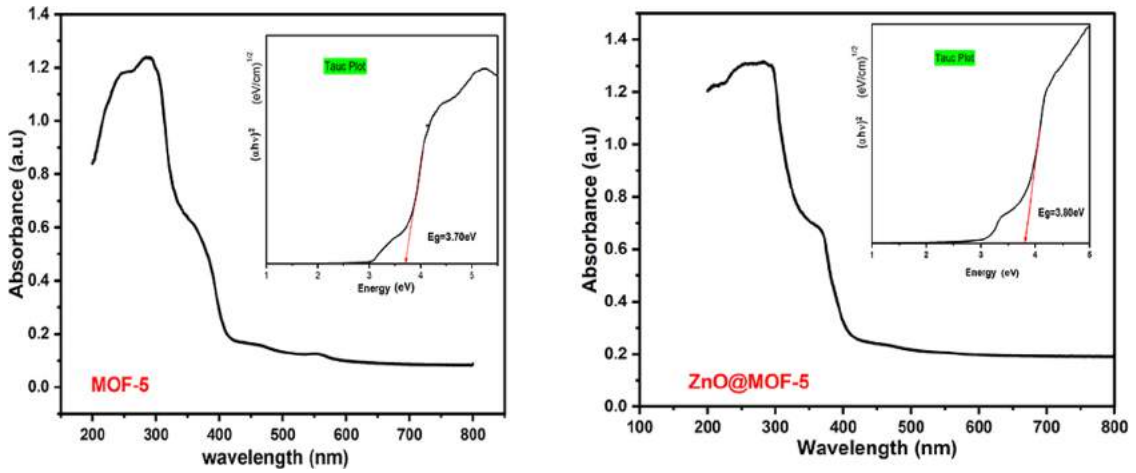

Figure 3. UV−visible spectra and Tauc plots of Zn-MOF-5 and ZnO@MOF-5.

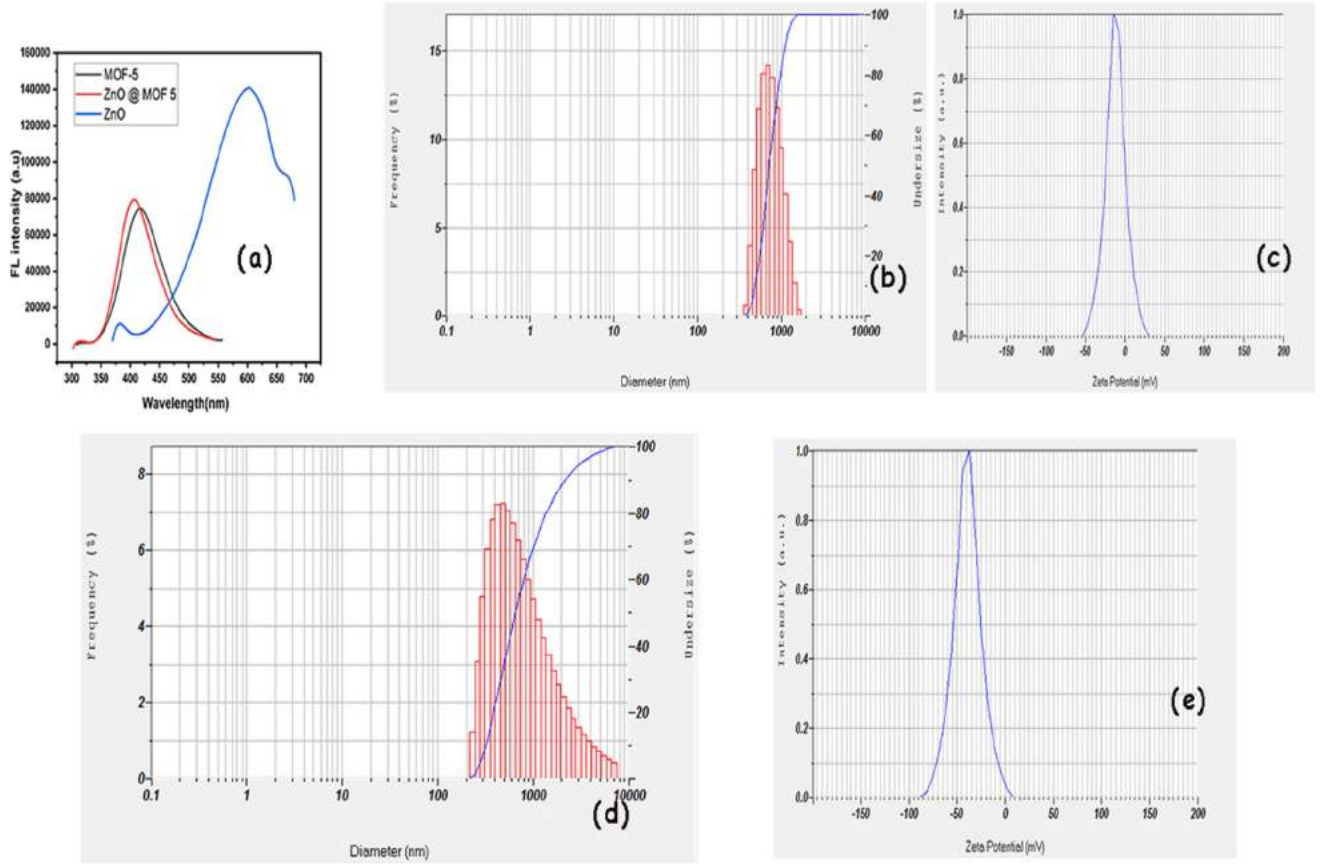

Figure 4. (a) PL spectra of analytes, (b,d) diameter distribution diagrams of MOF-5 and ZnO@MOF-5, and (c,e) variation of the zeta potential of MOF-5 and ZnO@MOF-5.

above-mentioned reasons. The zeta potential variation graphically presented in Figure 4c shows that values for MOF-5 and the nanocomposite are −12.1 and −23 mV with conductivity values of 0.085 and 0.092 ms/cm. A higher negative value of the zeta potential corresponds to deposition of ZnO onto the framework structure. The net negative value of the zeta potential may be due to the net negative charge localized on the MOF surface due to the presence of carboxylic groups on terephthalic acid.

X-ray Photoelectron Spectroscopy. To explain the binding energy distribution among different energy levels, XP spectra are taken, and the survey scan and deconvoluted spectra are shown in Figure 5a−e.

From the XP survey scan, spectral binding energies of different orbitals of zinc, carbon, and oxygen are noted. Intense peaks at binding energy values of 1043.88 and 1020.98 eV correspond to the terms $2p_{1/2}$ and $2p_{3/2}$, respectively[10] (Figure 5c). The sharp peak at 978.39 eV in the XP spectra of MOF-5 corresponds to the presence of free Zn^{2+} ions on the framework topology. The absence of the same peak on the spectra of ZnO@MOF-5 is attributed to the absence of free metal ions on the surface topology that may be utilized for

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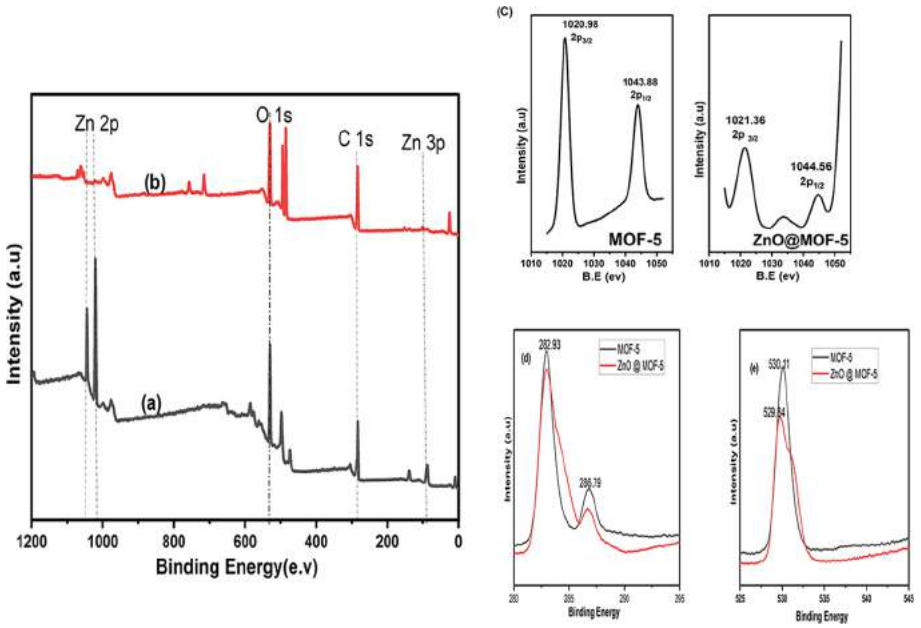

Figure 5. X-ray photoelectron survey spectra of (a) MOF-5 and (b) ZnO@MOF-5; deconvoluted XP spectra of (c) zinc 2p, (d) carbon 1s, and (e) oxygen 1s.

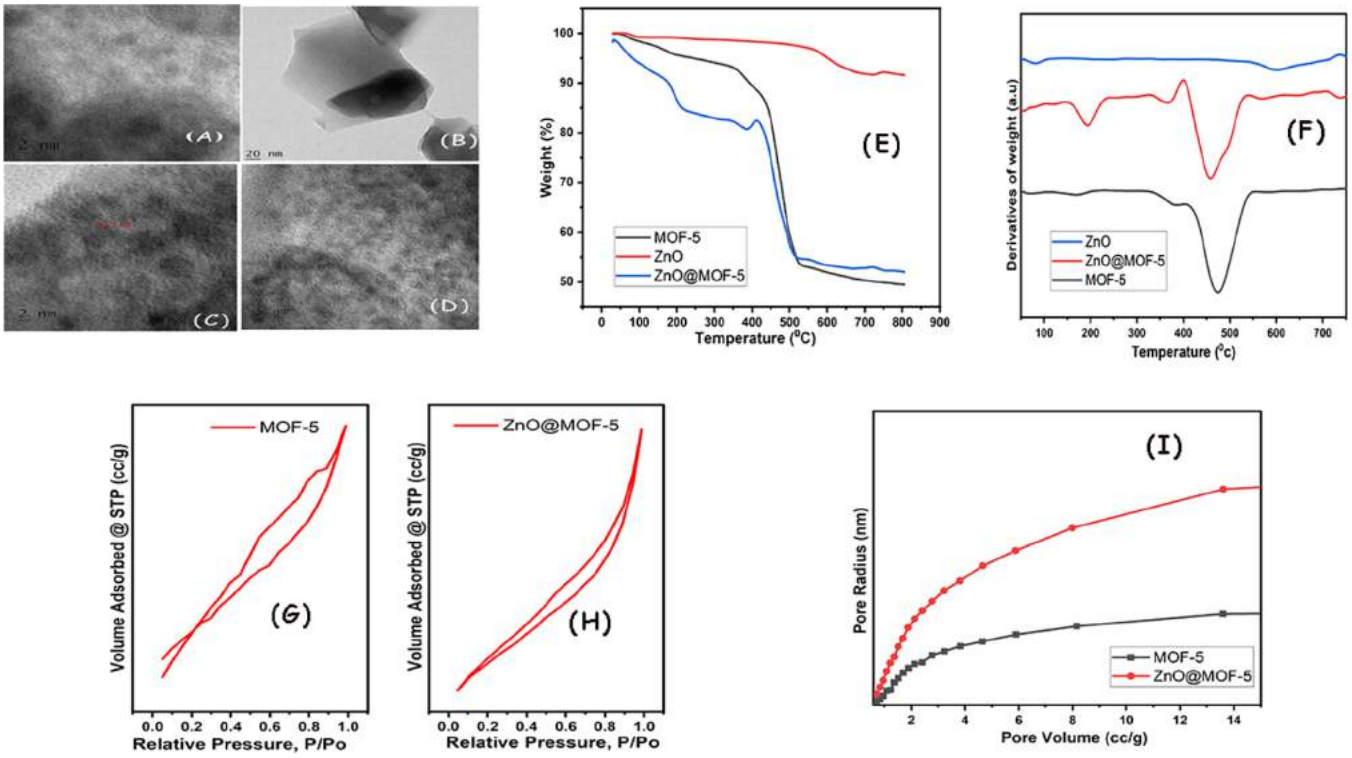

Figure 6. (A,B) FETEM images of MOF-5, (C,D) FETEM images of ZnO@MOF-5, (E) thermograms of synthesized compounds, (F) DTA of analytes, (G,H) BET adsorption isotherms of the MOF and the MOF nanocomposite, and (I) pore radius-to-pore volume distribution of synthesized samples.

bonding with the ZnO particles loaded. The intense peak at a BE value of 285.37 eV corresponds to the presence of 1s orbitals of carbon atoms of the terephthalate framework structure. The deconvoluted XP spectra of zinc show the shifting of binding energy values and a decrease in the intensity of peaks that may be due to the binding interactions of ZnO nanoparticles. The binding energy of O 1s is changed from 530.11 to 529.84 eV when encapsulation of ZnO occurs onto the framework structure, which further confirms the interaction of ZnO. More details of the bonding interactions can only be interpreted through Auger electron spectroscopy, which has to be done later.

Transmission Electron Microscopy. Transmission electron micrographs of the synthesized samples gave topographical as well as microcrystalline analysis of the synthesized samples and are shown in Figure 6A–D. In the micrograph

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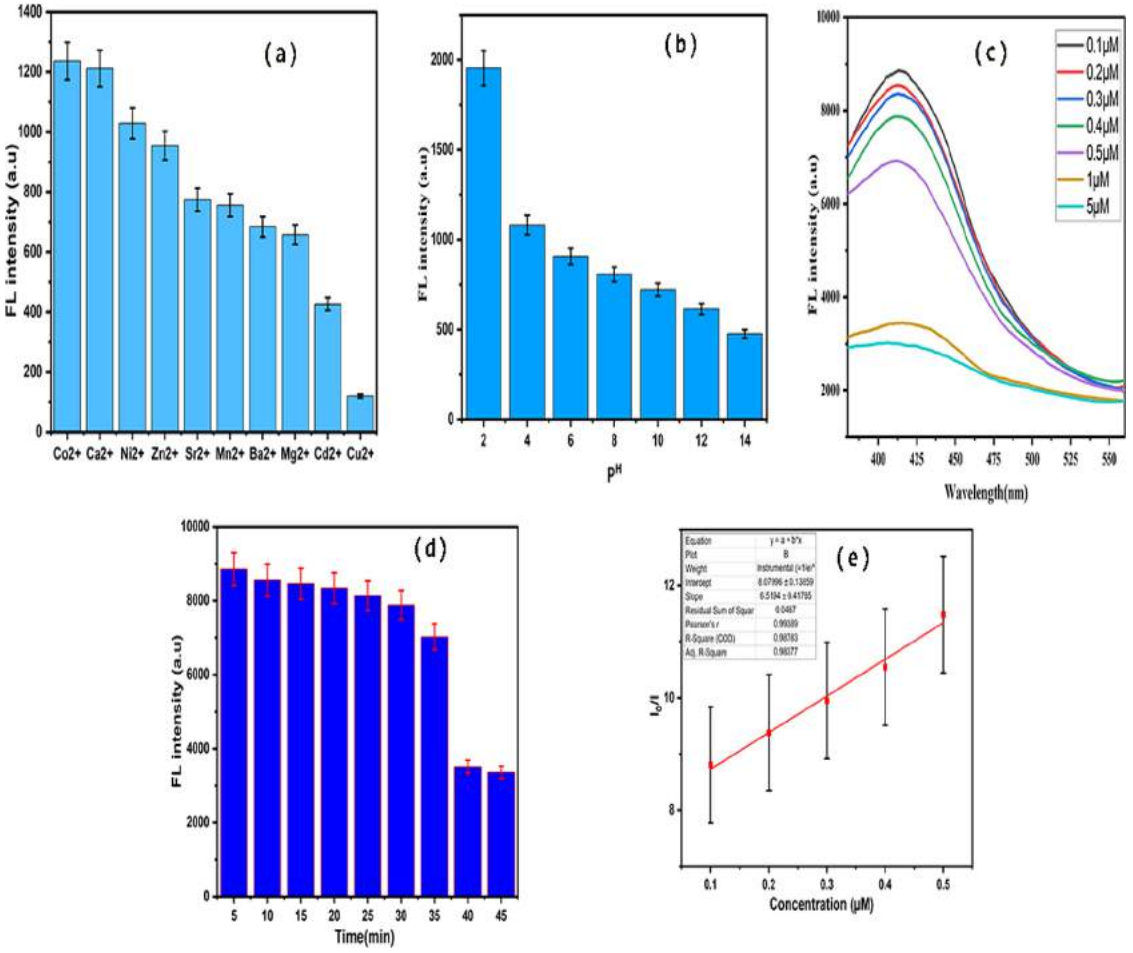

Figure 7. (a) Variation of fluorescence intensity in the presence of divalent metal ions. (b) Variation of fluorescence intensity with the change in pH values. (c) Variation of fluorescence intensity with concentration. (d) Change in intensity of fluorescence with variation in time. (e) Stern–Volmer plot.

taken at a resolution of 2 nm, similar types of grains represent similar planes oriented in different directions. Hence, the MOF is polycrystalline in nature. At low magnification, TEM images will resemble SEM images, and the structure of the MOF resembles a thin flaky shape. TEM images of ZnO@MOF-5 are shown in Figure 6C,D. The images clearly indicate the deposition of particles onto the motif of MOF-5, and the pore size is found to be almost 0.23 nm, which is in good agreement with the data obtained from the BET analysis. The micrograph obtained at a resolution of 5 nm indicates the presence of different grain structural patterns, which resemble the different microcrystalline planes present in the MOF nanocomposite ZnO@MOF-5.

TG-DTA Analysis. TGA and DTA diagrams of the analytes are given in Figure 6E,F. The thermal stability as well as phase purity of the analytes was studied by means of thermogravimetric analysis (TGA). The compounds were heated from a low temperature till 800 °C. Degradation temperatures were assessed, and corresponding decomposition temperatures were noted. The metal–organic framework shows one-stage decomposition at 474.55 °C with a weight loss of 34%, which is attributed to the destruction of the organic framework present. The MOF composite shows maximum weight due to the incorporation of zinc oxide nanoparticles. For zinc oxide nanoparticles, the decomposition starts at 599 °C, which confirms the higher thermal stability of metal oxides and suggests the possibility of formation of the crystalline nature of ZnO above 599 °C. The composite shows decompositions at temperatures of 192 and 457 °C with weight losses of 7 and 28% and suggests the extra thermal stability as compared to the pure organic framework.

BET Surface Area Analysis. Brunauer–Emmet–Teller surface area analysis was performed to investigate the surface topology, and BET adsorption isotherms of analytes are shown in Figure 6G,H. The pore size-to-pore volume distribution of different synthesized samples is shown in Figure 6I. The obtained graphs after the sorption measurements resemble a type 4 isotherm, which indicates that the samples are mesoporous in nature. Multipoint BET results shows that MOF-5 and ZnO@MOF-5 have surface areas of 3.050 and 9.335 m^2/g, respectively. The increase in the surface area of the sample is attributed to the incorporation of ZnO onto the lattice surface. The surface area of MOF-5 is comparatively very low as compared to the reported one and may be due to exposure to a humid atmosphere.[33] The Barrett–Joyner–Halenda (BJH) adsorption isotherm gives the distribution of the pore volume with the pore radius. The total pore volume of MOF-5 is 5.03×10^{-3} cc/g at a relative pressure of 0.98869 atm, and that of the composite is 1.46×10^{-2} cc/g at a relative pressure of 0.98590 atm. Evident from the BJH adsorption isotherm, ZnO@MOF-5 shows a better pore radius-to-pore diameter ratio than MOF-5 alone and suggests the surface

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ACS Omega 2022, 7, 13031–13041

functionalization of ZnO nanoparticles rather than the encapsulation of nanoparticles due to a greater number of open channels in the composite.

Sensing of Copper(II) Ions and Luminescence Quenching. *Sensing of Divalent Metal Ions.* Sensing of the analyte ZnO@MOF-5 toward various metal ions was investigated. Equimolar concentrations of divalent metal ions such as Co^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Sr^{2+}, Mn^{2+}, Ba^{2+}, Mg^{2+}, Cd^{2+}, and Cu^{2+} were prepared for this purpose. The FL intensity of the analyte in various divalent cation solutions was recorded and is shown as a bar diagram (Figure 7a). The bar diagram of ZnO@MOF-5 showed good luminescence sensing activity toward different inorganic metal ions. The study further suggests the ultrasensitive ability of the porous analyte toward the detection of different inorganic metal ions in micromolar concentrations. The synthesized analyte showed the lowest sensing activity toward the Co^{2+} ion and a higher sensing activity toward the presence of Cu^{2+}. For understanding the relative power of the analyte toward the ultrasensitive detection as well as probing of metal ions, the quenching efficiency was calculated for each inorganic metal ion. The quenching efficiency of copper ions toward FL emission of ZnO@MOF-5 was again assessed by the Stern−Volmer equation, $I_0/I = K_{sv}[Q] + 1$. Here, I_0 and I represent the FL emission intensity of the analyte before and after the addition of cupric chloride solution. [Q] is the molar concentration at which the quenching process had been carried out, and K_{sv} is the quenching constant, which determines the efficiency of the MOF composite as a probe for sensing the presence of copper ions at the microscopic level. The higher the value of the constant K_{sv}, the greater the quenching efficiency. The fluorescence quenching efficiency was calculated by $(I_0 - I)/I_0 \times 100$. The quenching efficiencies of ZnO@ MOF-5 toward various metal ions such as Co^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Sr^{2+}, Mn^{2+}, Ba^{2+}, Mg^{2+}, Cd^{2+}, and Cu^{2+} were obtained to be 98.44, 98.47, 98.70, 98.80, 99.0, 99.05, 99.14, 99.17, 99.46, and 99.85%, respectively. The results suggest that the prepared analyte can be used as an effective tool for sensing different divalent cations with high accuracy.

Effect of pH Values toward the Sensing Ability of Cu^{2+} Ions. For optimizing the reaction conditions of sensing, solutions of copper having different pH values (range between 2 and 14) were prepared. The analyte showed different sensing properties as well as different quenching efficiencies toward the detection of the presence of copper ions in aqueous solutions. The variation in intensity of fluorescence with the change in pH values was recorded and is shown as a bar diagram (Figure 7b). Quenching efficiencies calculated were 97.55, 98.64, 98.86, 98.99, 99.09, 99.22, and 99.40% at pH values of 2, 4, 6, 8, 10, 12, and 14, respectively. It is clear that the analyte shows a quenching efficiency of more than 90% in the acidic range as well as in the basic range. It further suggests the better sensing efficiency of the analyte in both acidic as well as basic conditions. At a pH value of 14, ZnO@ MOF-5 shows better sensing with a quenching efficiency of 99.40%. Here, the quenching efficiency gradually increases with the increase in pH values of the medium.

Effect of Concentration on Sensing of Cu^{2+} Ions. The chemical environment at which fluorescence quenching occurs plays a significant role in the experimental part. The reaction is carried out in the presence of phosphate buffered saline (PBS), which is the best one suggested by Hu et al.[34] for maintaining the pH value of the reaction medium. The PL spectra of the analytes after the successive addition of cupric chloride solutions in the concentration range of 0.1−5 μM are shown in Figure 7c. Excitation at 282.46 nm shows an emission at the range of 400−420 nm, which is in accordance with the emission values of the MOF as well as the ZnO@MOF-5 composite. The entrapment of copper ions onto the ZnO@MOF-5 framework may be due to the inherent porous nature of prepared composites. Occlusion or adsorption of Cu^{2+} within the crystal lattice of the porous composite framework leads to the decrease in intensity of the fluorescence spectrum. Mathematically, K_{sv} calculated from the Stern−Volmer equation, $I_0/I = K_{sv}[Q] + 1$, is found to be 5.09×10^{6} M^{-1}, which is a far higher value than those of the conventional MOF composites that are used as sensors.[35] It predicts the high degree of quenching and binding interaction of copper towards the ZnO@MOF-5 composite. The graph (Figure 7e) shows the relationship between I_0/I against the molar concentration, which is linear with a high degree of linear correlation with an R^2 value of 0.9878. The quenching efficiencies calculated are 88.95, 89.44, 90.23, 91.24, 91.35, 95.66, and 96.20% for concentrations of copper ions ranging from 0.1 to 5 μM. The higher the copper ion concentration, the higher the quenching efficiency; it predicts the possibility of the corresponding composite to act as a good sensing agent. The variation of fluorescence intensity with respect to time is shown as a bar diagram in Figure 7d. It is evident from the graph that as aging occurs, the fluorescence quenching power increases.

The Stern−Volmer plot (Figure 7e) shows a linear change of I_0/I with the concentration of the analyte Cu^{2+} ions. The limit of detection (LOD) and the limit of quantification (LOQ) in the sensing experiments were calculated by the same S−V plot (Stern−Volmer plot). The standard deviation of the intercept is given by the following:

$$\text{standard deviation of the intercept} = (\text{standard error of the intercept}) \times n^{1/2}$$

Here, "n" represents the number of measurements taken. The limit of detection (LOD) can be calculated by the following:

$$\text{LOD} = 3.3 \times (\text{standard deviation of the intercept/slope})$$

Here, slope represents the slope of the line obtained in the S−V plot. The LOD is calculated to be 0.185 μM. The value represents the lowest concentration of the analyte that can be calculated experimentally with a 95% accuracy. The value obtained is in good agreement with the experiments too. The value further suggests the better sensing power of the analyte toward the detection of the presence of Cu^{2+} ions in micromolar quantities.

Sensing of Cu^{2+} Ions with Variation in Time. Variation in the sensing activity of the analyte with time toward the sensing of copper ions in aqueous solution is analyzed. As the time progresses, the intensity of the fluorescence emission of ZnO@MOF-5 decreases. This may be due to the slow diffusion of copper ions into the vacant voids present in the hybrid structure of ZnO@MOF-5. Other plausible mechanisms have been suggested at the end of this manuscript. The quenching efficiency of the analyte toward the inorganic metal moieties increases with the increase in the time. Sensing experiments were done by varying time from 5 to 45 min with 5 min intervals, and the results obtained are shown in Figure 7d as a

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ACS Omega 2022, 7, 13031−13041

bar diagram. The maximum quenching efficiency of 95.77% was obtained toward the detection of Cu^{2+} ions.

Plausible Binding Mechanism of the ZnO@MOF-5 Composite with Cu^{2+} Ions Leading to a "Turn-Off Mechanism". We hereby suggest three possible mechanisms for the quenching of fluorescence after each successive addition of cupric chloride solutions of varying concentrations. First, the mechanism can be explained on the basis of the interaction of metal cations and ligands. The fluorescence emission peak at 413 nm may correspond to the ligand-to-metal charge transfer (LMCT) process from terephthalic linkers to Zn^{2+} metal nodes. The uncoordinated carboxylate groups on the terephthalate linker present in the channels of the MOF composite provide a binding site for copper ions. The electronic structure of the linker is perturbed due to the incorporation of Cu^{2+}, which may in turn effectively suppress the energy transfer from the ligand to the metal (LMCT) resulting in luminescence quenching. The FL intensity greatly depends upon the identity as well as the concentration of metal ions. Compared to alkali and alkaline-earth metals, the presence of d block elements plays a vital role in the fluorescence intensity maxima. Among the other transition metals, the presence of Cu^{2+} has more significance.[34] The fluorescence intensity of copper ion-incorporated ZnO@MOF-5 solution of 0.1 μM concentration is 8865 a.u., which is a far smaller value than that of the intensity of the blank of 80,243.35 a.u. This value itself suggests the higher quenching efficiency of the copper ion even at its micromolar-level presence.

The second mechanism that describes the FL intensity quenching deals with the probability of collapse of the metal−organic framework structure after the interaction of the terephthalic acid ligand with copper cations. The decrease in the fluorescence intensity can be explained on the basis of the electron transfer process occurring in the composite ZnO@MOF-5.[36] The electrons present on the framework structure of the composite get excited on irradiation with light. These excited electrons may be transferred to the unoccupied energy levels of ZnO, which will further move down to the metal center zinc ions present in the framework, and the fluorescence will develop. Quenching of luminescence intensity during the addition of cupric chloride solution can be explained as suggested. When the cupric solution was added to the ZnO@MOF-5 composite, oxygen atoms present in the carboxylic group of 1,4-BDC linkers coordinate with Cu^{2+} ions, which in turn results in the blocking of the electron transfer process (ET) occurring in the composite due to the collapse of the framework structure.

The third mechanism for the decrease in luminescence intensity in the composite may be due to the replacement of zinc atoms of ZnO@MOF-5 by copper ions of cupric chloride solutions.[37] This mechanism may be more convincing and applicable in our ZnO@MOF-5 system due to the increase in the ratio of the pore radius to the pore volume as indicated from BET surface analysis and also from the decreasing XPS binding energy values of Zn (2p). The possibility of encapsulation or occlusion of copper(II) cations to ZnO nanoparticles present in the pores and further change to CuO can thus be discarded and there comes the possibility of isomorphous displacement of zinc of the framework by copper atoms, and this change in the luminescence center will result in the decrease in the fluorescence intensity of analytes. The explanation of the suggested binding mechanism of the analyte with copper(II) cations has to be further studied and confirmed through XPS, XRD, and FTIR measurements.

CONCLUSIONS

A luminescent MOF composite called ZnO@Zn-MOF-5 was prepared by means of a solvothermal method for the quantitative trace analysis of Cu^{2+} ions in water medium. The extensive porous nature and the isoreticular framework structure of the nanocomposite make it a versatile fluorescent probe for the detection of copper ions from drinking water at the microscopic level. The feasibility of the same is tested from a level of 0.1 to 5 μM cupric chloride solution, and the intensity of FL emission is shown to be decreasing with increasing copper ion concentration. As the time proceeds, the quenching efficiency of the analyte toward the detection of Cu^{2+} ions increases, which further suggests the nature of time-bound detection and elimination of Cu^{2+} ions in aqueous media. As the pH value increases, the sensing ability of the analyte seems to be increasing, which also suggests the higher activity of the analyte toward the sensing at acidic as well as basic pH ranges. The FL turn-off mechanism is suggested due to the binding interaction of copper ions with the ZnO@MOF-5 composite. The quenching efficiency of ZnO@MOF-5 is 96.20% at a 5 μM cupric chloride concentration. The quenching of luminescence intensity in the composite may be due to the possibility of isomorphous displacement of Zn^{2+} of the framework by copper(II) cations. This suggested mechanism may be more applicable in the synthesized ZnO@MOF-5 system, which has to be further complemented by XRD analysis and FTIR and XPS measurements. The property of the unique rate of adsorption can be extended to fabrication of nanosensing probes for the microlevel analysis as well as quantification of inorganic pollutants.

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Notes

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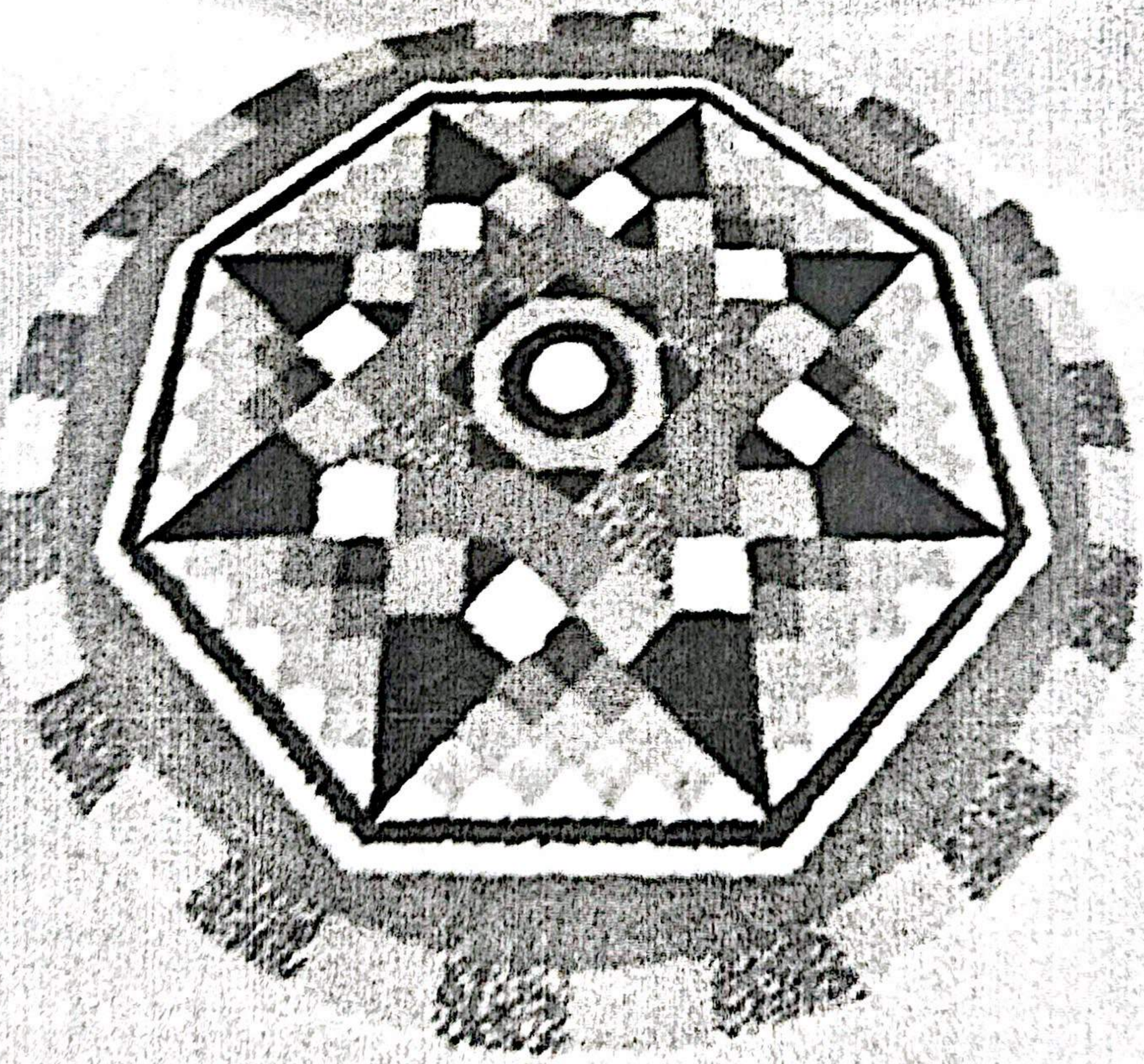

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शोध सरोवर पत्रिका

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इस अंक में

यू जी सी से अनुमोदित पत्रिका

संघर्षशील नारी की जीवंत गाथा 'सकुबाई' नाटक

• डॉ.राजेश कुमार.आर

विख्यात नाटककार नादिरा ज़हीर बब्बर का चर्चित नाटक है 'सकुबाई।' नाटककार नादिरा जहीर बब्बर का जन्म 1948 जनवरी 20 को हुआ। 'एकजुट' नादिरा ज़हीर बब्बर की अपनी नाट्य संस्था है। आथेलो, तुगलक, जसमा ओढन, संध्या छाया आदि नाटकों में नादिरा जहीर बब्बर ने केंद्रीय भूमिकाएँ निभायीं। राजनेता और हिन्दी फिल्मों के अभिनेता राज बब्बर की पत्नी है नादिरा जहीर बब्बर। सुप्रसिद्ध चित्रकार मकबूल फिदा हुसैन के जीवन पर आधारित नाट्य रचना 'पेंसिल से ब्रश तक' का निर्देशन नादिरा जहीर बब्बर ने किया। धर्मवीर भारती की कालजयी कृति 'कनुप्रिया' एवं 'अंधायुग' पर आधारित नादिरा जहीर बब्बर द्वारा निर्देशित नाटक है 'इतिहास तुम्हें ले गया कन्हैया।' नादिरा जहीर बब्बर द्वारा निर्देशित चर्चित अन्य नाट्य रचनाएँ हैं -'पेंसिल से ब्रश तक', 'इतिहास तुम्हें ले गया कन्हैया', ऑपरेशन क्लाउडबर्स्ट आदि।

'सकु बाई' नाटक का मुख्य पात्र है, शकुंतला (सकु बाई)। शकुंतला 'सकु बाई' नाम से हमारे सामने आती है। आजीविका कमाने के लिए गाँव से शहर में आनेवाली लाखों औरतों की प्रतिनिधि के रूप में सकू बाई का प्रस्तुतीकरण हुआ है। विश्रुत नाटककार नादिरा जहीर बब्बर कृत 'सकुबाई' नाटक में उच्च वर्ग के जीवन के विरोधाभास को उजागर किया गया है। बारिश में अपने घर को ठीक करने के बजाय दूसरे के घरों को ठीक करने की एक स्थिति सकुबाई के किरदार में दिखाई देती है। साथ ही मालिकिन के बेटे पामोल को दूध पिलाने के लिए उसके पीछे-पीछे दौड़ लगाना और फिर भी दूध नहीं पीना एक रोचक दृश्य रहा। चंद रुपयों के खातिर सकुबाई की मनोदशा परिवार के पालन-पोषण की विवशता को दर्शाती है। वहीं स्वयं के घर में एक गिलास दूध के पीछे दस हाथों की अड़चन गरीबी और विवशता का प्रतीक रही है। यह नाटक हमें सोचने पर मज़बूर करता है कि हम में से कितने लोग वास्तव में श्रम की गरिमा का मूल्य जानते हैं और उसका कद्र करते हैं।

सकुबाई सिर्फ एक घर में काम करनेवाली महिला की कथा ही नहीं है बल्कि हर उस महिला की कथा है जो जीवन के कठिन दौर से गुज़रकर भी मुस्कुराना नहीं छोड़ती। नाटक की कथा नारी चेतना से जुड़ी हुई है, यह सकुबाई नामक चरित्र के इर्द-गिर्द घूमती है, जो कि एक नौकरानी है और उसके साथ उसके ही मामा ने बचपन में बलात्कार किया था, बाद में उसकी शादी होती है। लेकिन उसका पति भी उसे अकेले छोड़ देता है, इस बड़े दुख और गरीबी से लड़ती हुई सकुबाई जीवन में हार नहीं मानती वह और लोगों के घरों में काम कर अपनी बच्ची को पालती है और उसे बड़ी लेखिका बनाती है।

सकुबाई हमें अपने घरों में काम करनेवालों के जीवन में झाँकने का मौका देती है। यह नाटक बहुत छोटी उम्र में रोटी कमाने केलिए बाध्य होकर शहर में आई सकुबाई के जीवन और समय को बड़ी दक्षता में दर्शाता है। घर के काम करने के साथ-साथ वह कभी अंतरंग मित्र, विश्वासपात्र, सलाहकार और कभी चौकीदार की भूमिकाएँ भी निभाती है। सकुबाई अपनी ज़िन्दगी के अनुभवों और कारनामों का विस्तृत ब्योरा स्वयं बहुत सूक्ष्म परिहास के धागों में पिरोकर प्रस्तुत करती है।

इक्कीसवीं शताब्दी का हिन्दी नाटक रंगमंच अपने आप में बहुत बड़ा कैनवेस है। इस लंबे काल की नाट्य यात्रा में बहुत सारे उतार-चढ़ाव और कई दिलचस्प मोड़ आये हैं। नादिरा ज़हीर बब्बर के नाटकों की अपनी विशेषताएँ हैं। इनकी भाषा की रेंज का फलक अपने आप में अनूठा और बड़ा है। पारिवारिक,राजनैतिक,

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साठोत्तरी मलयालम कहानी और कहानीकार

डॉ राजेश कुमार आर

आधुनिक मलयालम के सर्वाधिक परिचित एवं प्रख्यात साहित्य विधा है कहानी। राष्ट्रीय, सामाजिक एवं सांस्कृतिक परिस्थितियाँ बदलने के साथ-साथ साठोत्तरी कहानी में भी बदलाव आ गया। आधुनिक कहानियाँ मानवजीवन का प्रतिबिंब मानी जाती है। मानव जीवन के प्रत्येक युगीन यथार्थ को कहानी समाज के सामने कलापूर्ण एवं भावात्मक शैली में प्रस्तुत करती है। आज की कहानी ज्ञानवर्धन एवं मनोरंजन की शक्ति से भरपूर है उसका अपना इतिहास है, विकास है, चेतना है। मलयाळम में कहानी-साहित्य का एक विकसित रूप है, एक स्वस्थ परंपरा है साठोत्तरी मलयाळम कहानियों के बारे में विख्यात कहानीकार एम.टी.वासुदेवन नायर कहता है- 'साठोत्तरी या आधुनिक कहानी, कविता के समान पूर्णता की प्राप्ति को लक्ष्य करके लिखी जाती है। कहानी को अधिकतम सशक्त बनाना उसका लक्ष्य है। शिल्प और शैली में साठोत्तरी कहानियाँ एकदम विभिन्न है। कहानियों में जो परिवर्तन पाश्चात्य साहित्य में दिखाई देता है, समान परिवर्तन मलयाळम कहानियों में भी विद्यमान है।

साठोत्तरी मलयाळम कहानी का केंद्र ग्रामीण जीवन से हटकर शहर तथा महानगर बन गया। इस काल में धर्म और संयुक्त परिवार के बंधन से व्यक्ति मुक्त हो गया। अपनी कहानियों द्वारा जीवन की निरर्थकता एवं सारशून्यता को व्यक्त करने की कोशिश की है हर एक कहानीकार ने। वास्तव में साठोत्तरी कहानीकार ने समाज केलिए नहीं लिखा, लेकिन अपने लिए लिखने में वे अतीव तत्पर थे। घटनात्मक शैली में वर्णित कहानी के स्थान पर मनोवैज्ञानिक धरातल पर लिखी कहानियाँ आ गयी।

सन् १९६० के बाद ही आधुनिक मलयाळम कहानी का सर्वांग पूर्ण विकास हुआ था और इसके अग्रगण्य कहानीकार थकषी शिवशंकर पिल्लै एम.टी.वासुदेवन नायर, एस.के.पोट्टेक्काट, ओ.वी.विजयन, वैक्कम मुहम्मद बशीर आदि थे। तकषी शिवशंकर पिल्लै, पोट्टेक्काट, वैक्कम मुहम्मद बशीर और केशव देव के उपन्यास साहित्य रूप के उत्तम के साथ साथ साहित्यकार आपस में राजनैतिक धरातल पर विभाजित होकर रह गये थे। निर्वैयक्तिकता, अजनबीपन, अराजकता आदि का शिकार हुआ। तकषी शिवशंकर पिल्लै के विषयों और पात्रों के अनुभवों का दायरा न होकर समाज रूप में खड़े रहने की कोशिश की। अपने अनुभवों से इधर-उधर होकर अपने आने-जाने हुए में वे जीवन को चित्रित करते है। साठोत्तर कहानीकार रचनाकार परंपरागत रचना प्रणाली और शैली से विमुख थे।

वास्तव में साठोत्तर कहानीकारों ने मलयाळम कहानी साहित्य-क्षेत्र में नवीन दिशाएँ

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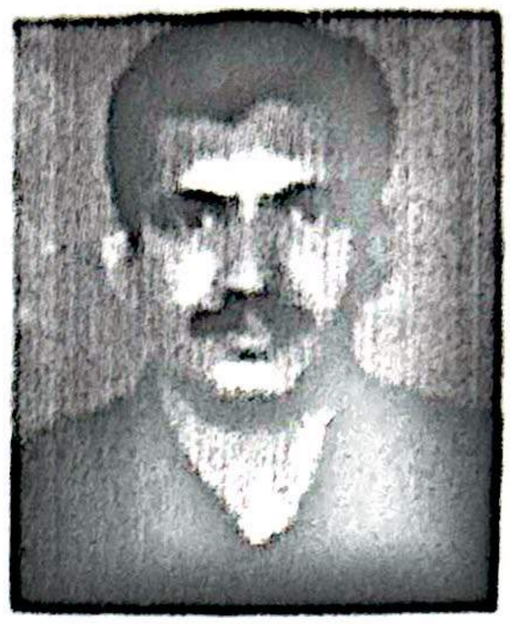
इस अंक में....

मुखपृष्ठ - स्व. प्रेमचन्द

हिन्दी एकांकी नाटक : एक सामान्य परिचय



डॉ.राजेष कुमार.आर

समकालीन हिन्दी एकांकी की स्थिति बहुत उत्साहजनक नहीं है। चाहे नाट्य रचना हो या रंगमंच, सब तरफ़ निराशा का वातावरण है। डॉ. गिरीश रस्तोगी उपर्युक्त प्रस्ताव का समर्थन करते दिखते हैं - "नाट्य-लेखन और रंगमंच में लगातार जो संवाद टकराहट, उत्साह, प्रतिक्रियायें अपेक्षित हैं, वह नितांत प्रसुप्त हैं।" आधुनिक काल में एकांकी के परंपरागत रूप का ह्रास हुआ है और उसके नये-नये रूपों का विस्तार हुआ है। स्वाधीनता के बाद जो सांस्कृतिक व साहित्यिक उत्साह और ऊर्जा का विस्फोट हुआ था, जिसके तहत प्रायः प्रत्येक महाविद्यालय और विश्वविद्यालय में वार्षिक सांस्कृतिक व साहित्यिक आयोजन होते थे, उनमें एकांकी नाटकों का मंचन भी अनिवार्य जैसा था।

छायावाद युग तक हिन्दी एकांकी दो सीमांत पार कर चुका था। १९३६ में दिल्ली में और १९३८ में लखनऊ में आकाशवाणी के अस्तित्व में आने के फलस्वरूप पहले उर्दू-लेखकों और फिर १९४० के आसपास हिन्दी लेखकों को भी रेडियो पर एकांकियों के प्रसारण का अवसर प्राप्त हुआ। चंद्र गुप्त विद्यालंकार का कहना है कि "मेरी स्थापना यह है कि एकांकी नाटक की कोई निश्चित और निजी टेकनीक न तो अभी तक बन पायी है और न बन सकती है।" लेकिन उपेंद्रनाथ अश्क की राय में एकांकी को नाटक, कहानी या उपन्यास से पृथक एक स्वतंत्र विधा मानना ही समचीन है। जैनेंद्र ने अपना मंतव्य व्यक्त करते हुए लिखा है कि भारत में एकांकी, परिस्थितियों की सहज उपज नहीं है, उसपर पाश्चात्य प्रभाव है।

आधुनिक हिन्दी एकांकियों में कथ्यगत संवेदना, रूपबंध और दृष्टि को लेकर गुणात्मक परिवर्तन परिलक्षित होता है। आज का एकांकी समग्र परिवेश में फैल कर देश और काल की प्रामाणिक चेतना में पाठकीय संवेदना को झकझोर देता है। समय और समाज की समस्याओं प्रश्नाकुलताओं, चुनौतियों, अंतर्विरोधों, विसंगतियों, विद्रूपताओं और आधुनिक समाज की जटिलताओं, यंत्रणाओं को व्यक्त करने के लिए एकांकी से उपयुक्त और समर्थ माध्यम आज दूसरा नहीं है। छायावादोत्तर काल में भुवनेश्वर के कुछ ही एकांकी प्रकाशित हुए जैसे 'तांबे के कीड़े', 'आजादी की नींद', 'सिकंदर' आदि। लेकिन रामकुमार वर्मा के अधिकतम एकांकी संकलन 'रेशमी टाई', 'चारुमित्र', 'विभूति', 'सप्तकिरण', 'रजत रश्मि', 'दीपदान', 'रिमझिम', 'इंद्रधनुष', 'पांचवां स्तंभ', 'कौमुदी-महोत्सव', 'मयूर पंख', 'जुही के फूल' आदि १९४० के बाद के प्रकाशन है। डॉ. अजीत कुमार द्वारा संपादित 'हिन्दी साहित्य का इतिहास' के अनुसार

I C E M I T
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Interdisciplinary approach in teaching English for specific purposes

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Abstract

Combining different areas of study has always been a useful approach and a necessary tool in modern teaching. When teaching language for specific purposes, it is one of the most productive ways to modernise the learning process and implement the theory into practice. One example of interdisciplinary approach in teaching language for specific purposes is combining the courses Sociology of Sport together with Business English course in terms of organising field class which is aiming to expose students to real English in use environment and giving them an oportunity to explore sociological aspects relevant to their studies. Students of sports management conduct a semi-structured interview about perception of Split as a city of sports among foreign tourists in local area and thus learn how to research the relevant topic in real life sourrounding, report back about the results of the interview and use English language throughout all activities.
***Keywords*:** *English language, interdisciplinary approach, interview, sociology of sport*

1. The importance of an interdisciplinary approach in the process of learning and education

Taking into account the increasing importance of achieving measurable outcomes in the process of education and the importance of acquiring practical, concrete, applicable skills that are the best preparation for professional and personal life, it is difficult to imagine teaching that could truly meet all the quality criteria without an interdisciplinary approach. By combining different professions, fields or scientific disciplines, different perspectives and methods, it is possible to achieve layering, gain a clearer insight into the issue, holistic approach, more possibilities of solving tasks and greater creativity, both in creating and adopting teaching content.

Interdisciplinary approach is particularly important in the process of higher education, where teachers are expected to understand several areas, and students are strengthened by intrinsic motivation to learn in new ways. “The use of an interdisciplinary approach in the learning process in higher educational institutions allows the formation and development of both scientific and professional thinking of students, and contributes to the formation of interdisciplinary knowledge that is necessary to solve complex scientific and technical problems.” (Salnaia et al., 2021, p. 1337). It is also important to add social problems to this definition, given that students are an important part of society that polytechnics and faculties, among other things, educate for social engagement, i.e., social contribution.

Many innovative learning methods, such as for example, neurolinguistic programming, have shown that students have significantly increased motivation to learn, they have improved memory and greater ability to reproduce material if they use multiple senses in the learning process (e.g., in addition to visual and auditory uses and kinesthetic, olfactory or gustatory representation systems).

Interdisciplinary learning, as well as learning through field work, with a specific task related to the area of interest of students, does just that – it offers students more opportunities to engage in the learning process, offers them experience, activates more senses, and the result is efficiency – in understanding, acquiring new skills and applying what has been learned.

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American sociologist Randall Collins has divided education throughout history into three different types: education for practical skills, education for belonging to a status group and education under the control of bureaucracy. Education for practical skills, as Fanuko says (Fanuko, 2013) took place in the process of work, without major formalization, in a way that students observed, noticed, listened and repeated in order to master the skills that an experienced master demonstrates. Throughout history, such education was acquired at work, in practice, during the performance of various jobs, but the school, or some other formal institution such as a higher education institution, was not a place for the acquisition of practical skills. Nevertheless, education is changing, developing according to the needs of users, but also the labor market.

Some educational institutions continue to foster a "classical" *ex cathedra* approach to students and one-way learning method in which the lecturer speaks and the audience listens, without questioning and without interaction. However, there are fewer and fewer of them. In addition, our interdisciplinary learning that takes place in the field is far from this *ex-cathedra* approach.

When combining different areas of study in interdisciplinary manner, the learning process becomes a cooperation between students and teachers and students among themselves. It encourages creativity, teamwork and also forces students to take a more active role in the learning process. In terms of learning foreign language for specific purposes, this type of approach is crucial in order to show students how they will apply language skills in their future jobs.

2. Field work as a method of socialization

Modern teaching should take into consideration that teaching is not a mere transfer of data. “In the broadest sense, education is simply an aspect of socialization: it involves acquiring knowledge and learning skills. Intentionally or unintentionally, education often affects the creation of beliefs and moral values.” (Haralambos et al., 2002, p. 774). According to Ivan Illich, (Haralambos et al., 2002, p.781) “education should be a liberating experience in which individuals explore, create, take initiative, judge and reason, and fully develop their abilities and talents.”

Although Illich's idea is already quite old, and his approach in which he advocates the abolition of formal education because it "only harms" is radical, it is still an educational reality today in many cultures, but also in many educational institutions. This is far from the priority that he even then put forward, and this is very concrete - learning skills useful for life. To the question of who should teach Illich’s answer is logical – teachers of skills.

American sociologist Talcott Parsons (according to Haralambos, 2002, p. 779) proved in the 1950s that school, after primary socialization in the family, is a focal means of socialization, an institution that acts as a bridge that prepares for the transition from the role of a student to the role of an adult. An educational institution such as polytechnics or faculty, for many is another transition, another bridge that also has the function of a socialization agent, only the focus is more on preparing the student for the world of work, for the professional roles they will have.

Apart from the importance of interdisciplinary approach for students individually, the importance of real-life interaction and communication in which there is no screen, no distance between the speaker and the interlocutor, is not negligible at all. The pandemic situation has seriously put face-to-face communication aside, one in which you have a multitude of opportunities to navigate, but also a multitude of potential mistakes and false impressions. Therefore, classes that involve real interaction are certainly important, and for many students accustomed to the ease of studying and communicating in front of a screen, this is a real-life exercise.

Learning a language in the classroom, among fellow students, is not a particular challenge for many, and the level of motivation depends mostly on their own, intrinsic motivation, and the rest on the skills of the lecturer. The field work, therefore, is a challenge in itself. Achieving real communication, in a foreign language, with strangers, requires more concentration, stronger motivation, better resourcefulness and a dose of courage.

Zygmunt Bauman, a Polish sociologist in Eric Gandini's "The Swedish Theory of Love" (2015) makes it clear how much socialization is desperately needed by people, how important it is to get out of one’s safe zone and start a conversation. Given the growing need and inclination of Western societies for individualism, autonomy and independence, in addition to socialization, interaction skills, people lose their collective identity, the sense of belonging to a certain social group, the sense of "We". “It is untrue that hapiness means trouble free life, happy life means overcoming troubles…you confront challenges, you try your best…and then you get the moment of happiness. This thing can’t be provided by the state… you have to be among other people” – says Bauman and then concludes that “at the end of independence there is emptiness in life, meaningless of life and unimaginable boredom.”

There are many advantages of interdisciplinary approach and field teaching, but in the process of agreeing among teachers and merging areas, it is necessary to pay extra attention to choosing the best method of learning, especially when it comes to language learning, and learning a language for specific purpose.

3. Teaching language for specific purpose

When teaching English for Specific Purposes one must focus on the reason why the teaching process is taking place. It is not just to master the structures of language and achieve general communication, but to prepare the students for their work and their careers. Classrooms can offer a certain framework for practicing skills and gaining vocabulary necessary for understanding and communicating, but it lacks real life experience and conditions which students will encounter in their work. For that reason, one of the best methods for achieving such conditions is the CLIL method.

3.1. CLIL Method

One of the most effective methods of the learning process which includes interdisciplinary approach is the method of content-language integrated learning. "This method allows you to effectively design the process of learning a foreign language, using an interdisciplinary integrative framework, especially in the framework of the ESP academic discipline (Arnó-Macià & Mancho-Barés, 2015; Dalton-Puffer et al., 2011; Llinares et al., 2012; Temirova, & Westall, 2015; Tokareva, 2018; Tsimerman, 2018). There are several main characteristics of the method of content and language integrated learning: mutual integration of the content of the academic discipline and a foreign language; the target language is only a vehicle for the study of professional disciplines (vehicular language); professional communication is an environment for natural learning of a foreign language; professional communication is primary, and grammar is secondary (if grammatical errors do not impede communication) (Salnaia Leia, et al. 2021, p 1339). When teaching ESP, one must be aware that students learn a foreign language in order to gain a tool to communicate non-language related subjects. Furthermore, the ability to actively use the English language in a certain area of study is a crucial requirement in labour market today. That is why CLIL method provides one of the best ways to expose students to reality of using the English language in business environment.

The field work carried out at University of Applied Sciences Aspira among students of Sports Management included this method and since students were involved both in Sociology of Sport and Business English course, interdisciplinary approach was organized in a way that includes the content – reasearching about the role of sport in the local community and the language – English.

4. Foreign language speaking anxiety and field work

The field work concerned included some challenges. When presented to the students, some had questions which revealed uncomfort about having a task which includes speaking English to real people in real life. The fear of leaving the comfort of classroom and starting a communication in a foreign language with other than peers is real. The phenomenon called foreign language speaking anxiety is something that foreign language teachers encounter very often. Since learning a foreign language includes communication, it is often the case that some students can communicate freely in their mother tongue, but cannot achieve a proper communication in a foreign language. However, it is important to stress that the focus is on students who do not lack the basic language skills to achieve communication, but their anxiety prevents them from starting communication. The reason for this anxiety is mostly the fear of making mistakes and the embarassement that arises from it. Mohamad & Wahid (2009, p. 74) mentioned in their study that "most of the students were concerned about various kinds of evaluative situations in which their knowledge and performance of English will be monitored by people around them." And with this fear in mind, many students seem reluctant to participate in any activity that involves speaking. However, the activity conducted among students of Aspira included team work which helped them disperse responsibility and not feel such discomfort about the task.

5. Sociology of sport and business English feld work example

Sociology of Sport is a course in which the focus is on understanding the relationship between society (social institutions, organizations, groups) and sports (sports organizations, groups). One of the important topics in the field of sociology of sport is certainly the mutual influence between sports and tourism. Since tourism is one of the most important industries in Croatia, increasing popularity of Split as a tourist destination and the rich history of Split as a sports' city, merging these two branches is an actual, sustainable and logical step that has enabled students to acquire practical and applicable knowledge in areas of their interests and studies. During field work, students have the opportunity to realize qualitative research and thus, acquire concrete skills, get a deeper insight into the topic that they will professionally deal with in the future, understand the wider context in which the relationship between sports and tourism takes place, and get guidance for further development of research. Given the topic and tourists as a target group, this task would not have been possible without business English. Thus, by learning about sociology of sport students are practicing vocabulary and grammar structures in real life surrounding. Instead of organising role-play in the classroom, students are not role-playing, they are actually communicating with real people about specific topic related to their studies.

In our example of interdisciplinary approach, the language – Business English was combined with Sociology of Sport. Students were from the Departments of Sport and Tourism, so we have put the management of these two areas in the subject of research. The task students received was to examine the perception of tourists about Split as a sports city. The task involved first preparing questions for a semi-structured interview, agreeing on roles and division of tasks, and finally creating questions in English in accordance with the goal. It is also important to note that students were both Croatian and international, which made the use of English crucial in cooperating within the team, as well as in performing the task itself.

Students were instructed to find tourists who are willing to participate in the task, talk to them, meet them, ask them few questions. In other words, they had to make a meaningful conversation in English with people outside classroom about specific topic related to their field of studies and return with answers which can give them insight about important aspects related to Sociology of Sport.

The semi-structured interview method was chosen in order for students to have the opportunity to be more informal in the conversation, follow the course of the conversation and change the direction of the conversation, following the respondents' replies, and to have enough space for informal communication with the aim of better getting to know the respondents, their views, their origin and culture. Additionally, English is not the native language of any of the students, which is certainly a better option for group homogeneity and equality of roles.

Students were divided into smaller teams, into groups of three or four, and the groups are usually composed of a combination of Croatian and international students. In this way, by combining language areas, smaller groups and combining language areas reduces the risk of diffusion of responsibility. The group has a significant positive contribution to the behavior and motivation of the individual, but there are also negative effects. In a group, there is more often a decrease in the motivation of members and non-execution of tasks, and there is a rare occurrence and diffusion of responsibility. ”The diffusion of responsibility is manifested in a way that each individual, due to the presence of others, may feel a lesser obligation to, for example, come to the rescue. The larger the number of people in one place and the more distant the relationship between them, the less the sense of responsibility” (Reić, et al. 2020). In real communication, in which each of the students had a specific task to fulfill, the students had to speak, they had to practice discussing the topic/issue they were studying and also how to discuss it in English.

In teams, they went around the city performing semi-structured interviews with tourists in the city researching their opinion about Split as a sports city. The activity was done in English language.

6. Results of field work

Fieldwork itself is, for the vast majority of students, interesting. Getting out of the classroom, changing the environment is certainly an advantage in the process of mastering new tasks. In our case, field classes are in the city center, the most beautiful part of the city, which is also the place visited by tourists the most – the target group of our examiners. The vibrancy and diversity of the city center is certainly an environment in which learning and acquiring new skills is fun, but also memorable. Such an informal atmosphere also contributed to lowering the anxiety of speaking in a foreign language.

“Schools exist to serve students and to expand their skills and knowledge. Still, there are many dynamics within a school that may undermine that primary objective. The role expectations of anyone in the status of student can be complicated by variables such as ethnicity, gender, sexual orientation, and socioeconomic standing” (Ballantine et al., 2018, p. 337)

The inclusion of international students in a group of Croatian students within the framework of the institution, the classroom, is always challenging. If it is a larger group of students, there is often a diffusion of responsibility in which those students who are reluctant to speak English or who are simply lazier, leave this "obligation" to their colleagues. Also, after classes, students disperse and there is no further interaction. The result is most often - international students are on the sidelines, in their own groups.

Such contexts, in which they are put in the same situation, where they are now one group, one collective in which the feeling of "we" is created, and the tourists they examine are "they" is definitely a much more efficient way of integrating international students and homogenizing the group in general. The task they get connects them, creates a sense of closeness, they have at that moment the same goal, the same interests and equal roles. Furthermore, everyone must speak a non-native language.

Moreover, when students finished the task, many approached and reported that they did not expect to be so successful in communication and many of them who previously expressed anxiety about the task returned vividly impressed by their own achievement. It is important to note that students were not forced to communicate because other team members could

conduct an interview if one felt discomfort. Thus, the idea of allowing them to start conversation when they feel ready actually made them more willing to participate.

7. Conclusion

This kind of teaching has many more advantages and results than one might assume at first. There are clear, visible goals of an interdisciplinary approach and combining Business English and Sociology. In ESP context this field work provides an example how language can be intentionally put outside the focus but it still remains a crucial part of the task, a tool without which the task cannot be done. However, there are also those advantages that are not, perhaps, obvious at first, but are not less important. The outcomes of this kind of class are using business English in real situations with real people in an international context, learning how to set up research drafts, how to perform a semi-structured interview and understanding research thinking. It also contributes to practicing social skills, both with people who were interviewed and among the members of the team.

This type of interdisciplinary approach strengthens individual motivation, it brings students into real interaction and communication and contributes to homogenization of the group and integration of foreign students. While establishing contact with new people students also get the opportunity to meet other cultures, practice cultural relativism, and thus connect sports and tourism as two extremely important branches and learn how to deal with foreign language speaking anxiety.

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CONTENTS

CONTENTS

10 As in a biography, the locus of the narrative is the subject K.T.N. Kottoor. The political and social turmoil, mystifying locale and other well-knitted characters are shadowed by the protagonist.

74 Multiplication Table- the only aphoristic system which controls the progress of mankind and the natural laws of development and which is free from weakening emotions. He, with single-mindedness, chanted the memorised Multiplication Table for 2 and 4.

101

51

39 This "indecent" behaviour of the woman of noble birth can be legitimised only when it is attached to the stereotype of a devadasi dancer known as morally loose.

59

69

Inclusive
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The Rhetoric of the Depressed Past: An Enquiry into the Oral History Interviews of the Women Tribal Leaders of Narmada

Chitra V.S. & Aditya Nair S.P.

Abstract

The stability of particular groups of the population can occasionally be impacted by government-sponsored development projects in a democracy. One such large-scale project that upset the balance of the locals, primarily the tribal people who had settled along the banks of the Narmada River, was the Sardar Sarovar Multi-purpose Project. Even though non-profit groups like the Narmada Bachao Andolan, led by intellectuals and social activists like Medha Patkar and Arundhati Roy, have attracted attention on a global scale, the hardship experienced by the indigenous inhabitants has frequently been given second-class treatment. An effort by Nandini Enquiry Oza called "Oral History Narmada" aims to give a voice to the suffering and struggles of a group of people who are still marginalized because there is no effective way for them to express their resistance. The main focus is on Nandini Oza's oral history interviews with two tribal women who were protestors and NBA leaders. It chronicles the lives of tribal women who were intertwined with their ecology and whose way of life in a democratic society has been endangered, uprooted, and stripped of their homes. It is crucial to comprehend how oral history gives marginalised people the authority to resist and gives them a place to start a conversation with people in hegemonic roles. The testimony of these indigenous women supports the sustainability of the environment in the face of development projects, but they fall short in practice, and they make a case for pursuing environmental justice in a representative democracy.

Keywords: *Ecology, Environmental Justice, Indigenous Women, Resistance, Oral History*

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Possession, Repossession and Dispossession in David Malouf's *Harland's Half Acre*

VIDYA RAJAGOPAL

Abstract

Generally considered to be the literary successor of Patrick White, David Malouf is a distinguished Australian writer of considerable versatility. He depicts with amazing dexterity and with a sense of realism, the inner workings of the complex minds of people, who seldom articulate their feelings and emotions. Each of his novels portrays a myriad of experiences that play a crucial role in the making of present-day Australians. The novel, Harland's Half Acre, narrates the story of a man who endeavours to recover the land of his ancestors – acres and half acres squandered by them. Here Maloufmakes an exploration into unchartered territory – the paradoxical lives and experiences of European Australians. They are often torn between two worlds – the distant, unfamiliar lands and a strange new land that nurtures them. The novel reputed to be one of the epic dimensions delineates a single man's struggles throughout his life and in such an effort, Malouf portrays Australian history in a microcosm. The article probes the various vicissitudes and tribulations in the life of the protagonist, along with the loss of a city's innocence and the end of an era. It also traces the physical and spiritual landscape of Australia, a changing Brisbane – from a colonial outpost to a nation becoming a part of a new changing world.

Keywords: Australian history, European Australians, Possession, Physical and Spiritual Landscape.

Australian literature often reflects an encounter between the existing social pattern and the new social fabric introduced by the white settlers. The patterns of Australian life were moulded in literature

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THE JOYS OF MATERNAL EXPERIENCE: MOTHERHOOD AND MOTHERING IN BUCHI EMECHETA, FAY WELDON AND R. K. NARAYAN

Vidya Rajagopal

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Abstract: *Motherhood is a glorious life force that imparts new possibilities and provides a new dimension to the very existence of women. Being a mother, imparts a sense of fulfilment to a woman's life. The love of a mother is selfless and unconditional, no matter to which cultural milieu she belongs. The method adopted by various novelists who deal with the problem of motherhood vary strikingly, and they embody realism, anti-realism and fantasy as distinctive features of their style. They depict motherhood as an experience that affords immeasurable pleasure and a sort of ambiguous power. The paper highlights three different aspects of motherhood enshrined in Madeleine, Savitri and Nnu Ego. These novels also portray the home as the hub of the power-struggle between the sexes.*

Keywords*: Motherhood, Mothering, Motherliness, Power and Vulnerability, Instincts, Femininity*

The attribution of divinity to mother is essentially an Indian concept. It glorifies mother as a divine form, elevating her to a level of a goddess. Nature is conceived of as a foster mother who nurtures and protects all created things. The 'Shaktheya' cult is the most logical manifestation of the Indian mode of worshipping the universal mother. The Indian outlook on woman is shaped and nurtured by the perception of divinity in feminine form. For example, Shakthi is the counterpart and complement of Shiva. This angle of vision is the pivot of the Indian literary concept of womanhood, and the cardinal virtue of Indian philosophy. The glorification of the feminine principle underlies all classical mythologies, but not in relatively new and revealed religions.

According to Andrea O'Reilly, "motherhood refers to the institution of motherhood, which is male-defined and male-controlled, and mothering refers to experiences of mothers which are female-defined and female-centred" (97). The role of mother, in all its depth and vicissitudes, can be entered through giving birth, adoption or marriage to a child's father. The duties and rights of motherhood vary considerably. They depend on various factors like the mother's position in society, her nature, age, race, marital status, sources of support and so on. The gender, the order of birth, physical condition and behaviour of the child influence the mother. That mothers parent differently from fathers is a matter to be attributed to both physiological and social factors, and feminist scholars have bestowed a lot of attention on this subject. It may be noted that motherhood is more than a biological event. Why women are willing to become mothers is a question answered by Chodorow with the help of psychoanalytic theory, by Lorber and Coser from a sociological point of view, and by Rossi with reference to the interplay between biology and social structure. Although medical advances have enlarged the potential for choice over whether and when to have children, societies vary in whether or not such action should be encouraged. For the most part, women's decisions are constrained by policies created and maintained by men for political, economic or religiously guided goals. The concept of fertility seems to be mandated in some parts of the world but suppressed in others.

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CONFLUENCE OF AESTHETICSAND RITUALS: SOCIOCULTURAL RELEVANCE OF PADAYANI AS AN ARTFORM

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Abstract

Living in harmony with nature lies at the root of Indian culture. Conservation of nature and natural resources is ingrained in the Indian psyche and faith and this is reflected in the religious practices, folklore, art and culture. Kerala is a land of colourful festivals, rituals, myth and folksongs that reveal the intimate sense of harmony and togetherness that existed here. Padayani is one such ritualistic art form practised in the Central Travancore regions of Kerala and it is dedicated to Goddess Bhadrakali. The central narrative of Padayani is unity in diversity and it reinforces the solidarity among human beings. But this art form has failed to reach out to the masses as it is restricted to certain areas only. Promoting this colourful rural artform will help to spread far and wide, the rich cultural heritage of Kerala.This article makes an attempt to explore the various aspects of Padayani and highlights the need for reviving and restoring this art form to its former glory, which otherwise would fade into oblivion.

Keywords: *Padayani, Folklore, Ritualistic Art form, Cultural Heritage*

Kerala is a land of sylvan scenic splendor. Enchanting natural scenery is its hallmark. This tiny state has a resplendent cultural and artistic tradition. A cradle of art and architecture she has given birth to, and ardently patronized innumerable artistic forms which speak of the resilience and aesthetic sensibility of the people of Kerala. Hindu temples reputed for their architectural designs of incredible beauty and quiet sanctity have been congenial centers for fostering art and literature. Many literary and artistic forms have been susceptible to the impact of these divine centers. A variety of artistic forms sprang up and flourished in the vicinity of the temples.

Padayani is an art form which bears eloquent testimony to the amazing ingenuity and superb artistic genius of the people of Kerala. This artistic form is a judicious admixture of almost all the fine arts. It provides ample scope for music, dance and action , which with the accompaniment of various percussion instruments hold the audience spellbound. Rituals can be defined as any kind of gesture or action that is socially, culturally or religiously relevant. They are an indispensable part of our life and often serve as a mode of communication. The communication that happens through rituals and traditions stands out and differs remarkably from communication through languages. Rituals form a connecting link between the past and the present, uniting different generations and thus forming an inseparable connection between man and nature. Thus rituals Forman integral part of the cultural fabric of Kerala.

Padayani as an artistic form has a lot of scope for religious harmony. Various castes and communities of Kerala actively participated in this art form, even before the Brahmanical hegemony. In a state like Kerala, where caste discrimination was rampant, Padayanihas the unique distinction of being a caste free performance. People irrespective of their castes and communities, were keen to take part in this agrarian art form. Padayaniis a word which combines Pada(group of soldiers) and Ani (rows), both Malayalam words. It is said that the initial proponents of this art form were the 'ganakas ', the medicine men of Kerala, who visited households for psychological or spiritual healing. The ganakas were also practitioners of martial arts and these accounts for the martial arts being an integral part of Padayani.

Padayani is often performed during the period from January to May . It is believed that Padayani includes within its fold, all 64 art forms or 'Kalas' mentioned in the Shastras. This ritualistic dance is in commemoration of the dance performed by Lord Shiva and the other gods

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ARE THERE MILES TO GO BEFORE WE SLEEP?

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Abstract : This paper talks about how women's body has been disciplined by various agencies through all these years. The levels of subjugation, internalization, resilience and resistance that went through her to make her what she is. In that conflict, the role of power relationship is huge. The unequal power relations within the intimate power partner relationship had left her with the societal stigmatization of abortion. Her body is not her own, where she has the right to take a decision. Hence there is this immediate need to review the fluidity of gender needs.

Key Words: Biological Essentialism, Patriarchy, Power Dynamics, Gender sensitization, Gender trouble, Sexualities

"How come when it's us, it's an abortion, and
when it's a chicken, it's an omelette?"
George Carlin

When Carlin cracked this statement as a joke, the people who might have been there, or those who saw this later might have laughed so hard. But pondering more into this dark humour lies the intricacies of womanhood. From the day a "she" is born, limb by limb estimations are done. And this structured existence gets shattered when she decides to think for herself. At that point the science of gender gets to work.

Essentialism as we know it has always spoken of the necessary factors that make a man "a man" and a woman " a woman". Women`s essence is thought to be and is normally recognized with her traits regarded as being mainly feminine. These thoughts of femininity are typically associated with biology and there are also certain subject mental traits like compassion, nurturing, empathy, support, non-competitiveness, etc, by which a woman is constantly analysed and judged. These essential criteria that make a woman, force her to deconstruct her mind and body throughout her life. This is how gender ideology works obliquely.

According to the gender ideology models, the division of family roles is driven by men's and women's gender beliefs. This approach proposes that couples with traditional gender ideologies assign tasks and roles along traditional lines, with the father serving as a breadwinner and the mother as a primary caregiver. This ideology of biological essentialism was demystified by the strong waves of feministic ideologies. There is a popular saying which strongly agrees with the above lines, "No woman can call herself free until she can choose consciously whether she will or will not be a mother"(Sanger). Sanger is one of the strong writers who upheld the idea of woman and childbirth control through her periodical publication, *The Woman Rebel.*

The idea of abortion is still considered a taboo in eastern part of the world, especially in the once advanced civilization, now known as India. The cultural and societal stigmatization of abortion has a key role in the increase of population in India. India before the 70s considered abortion as an offense, as the murdering of a child. But this was removed and MTP or Medical Termination of Pregnancy was established. The MTP law which was amended in the year 2021 legally allows a woman to choose for an abortion if she wishes to do show. Even when the law is set to assist woman in choosing a life of her choice, abortion is not promoted or any woman who wishes to do so is projected as a woman of bad character.

The social stigma around abortion as well as the changing perception is reflected and propogated through the popularly accepted visual treat. For instance, the movie *Kanakanmani*, a 2009 horror thriller directed by Akku Akbar, starring Jayaram and Padma Priya and the movie *Sara's*, 2021 movie directed by Jude Anthony Joseph, starring Anna ben and Sunny Wayne. Both

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CAUGHT BETWEEN TWO WORLDS: GEORGE RYGA'S THE ECSTASY OF R JOE AS APLAY ON SURVIVAL AND VICTIMISATION

Dr. Vidya Rajagopal
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Abstract

George Ryga, in his seminal play The Ecstasy of Rita Joe exposes the desperate and hapless of a forgotten people – Canadian Indians. Ryga's drama unveils the detailed portrait of an inhum and destructive social process, slowly working its way towards the total annihilation of the li and dreams of a young native woman, Rita Joe. Ryga vividly bringsout the tragic consequenc of the cultural divide that separates the aboriginals and the non-aboriginals in Canada. In th hierarchy of the dominant culture, native women are at the very bottom. For women like Rita Joe the world is a dangerous place – dangerous and different from the one she had envisioned and experienced so far. The dramatist also makes subtle references to the historical dispossession of the First Nations People of Canada as a result of British and French colonization.

Keywords: Aboriginals, Indigenous, Imperialism, Marginalization, Appropriation, Cultural alienation

Canada is a land of many provinces, inhabited for millennia by various groups of aboriginal people. In a multicultural society like Canada, national identity can be evolved only in mosaic. A significant and indigenous drama theatre has come into existence in Canada only in the 20th century. George Ryga's plays are landmarks in the annals of Canadian drama in the sense that it is he who brought them to the centre stage, investing them with a touch of modernism. Credit goes to him for bringing to the forefront the relevance and significance of Canadian mythology by creating and identifying the archetypes based purely upon it. It was his conviction that a full-fledged theatre can play a vital role in fostering a sense of national unity and development. By exploiting the potential of the theatre, Ryga's voice has become a veritable call for struggle against oppression and exploitation in its ugly manifestations. Most of his plays mirror the interaction of individuals or societal groups of different cultural values with uncharitable alien forces. The Canadian natives had to bear the brunt of white imperial oppression and their futile struggle for the possession of their legitimate rights finds its reflection in Ryga's works.

The plight of the Canadian natives was so miserable that they were completely at the mercy of the foreign elements to obtain sanctions to present plays in their native language. But some concerted effects were made in the direction of creating an indigenous theatre, which would reflect the troubles and tribulations in the minds of the Canadian people.

But these attempts made by a brave few sounded like cries in the wilderness simply because of a

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Validating the Essence of Bhagavad Gita in Modern Times through TA

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Abstract

In this paper, the transaction between Arjuna and Lord Krishna in the age-old wisdom called Bhagavad Gita is being analysed along the lines of the Transactional Analysis theory of Eric Berne. There are two aims for the paper. 1. To analyse the transaction between Krishna and Arjuna in tune with the TA theory by Eric Berne. 2. To find out about the Universality of Human Behaviour by such correspondence and hence suggest the application of the wisdom of Gita in Counselling. The ego state of Arjuna before the discourse and later is analysed. The Processes used by Lord Krishna to make the ego state change in Arjuna are looked also into. The life script of Arjuna, the role of different Yoga systems etc are analysed. Three modes of material nature are compared and contrasted with the three ego states. Adult Autonomy as achieved by Arjuna and the state of Satwa is compared. Finally, the Universality of the Bhagavad Gita and the use of the Counselling tips got from the Bhagavad Gita are discussed.

Key terms:

Bhagavad Gita, Transactional Analysis, Ego state, Life script, Autonomy, Three Modes Of Material Nature

Paper

'Transactional Analysis (TA) is a theory of personality and a systematic psychotherapy for human growth and transformation,' according to the International Transactional Analysis Association. Transactional Analysis is a theory propounded by Eric Berne in 1957. Ego states, Three types of transactions, Life script, Life positions, and Games are the fundamental themes of Eric Berne's theory. Bhagavad Gita is the distilled spiritual essence of the Vedic scriptures. Vedic scriptures consist of 4 Vedas, 108 Upanishads 18 Puranas and two Itihasas, and the essence of the Vedic scriptures is a manual for human behaviour. Its 'distilled essence' is a guide to human behaviour. Written by Vyasa the Bhagavad Gita talks largely on the nature of the soul, yoga systems, the three modes of nature, and so on, within the framework of 18 chapters and 701 verses (shlokas). The Gita represents chapters 25-42 of the Mahabharata, which contains 100,000 shlokas.

Bhagavad Gita is spoken in the war field by Lord Krishna to a depressed Arjuna has been referred to many times as psychotherapeutic intervention. (Murthy,1985). Bhagavad Gita is almost in its entirety the dialogue between Lord Krishna and Arjuna (the Pandava Prince) on the battlefield (war between the Pandavas and the Kauravas).. The discourse – one of the greatest philosophical and religious dialogues known to man – took place just before the outbreak of war, a great fratricidal conflict between the hundred sons of Dhrtharastra (known as Kauravas) and their cousins the Pandavas or sons of Pandu on the opposing side. (Prabhupad,1972).

The situation of Arjuna by the end of the first chapter is pitiable. *tatrāpaśhyat sthitān pārthaḥ pitṝn atha pitāmahān/āchāryān mātulān bhrātṝn putrān pautrān sakhīṁs tathā/śhvaśhurān suhṛidaśh chaiva senayor ubhayor api/*(After seeing within the midst of the armies of both parties, his fathers, grandfathers, teachers, maternal uncles, brothers, sons,

On the Vertex Position Number of Graphs

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Abstract

In this paper we generalise the notion of visibility from a point in an integer lattice to the setting of graph theory. For a vertex x of a connected graph G, we say that a set $S \subseteq V(G)$ is an *x-position set* if for any $y \in S$ the shortest x, y-paths in G contain no point of $S \setminus \{y\}$. We investigate the largest and smallest orders of maximum x-position sets in graphs, determining these numbers for common classes of graphs and giving bounds in terms of the girth, vertex degrees, diameter and radius. Finally we discuss the complexity of finding maximum vertex position sets in graphs.

Keywords: geodesic, vertex position set, vertex position number, general position
2000 MSC: 05C12, 05C69

1. Introduction

All graphs considered in this paper are finite, undirected and simple. For a graph G we will denote the subgraph induced by a subset $S \subseteq V(G)$ by

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$G[S]$. The *distance* $d(u, v)$ between two vertices u and v in a connected graph G is the length of a shortest u, v-path in G; any such path is called a *geodesic*. The distance is a metric on the vertex set V. The diameter $\mathrm{diam}(G)$ of a connected graph G is the length of any longest geodesic. For any vertex u of G, the *eccentricity* of u is $\mathrm{e}(u) = \max\{d(u, v) : v \in V\}$. A vertex v of G such that $d(u, v) = \mathrm{e}(u)$ is called an *eccentric vertex* of u. The neighborhood of a vertex v is the set $N(v)$ consisting of all vertices u which are adjacent with v. A vertex v is *simplicial* if the subgraph induced by its neighborhood $N(v)$ is complete; we will denote the number of simplicial vertices of a graph G by $\mathrm{s}(G)$ and the set of all simplicial vertices of G by $\mathrm{Ext}(G)$. A set of vertices in a graph is *independent* if no two vertices in the set are adjacent; the independence number $\alpha(G)$ is the number of vertices in a largest independent set of G. A graph is a *block graph* if every maximal 2-connected component is a clique. For basic graph theoretic terminology not defined here we refer to [4, 6].

Visibility and illumination problems are among the most attractive and interesting research topics in combinatorics, geometry and number theory [3]. Such problems have been studied intensively in the context of the integer lattice; a set Λ of points of the lattice is *visible* from a point x if for any $y \in \Lambda$ the line segment from x to y contains no other points of Λ. A well-known result from elementary analytic number theory first proved by Sylvester [19] states that the density of the set of points in the integer lattice that are visible from the origin is $\frac{6}{\pi^2}$ [2]. In particular, in Chapter III of [14], it is shown how to place a set of points with positive integer coordinates (i, j), $j \leq i$, in such a way that each point is visible from the origin $(0, 0)$, by also maximising the number of points with the same abscissa. This construction has interesting relations with the Farey series and Euler's totient function ϕ. Other interesting visibility problems in integer lattices can be found in [9, 13].

In recent years the algorithmic component of visibility problems has attracted great attention under the name *art gallery* or *watchman* problems, which lie in the intersection of combinatorial and computational geometry [18]. Art gallery problems, theorems and algorithms are so named after the celebrated 48 years old problem posed by V. Klee. In 1973 he asked the following question: 'What is the minimum number of guards sufficient to cover the interior of an n-wall gallery?'. This problem was solved by Chva'tal and subsequently by Fisk. By creating idealised situations such as obstacles, guards, etc., the theory succeeds in abstracting the algorithmic essence of many visibility problems.

Taking our inspiration from the result of Sylvester [19], in this paper we consider a generalisation of 'local visibility problems' to the context of the general position problem in graph theory. The general position problem originated in Dudeney's no-three-in-line problem [8] and the general position subset selection problem [10, 17] from discrete geometry. These problems were generalised to graphs independently in [5] and [15]. A set S of vertices of a graph G is in *general position* if for any $u, v \in S$ any u, v-geodesic does not intersect $S \setminus \{u, v\}$. The *general position number* $\mathrm{gp}(G)$ of G is the number of vertices in a largest general position set in G. We refer the reader to [1, 16, 20] for more information on the general position problem.

In a recent paper Di Stefano [7] introduced the concept of a *mutual visibility set* in a graph; a set S of points in a graph G are *mutually visible* if for any $u, v \in S$ there exists a shortest u, v-path in G that does not pass through $S \setminus \{u, v\}$; the *mutual visibility number* $\mu(G)$ of G is the number of vertices in a largest mutual visibility set in G. In [7] the mutual visibility number of some classes of graphs are determined and it is shown that the problem of finding a largest mutual visibility set is NP-complete for general graphs.

We now study a 'local' version of these problems using a parameter that we call the *vertex position number* of a graph. The plan of this paper is as follows. In Section 2 we provide some bounds on the vertex position numbers of a graph. In Section 3 the vertex position numbers of some common classes of graphs are determined. We characterise the graphs with very large or small vertex position numbers in Section 4. Finally in Section 5 we consider the computational complexity of finding the vertex position number of a graph.

2. Vertex position sets in graphs

In this section we derive bounds for the vertex position numbers of a graph in terms of the minimum and maximum degrees, radius and diameter. First we formally define the vertex position numbers.

Definition 2.1. *For any graph G and a fixed vertex $x \in V(G)$, a set $S_x \subseteq V(G)$ is an* x-position set *if for any $y \in S_x$ no vertex of $S_x \setminus \{y\}$ lies on any x, y-geodesic in G. The* x-position number *of G is defined to be the maximum cardinality of an* x-position set *and is denoted by $p_x(G)$ or simply p_x. An* x-position set *of cardinality $p_x(G)$ is called a p_x-*set*. The maximum value of $p_x(G)$ among all vertices x of G is called the* upper vertex position number $\mathrm{vp}(G)$ *(or simply the* vertex position number*) of G. Similarly, the minimum*

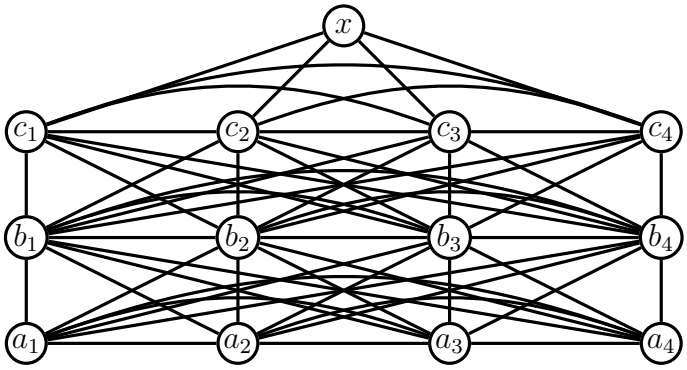

Figure 2.1

value of $p_x(G)$ among all vertices of G is called the minimum vertex position number $\mathrm{vp}^-(G)$ *of G.*

To illustrate these concepts, consider the graph G in Figure 2.1. We give the x-position numbers of G for representative vertices in Table 1, together with a (not necessarily unique) x-position set. We see from the table that $\mathrm{vp}^-(G) = 4$ and $\mathrm{vp}(G) = 11$.

Vertex	p_x-set	$p_x(G)$
x	$\{c_1, c_2, c_3, c_4\}$	4
c_1	$\{x, c_2, c_3, c_4, b_1, b_2, b_3, b_4\}$	8
b_1	$\{c_1, c_2, c_3, c_4, b_2, b_3, b_4, a_1, a_2, a_3, a_4\}$	11
a_1	$\{a_2, a_3, a_4, b_1, b_2, b_3, b_4\}$	7

Table 1

Unless stated otherwise (for example in Theorem 2.13) we assume all graphs to be connected. However, Definition 2.1 also applies to disconnected graphs; if x belongs to a component C of a disconnected graph G, then any vertex y from another component D of G can be included in an x-position set, as there is no x, y-path in G. Hence in this case $p_x(G) = (n - |C|) + p_x(C)$.

For any vertex $x \in V(G)$ the set $\{x\}$ is an x-position set; however, by the convention in Definition 2.1, if G is connected, then x is not contained in any x-position set of order ≥ 2. Hence for any connected graph G with order $n \geq 2$ we have $1 \leq p_x(G) \leq n - 1$ for any $x \in V(G)$ and, more generally, a (not necessarily connected) graph G has $\mathrm{vp}(G) = n$ if and only if G has

an isolated vertex. These bounds are sharp: for any path P_n of length ≥ 1 we have $p_x(P_n) = 1$ for either terminal vertex, whilst for $n \geq 2$ we have $p_x(K_n) = n - 1$ for every vertex of a complete graph K_n. In this section we derive several bounds for the vertex position numbers in terms of various graph parameters. First we compare the vertex position number with the general position number.

Lemma 2.2. *The vertex position number and general position number of a graph are related by* $\mathrm{vp}(G) \geq \mathrm{gp}(G) - 1$.

Proof. Let S be a gp-set of G with $|S| = \mathrm{gp}(G)$. Choose a vertex $x \in S$. Then $S \setminus \{x\}$ is an x-position set, implying that $\mathrm{vp}(G) \geq p_x(G) \geq \mathrm{gp}(G) - 1$. ∎

The bound in Lemma 2.2 is met by the complete graph K_n. However, we now give an example to show that the numbers $\mathrm{vp}^-(G)$, $\mathrm{gp}(G)$ and $\mathrm{vp}(G)$ can be arbitrarily far apart. For $r \geq 2$ we define the vertex set of the graph $G(r)$ to be $\{u_{i,j} : 1 \leq i \leq 7, 1 \leq j \leq r\} \cup \{x\}$. Let $H(r)$ be the graph on the same vertex set as $G(r)$ with adjacencies defined as follows:

- $x \sim u_{1,j}$ for $1 \leq j \leq r$,
- $u_{i,j} \sim u_{i,j'}$, $1 \leq i \leq 7$, $1 \leq j, j' \leq r$ and $j \neq j'$, and
- $u_{i,j} \sim u_{i+1,j'}$ for $1 \leq i \leq 6$ and $1 \leq j, j' \leq r$.

Now define $G(r)$ to be the graph formed by deleting all edges to the vertices $u_{3,1}$, $u_{4,1}$ and $u_{5,1}$ except for the path $u_{2,1}, u_{3,1}, u_{4,1}, u_{5,1}, u_{6,1}$. See Figure 2.2 for an example. The minimum vertex position number of this graph is r (attained at the vertex x) and the vertex position number is $6r - 4$ (attained at the vertex $u_{4,1}$).

Lemma 2.3. *For $r \geq 3$, we have* $\mathrm{vp}^-(G(r)) = r, \mathrm{gp}(G(r)) = 2r, \mathrm{vp}(G(r)) = 6r - 4$.

This raises the question of how far apart the numbers $\mathrm{vp}^-(G)$ and $\mathrm{vp}(G)$ can be.

Problem 2.4. *Is the ratio $\frac{\mathrm{vp}(G)}{\mathrm{vp}^-(G)}$ bounded for connected graphs?*

We now bound the vertex position numbers in terms of the vertex degrees.

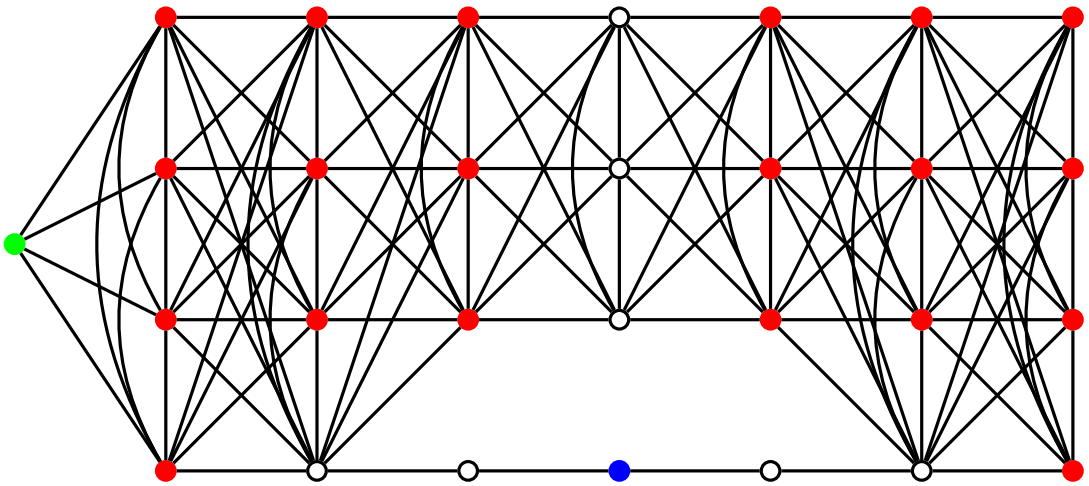

Figure 2.2: A graph with $\mathrm{vp}^- = r$ (green vertex) and $\mathrm{vp} = 6r - 4$ (blue vertex). A largest vp-set of the blue vertex is shown in red.

Lemma 2.5. *Let G have minimum degree δ and maximum degree Δ. Then $\mathrm{vp}^-(G) \geq \delta$ and $\mathrm{vp}(G) \geq \Delta$.*

Proof. It follows from Definition 2.1 that for any vertex x of G the neighbourhood $N(x)$ is an x-position set of G. Therefore for all vertices $x \in V(G)$ we have $p_x(G) \geq d(x)$. This implies that all p_x-sets have order at least δ and there exists a p_x-set with order at least Δ. ∎

We now generalise this result to sets of vertices at given distance from a fixed vertex; this leads to bounds on $p_x(G)$ in terms of the order n of G and the eccentricity $\mathrm{e}(x)$ of the vertex x.

Lemma 2.6. *For any vertex x of G with eccentricity $\mathrm{e}(x)$ the vertex position number satisfies $p_x(G) \geq \frac{n-1}{\mathrm{e}(x)}$. Thus $\mathrm{vp}^-(G) \geq \frac{n-1}{\mathrm{diam}(G)}$ and $\mathrm{vp}(G) \geq \frac{n-1}{\mathrm{rad}(G)}$.*

Proof. For $1 \leq t \leq \mathrm{e}(x)$, let V_t be the set of vertices at distance exactly t from x in G. Each of the sets V_t is an x-position set and one of them must have order at least $\frac{n-1}{\mathrm{e}(x)}$, so that $p_x(G) \geq \frac{n-1}{\mathrm{e}(x)}$. Since $\mathrm{rad}(G) \leq \mathrm{e}(x) \leq \mathrm{diam}(G)$ for all $x \in V(G)$ the result follows. ∎

This bound immediately characterises the graphs with vertex position number one.

Corollary 2.7. *A graph G satisfies* $\mathrm{vp}^-(G) = 1$ *if and only if G is a path. The only connected graphs with* $\mathrm{vp}(G) = 1$ *are K_1 and K_2.*

Proof. If x is the terminal vertex of a path P_n, then $p_x(P_n) = 1$. Conversely, if $\mathrm{vp}^-(G) = 1$, then by Lemma 2.6 we must have $\mathrm{diam}(G) = n - 1$, which implies that G is a path. By Lemma 2.5 any graph G with $\mathrm{vp}(G) = 1$ must have maximum degree $\Delta \leq 1$, which proves the latter statement. ∎

The argument of Lemma 2.6 also easily yields the vertex position number of the join of two graphs.

Corollary 2.8. *If G_i has order n_i and maximum degree Δ_i for $i = 1, 2$, then the vertex position number of the join is*

$$\mathrm{vp}(G \vee H) = \max\{n_1 + \Delta_2, n_2 + \Delta_1\}.$$

Proof. The diameter of G is two. For any vertex x in G_1 the set $V(G_2) \cup N_{G_1}(x)$ is an x-position set by Lemma 2.6 with order $n_2 + \Delta_1$, with a similar result for vertices y in G_2. Suppose without loss of generality that the largest vertex position set is attained at a vertex $x \in V(G_1)$. Then we can assume that a p_x-set contains a vertex of G_2, for otherwise $\mathrm{vp}(G) \vee H) = p_x(G \vee H) \leq n_1 < p_y(G \vee H)$ for any $y \in V(G_2)$, a contradiction. As a maximum p_x-set S_x contains a vertex of G_2, S_x cannot contain any vertex of $V(G_1) \backslash (\{x\} \cup N_{G_1}(x)$, so that $p_x(G \vee H) \leq n_2 + \Delta_1$. The result follows. ∎

Theorem 2.9. *For any connected graph G we have* $\mathrm{vp}^-(G) \geq \left\lceil \frac{\Delta+1}{3} \right\rceil$. *If G is bipartite, then* $\mathrm{vp}^-(G) \geq \left\lceil \frac{\Delta}{2} \right\rceil$.

Proof. Let G be a connected graph with maximum degree Δ and let x be a vertex of G with this degree. Let y be any vertex of G. If $y = x$, we have $p_y(G) \geq \Delta$, so suppose that $y \neq x$ and let $r \geq 0$ be the length of the shortest path from y to $N(x)$. Then it can be seen that the distance from y to any vertex of $\{x\} \cup N(x)$ is one of r, $r+1$ or $r+2$. It follows that one of the level sets of G in the distance partition with respect to y must have order at least $\frac{\Delta+1}{3}$. Hence $p_y(G) \geq \frac{\Delta+1}{3}$ and our proof is complete. If G is bipartite, then $N(x)$ is an independent set and the distance from y to any vertex of $N(x)$ is either r or $r+2$, so we can improve the bound to $\mathrm{vp}^-(G) \geq \frac{\Delta}{2}$ in this case. The constructions in Figures 2.3 show that both of these bounds are tight (in both cases x is a vertex with maximum degree and $p_y(G) = \mathrm{vp}^-(G)$). ∎

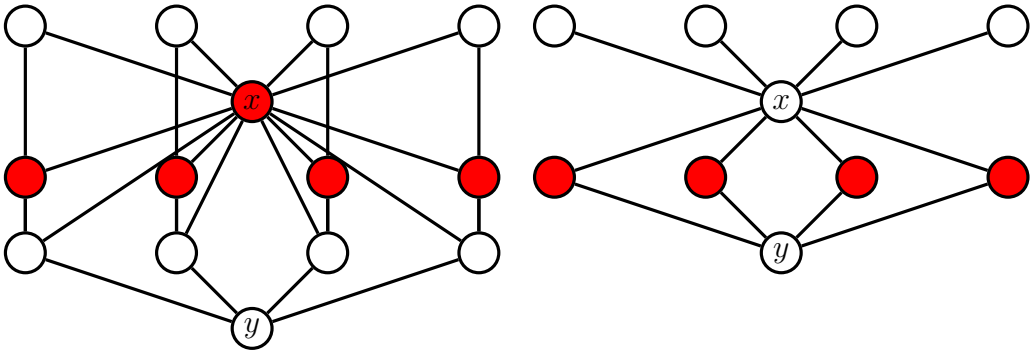

Figure 2.3: A graph with $\mathrm{vp}^-(G) = \left\lceil \frac{\Delta+1}{3} \right\rceil$ (left) and a bipartite graph with $\mathrm{vp}^-(G) = \frac{\Delta}{2}$ (right), with p_y-sets in red.

Now we give an upper bound for the vertex position number in terms of vertex eccentricity.

Lemma 2.10. *For any vertex x of G with eccentricity $\mathrm{e}(x)$, the x-vertex position number of G is bounded above by $p_x(G) \leq n - \mathrm{e}(x)$. Thus $\mathrm{vp}(G) \leq n - \mathrm{rad}(G)$ and $\mathrm{vp}^-(G) \leq n - \mathrm{diam}(G)$.*

Proof. Fix a vertex x of G with eccentricity $\mathrm{e}(x)$. Let y be an eccentric vertex of x, i.e. $d(x, y) = \mathrm{e}(x)$. Let $x = u_0, u_1, \ldots, u_{\mathrm{e}(x)} = y$ be an x, y-geodesic in G and S_x be an x-position set of G with order $p_x(G)$. Suppose that $u_i, u_j \in S_x$ for some i, j with $0 \leq i < j \leq \mathrm{e}(x)$. But then u_i lies on an x, u_j-geodesic, contradicting the fact that S_x is an x-position set. Hence any x-position set contains at most one vertex from the set $\{x, u_1, u_2, \ldots, u_{\mathrm{e}(x)}\}$. Thus $p_x(G) = |S_x| \leq n - 1 - \mathrm{e}(x) + 1 = n - \mathrm{e}(x)$. Thus $\mathrm{vp}(G) \leq n - \mathrm{rad}(G)$ and $\mathrm{vp}^-(G) \leq n - \mathrm{diam}(G)$. ∎

The following theorem improves the upper bound for $\mathrm{vp}(G)$ in Lemma 2.10.

Theorem 2.11. *For any graph G with $\mathrm{rad}(G) \geq 3$ we have $\mathrm{vp}(G) \leq n - \mathrm{rad}(G) - 1$.*

Proof. Suppose that G has radius $\mathrm{rad}(G) \geq 3$ and meets the upper bound in Lemma 2.10. Then the largest value of the vertex position number is achieved by a central vertex, call it u. Let S_u be any u-position set of order $n - \mathrm{rad}(G)$. By the argument of Lemma 2.10 there is a path P from u to one of its eccentric vertices such that P contains just one vertex of S_u and all vertices of $V(G) \setminus V(P)$ belong to S_u. As the shortest path from u to any

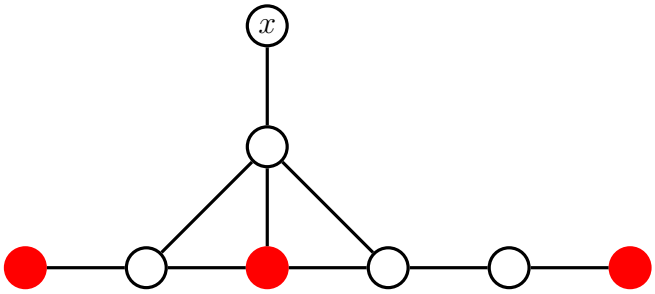

Figure 2.4: The boundary $\partial(x)$ (shown in red) is a p_x-set

vertex $x \in V(G) \setminus V(P)$ cannot pass through another vertex of $V(G) \setminus V(P)$, the shortest path from u to x consists of a section of P followed by an edge from P to x. Hence each vertex of $V(G) \setminus V(P)$ has an edge to P; however, this contradicts our supposition that u is a central vertex. ∎

A vertex v in a connected graph G is a *boundary vertex* of a vertex u if $d(u, w) \leq d(u, v)$ for each neighbour w of v. The set of all boundary vertices of u is denoted by $\partial(u)$.

Proposition 2.12. *For any connected graph G and any vertex $x \in V(G)$, the boundary $\partial(x)$ is an x-position set of G.*

Proof. Assume to the contrary that $\partial(x)$ is not an x-position set; hence there must be a geodesic $x = u_0, u_1, \ldots, u_i = z, u_{i+1}, \ldots, u_k = y$ such that $z, y \in \partial(x)$ and $z \neq y$. This shows that $d(x, u_{i+1}) > d(x, z)$, contradicting the fact that z is a boundary vertex of x. Hence $\partial(x)$ is an x-position set. ∎

It follows from Proposition 2.12 that for any $x \in V(G)$ the set $\mathrm{Ext}(G) \setminus \{x\}$ is an x-position set. The bound in Proposition 2.12 is tight for the vertex x in the graph in Figure 2.4, but this is not true in general. In fact for any $s \geq t$ if we take a vertex x in the partite set of order $t + 1$ in the complete bipartite graph $K_{s,t+1}$ then $|\partial(x)| = t$ but $p_x(K_{s,t+1}) = s$.

Finally we present a Nordhaus-Gaddum relation for the vertex position number.

Theorem 2.13. *For any graph G we have $n - 1 \leq \mathrm{vp}(G) + \mathrm{vp}(\overline{G}) \leq 2n - 1$. Both bounds are tight.*

Proof. Notice that one of G and $\overline{G}$ could be disconnected. Let x be any vertex of a graph G with degree $d(x)$. In the complement $\overline{G}$ the vertex x has

degree $d'(x) = n - 1 - d(x)$. By Lemma 2.5 we thus have

$$\mathrm{vp}(G) + \mathrm{vp}(\overline{G}) \geq p_x(G) + p_x(\overline{G}) \geq d(x) + n - 1 - d(x) = n - 1. \quad (1)$$

To show that equality holds, consider the cycle C_n for $n \geq 5$. If $n = 5$ the result is simple, as $\overline{C_5} \cong C_5$, so take $n \geq 6$. Label the vertices of the cycle $x_0, x_1, \ldots, x_{n-1}$, where $x_0 \sim x_{n-1}$ and $x_i \sim x_{i+1}$ for $0 \leq i \leq n-2$. As will be shown in Corollary 4.2, we have $\mathrm{vp}(C_n) = 2$. Consider the vertex x_0 (as $\overline{C}_n$ is vertex-transitive the choice is arbitrary) and let S be a largest x_0-position set. The degree of x_0 is $d(x) = n-3$, so that by Lemma 2.5 we have $\mathrm{vp}(\overline{C}_n) \geq n-3$. Suppose that a vertex x_i, $3 \leq i \leq n-3$, belongs to S; then as x_0, x_i, x_1 and x_0, x_i, x_{n-1} are shortest paths we must have $x_1, x_{n-1} \notin S$, so that $|S| \leq n-3$. Furthermore S cannot contain both vertices x_{n-2} and x_1 and likewise cannot contain both x_2 and x_{n-1}, so in any case $|S| \leq n-3$. Thus $\mathrm{vp}(\overline{C}_n) = n-3$ and we have $\mathrm{vp}(C_n) + \mathrm{vp}(\overline{C}_n) = n-1$.

Applying this argument to a vertex of maximum degree Δ and a vertex with minimum degree δ gives the stronger bound $\mathrm{vp}(G)+\mathrm{vp}(\overline{G}) \geq n-1+\Delta-\delta$, so we see that we have equality in Equation 1 if and only if G is regular and both G and $\overline{G}$ have vertex position number equal to their maximum degree.

Trivially for $n \geq 2$ we have $\mathrm{vp}(G) \leq n$, with equality if and only if G has an isolated vertex. Not both of G and $\overline{G}$ can have an isolated vertex, for if G has an isolated vertex, then $\overline{G}$ contains a universal vertex. Therefore we do not have equality in both $\mathrm{vp}(G) \leq n$ and $\mathrm{vp}(\overline{G}) \leq n$, so it follows that $\mathrm{vp}(G) + \mathrm{vp}(\overline{G}) \leq 2n-1$. Equality holds if and only if G contains an isolated vertex or a universal vertex. ∎

3. Vertex position numbers of certain classes of graphs

In this section, we determine the x-position number of certain standard classes of graphs.

Lemma 3.1. *Let x be a vertex of a connected graph G and $S_x \subseteq V(G)$ be an x-position set of G. If $C_1, C_2, \ldots, C_k$ are the components of $G[S_x]$, then there exist $r_1, r_2, \ldots, r_k$ such that $d(x, y) = r_i$ for all $y \in C_i$.*

Proof. Suppose that there is a component C of $G[S_x]$ and $y, y' \in V(C)$ such that $d(x, y) \neq d(x, y')$. Then, considering a shortest path from y to y' in $G[C]$, we see that there is a pair $z, z' \in V(C)$ such that $z \sim z'$ and $d(x, z') =$

$d(x,z)+1$. However, this implies that an x,z-geodesic followed by the edge $z \sim z'$ is a shortest x,z'-path that passes through z, a contradiction. ∎

Theorem 3.2. *If G is a bipartite graph, then* $\mathrm{vp}(G) \leq \alpha(G)$.

Proof. Let S_x be an x-position set of G and suppose for a contradiction that S_x is not an independent set. Then there are $y, z \in S_x$ such that $y \sim z$ in G. By Lemma 3.1 we have $d(x,y) = d(x,z) = r$ for some $r \geq 1$. A shortest x,y-path, a shortest x,z-path and the edge $y \sim z$ together constitute an odd circuit, implying the existence of an odd cycle; since G is bipartite, this is impossible and it follows that $p_x(G) \leq \alpha(G)$. ∎

Theorem 3.3. *For $r \geq 2$, let $K_{n_1,n_2,\ldots,n_r}$ be the complete multipartite graph with partite sets $V_1, V_2, \ldots, V_r$, where $n_i = |V_i|$ and $n_1 \geq n_2 \geq \cdots \geq n_r$. Set $n = \sum_{i=1}^{r} n_i$. Then if the vertex x lies in V_i, the x-position number is given by*

$$p_x(K_{n_1,n_2,\ldots,n_r}) = \max\{n - n_i, n_i - 1\}.$$

Thus $\mathrm{vp}(K_{n_1,n_2,\ldots,n_r}) = n - n_r$.

Proof. Let $x \in V_i$ and let S be a maximum x-position set of the graph. Set $V = \bigcup_{i=1}^{r} V_i$. Suppose that S contains a vertex $y \in V_i \setminus \{x\}$; for any vertex $z \in V \setminus V_i$ the path x, z, y is a geodesic, so that in this case $S \cap (V \setminus V_i) = \emptyset$. Thus either $S \subseteq V \setminus V_i$ or $S \subseteq V_i \setminus \{x\}$. Conversely, both of these sets are x-position sets by the argument of Lemma 2.6, which yields the claimed bounds. ∎

Theorem 3.3 shows that equality holds in the bound of Theorem 3.2 for all complete bipartite graphs.

Lemma 3.4. *Let G be a connected graph of order n. Then for each $x \in V(G)$ there is a maximum x-position set without cutvertices.*

Proof. Suppose that there is a maximum x-position set M containing a cutvertex $v \neq x$ of G. Let $C_1, C_2, \ldots, C_k$ be the components of $G \setminus \{v\}$, where $k \geq 2$. Without loss of generality we may assume that $x \in V(C_1)$. Then it follows that $M \cap V(C_i) = \emptyset$ for all $i = 2, 3, \ldots, k$. Let u_i be any vertex in C_i for all $i = 2, 3, \ldots, k$. If $k \geq 3$, then the set $M' = (M \setminus \{v\}) \cup \{u_2, u_3, \ldots, u_k\}$ is an x-position set with order greater than M, a contradiction to the maximality of M. Hence $k = 2$. Let u be a farthest vertex from v in C_2. Then u is not a cutvertex in G. Moreover, $M' = (M \setminus \{v\}) \cup \{u\}$ is a maximum x-position set containing fewer cutvertices than M; this implies the existence of a maximum x-position set without cutvertices in G. ∎

Theorem 3.5. *For any block graph G,*

$$p_x(G) = \begin{cases} \mathrm{s}(G) - 1, & \text{if } x \text{ is a simplicial vertex,} \\ \mathrm{s}(G), & \text{otherwise.} \end{cases}$$

Proof. First suppose that x is a simplicial vertex. Then it is clear that $\mathrm{s}(G) \setminus \{x\}$ is an x-position set in G. Hence $p_x(G) \geq \mathrm{s}(G) - 1$. On the other hand, in a block graph each vertex is either a cutvertex or a simplicial vertex. By the above lemma, G contains a maximum x-position set without cutvertices. Hence the result follows. ∎

Corollary 3.6. *For any tree T with ℓ leaves we have*

$$p_x(T) = \begin{cases} \ell - 1, & \text{if } x \text{ is a leaf,} \\ \ell, & \text{otherwise.} \end{cases}$$

Corollary 3.6 implies the following bound for the vertex position numbers in terms of the girth of the graph.

Theorem 3.7. *If a graph G has girth g and minimum degree $\delta \geq 2$ and there are N vertices at distance less than or equal to $\left\lfloor \frac{g-1}{2} \right\rfloor - 1$ from a vertex u, then $p_u(G) \leq n - N$.*

Proof. Set $r = \left\lfloor \frac{g-1}{2} \right\rfloor$. Fix a vertex u of G and consider the subgraph G' induced by the vertices at distance at most r from u. G' is isomorphic to a tree, possibly with some edges added between the vertices at distance r from u. It follows from Corollary 3.6 that the largest number of vertices from G' that can belong to a u-position set is the number of vertices at distance exactly r from u; hence there are at least N vertices missing from any u-position set and $p_u(G) \leq n - N$. ∎

Theorem 3.7 is tight for the Petersen and Hoffman-Singleton graphs by Lemma 2.6. Finally, we note that Lemma 2.5 gives the vertex position number of sufficiently large Kneser graphs. The Kneser graph $K(n, k)$ is the graph with vertex set equal to all k-subsets of $\{1, 2, \ldots, n\}$ with an edge between any two such subsets if and only if they are disjoint.

Theorem 3.8. *For sufficiently large n we have* $\mathrm{vp}(K(n, k)) = \binom{n-k}{k}$.

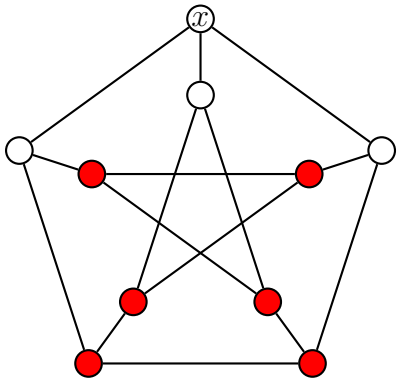

Figure 3.1: A largest x-position set (red vertices) in the Petersen graph

Proof. For $n \geq 3k$ the Kneser graph $K(n,k)$ has diameter two. Note that $K(n,k)$ is vertex-transitive, so $\mathrm{vp}(K(n,k)) = \mathrm{vp}^-(K(n,k))$ and we can without loss of generality consider the vertex $\{1,2,\ldots,k\}$; let S be a largest $\{1,2,\ldots,k\}$-position set. Lemma 2.5 gives $|S| = \mathrm{vp}(K(n,k)) \geq \binom{n-k}{k}$. Suppose that S contains a vertex at distance two from $\{1,2,\ldots,k\}$, say $\{1,2,\ldots,i,j_{i+1},j_{i+2},\ldots,j_k\}$, where

$$\{1,2,\ldots,k\} \cap \{1,2,\ldots,i,j_{i+1},j_{i+2},\ldots,j_k\} = \{1,2,\ldots,i\}.$$

As $\{1,2,\ldots,k\}$ and $\{1,2,\ldots,i,j_{i+1},j_{i+2},\ldots,j_k\}$ have exactly $\binom{n-2k+i}{k}$ common neighbours, we would have $|S| \leq \binom{n}{k} - \binom{n-2k+i}{k}$, which is a polynomial of degree $k-1$, whereas the vertex degree is a polynomial function of n with degree k. Thus for sufficiently large n compared to k the bound in Lemma 2.5 is best possible. ∎

Interestingly Theorem 3.8 implies that for large n the vertex position number of $K(n,k)$ is significantly larger than the general position number, as given in [11]. For small n Lemma 2.5 is not optimal; for example, as previously noted for the Petersen graph P (isomorphic to $K(5,2)$) the second neighbourhood of a vertex is a largest vertex position set and $\mathrm{vp}(P) = \mathrm{gp}(P) = 6$.

4. Characterisation results

We now make use of the bounds derived in Section 2 to characterise graphs with very large or very small vertex position numbers.

Corollary 4.1. *A connected graph G with order n satisfies* $\mathrm{vp}(G) = n-1$ *if and only if G contains a universal vertex, whilst* $\mathrm{vp}^-(G) = n-1$ *if and only if G is a complete graph.*

Proof. By Lemma 2.5 any universal vertex u has vertex position number $p_u(G) = n-1$. Conversely, by Lemma 2.10 any vertex u with $p_u(G) = n-1$ has eccentricity one and hence is universal. If $\mathrm{vp}^-(G) = n-1$, it follows that G is complete. ∎

Corollary 4.2. *A connected graph G satisfies* $\mathrm{vp}^-(G) = \mathrm{vp}(G) = 2$ *if and only if G is a cycle. Similarly* $\mathrm{vp}(G) = 2$ *only for cycles and paths of length* ≥ 2.

Proof. Let C_n be a cycle for some $n \geq 3$. As C_n is 2-regular, by Lemma 2.5 we have $\mathrm{vp}^-(C_n) \geq 2$. We now show that $\mathrm{vp}(C_n) \leq 2$. Let x be any vertex of C_n and suppose that there exists an x-position set S_x of C_n of order ≥ 3; we can assume that $x \notin S_x$. Let A be the set of antipodal vertices of x, i.e. the vertices of C_n at distance $\lfloor \frac{n}{2} \rfloor$ from x. We have $|A| = 1$ if n is even and $|A| = 2$ if n is odd. Let P_1 and P_2 be the two shortest paths from x to A. Then one of P_1 and P_2 (say P_2) contains distinct vertices $u, v \in S_x$. Hence either u is on the v, x-geodesic or v is on the u, x-geodesic, a contradiction. Hence $|S_x| \leq 2$ and, since x is an arbitrary vertex of C_n, we have $\mathrm{vp}^-(C_n) = \mathrm{vp}(C_n) = 2$.

Conversely, suppose that $\mathrm{vp}(G) = 2$; it follows from Lemma 2.5 that G has maximum degree $\Delta = 2$, so that G is either a path or a cycle. As $\mathrm{vp}^-(P_\ell) = 1$ for paths by Corollary 2.7, it follows that if $\mathrm{vp}^-(G) = 2$, then G is a cycle. ∎

Now we characterise some graphs with very large vertex position number.

Lemma 4.3. *A vertex u of a connected graph G with order n has $p_u(G) = n-2$ if and only if either i) u has degree $d(u) = n-2$, or ii) u has a neighbour v such that v is a cutvertex of G and $\{u, v\}$ dominates G, in which case the unique largest p_u-set of G is $S_u = V(G) \setminus \{u, v\}$.*

Proof. Let G be a graph with order n and let $u \in V(G)$ satisfy $p_u(G) = n-2$, with S_u a largest u-position set. If u is a universal vertex, then by Corollary 4.1 we would have $p_u(G) = n-1$, so u has degree $d(u) \leq n-2$. Hence by Lemma 2.10 u has eccentricity two. If $d(u) = n-2$, then $N(u)$ is a u-position set, so we can assume that $d(u) \leq n-3$. Hence $V(G) = \{u\} \cup N(u) \cup N^2(u)$ and $|N^2(u)| \geq 2$.

Let x, y be any vertices in $N^2(u)$. Suppose that one of these vertices, say x, has at least two common neighbours with u. If $x \in S_u$, then we must have $N(x) \cap N(u) \cap S_u = \emptyset$; however, this contradicts $u \notin S_u$, implying that $x \notin S_u$ and $S_u = V(G) \setminus \{u, x\}$, so that $N(u) \subseteq S_u$. As $y \in N^2(u) \cap S_u$ and has a neighbour in $N(u)$, this is also a contradiction. Therefore every vertex in $N^2(u)$ has just one neighbour in $N(u)$.

Suppose that $N(u) \cap N(x) = \{v\}$ and $N(u) \cap N(y) = \{v'\}$, where $v \neq v'$. Then $|S_u \cap \{v, x\}| \leq 1$ and $|S_u \cap \{v', y\}| \leq 1$, which, together with u, accounts for at least three vertices missing from S_u. Thus we must have $v = v'$ and there is a vertex $v \in N(u)$ that is the unique neighbour in $N(u)$ of every vertex in $N^2(u)$. Hence $\{u, v\}$ dominates G. Furthermore in any such graph $V(G) \setminus \{u, v\}$ is a u-position set, so that $\mathrm{vp}(G) = n - 2$. ∎

Theorem 4.4. *For $n \geq 4$, a graph G with order n satisfies $\mathrm{vp}^-(G) = \mathrm{vp}(G) = n - 2$ if and only if G is isomorphic to an even clique with a perfect matching deleted, i.e. if and only if $G \cong K_{2,2,\ldots,2}$.*

Proof. Assume that G is a graph such that $p_u(G) = n - 2$ for every $u \in V(G)$. Suppose that G contains a vertex u with degree $\leq n - 3$, so that by Lemma 4.3 u has eccentricity two and u has a neighbour v that is a cutvertex of G and $\{u, v\}$ is a dominating set of G. As $\mathrm{vp}(G) = n - 2$, G contains no universal vertex, so that there is a neighbour w of u such that $v \not\sim w$. Hence if $x \in N^2(u)$ we have $d(x, w) \geq 3$ and x has eccentricity at least three, so that by Lemma 2.10 we have $p_x(G) \leq n - 3$, a contradiction. Therefore every vertex of G has degree $n - 2$ and G is isomorphic to a K_{2r} with a perfect matching deleted. Conversely in such a graph every vertex has vertex position number $n - 2$. ∎

Theorem 4.5. *For $n \geq 4$, a graph G has $\mathrm{vp}^-(G) = n-2$ and $\mathrm{vp}(G) = n-1$ if and only if i) G is isomorphic to a clique with a non-empty, non-perfect matching deleted or ii) G is the join of K_1 with a disjoint union of cliques.*

Proof. Let G be a graph with $\mathrm{vp}^-(G) = n - 2$ and $\mathrm{vp}(G) = n - 1$. We can assume that G contains $r \geq 1$ universal vertices as well as at least two vertices with degree $\leq n-2$. If every vertex has degree either $n-1$ or $n-2$, then G is isomorphic to a clique with a matching deleted. To avoid the graph having $\mathrm{vp}^-(G) = \mathrm{vp}(G) = n - 1$ the matching is non-empty and to avoid having $\mathrm{vp}^-(G) = \mathrm{vp}(G) = n-2$ the matching is not perfect by Theorem 4.4.

Suppose that G contains a vertex u with $p_u(G) = n - 2$ and degree $d(u) \leq n - 3$. By Lemma 4.3 u has eccentricity two and has a neighbour

v that is a cutvertex. By Lemma 2.10 every vertex of G has eccentricity at most two, so, considering the vertices in $N^2(u)$, we see that v is a universal vertex. As v is a cutvertex, it is the unique universal vertex of G, so that every other vertex w of G must have $p_w(G) = n-2$. For any $w \in V(G) \setminus \{v\}$, let S_w be a w-position set of order $n-2$. Suppose that $v \in S_w$. Then S_w cannot contain w or any vertex from a component of $G - v$ not containing w; this impossible unless $G \cong P_3$, which has the stated structure, so we can assume that $S_w = V(G) \setminus \{w, v\}$ for each $w \in V(G) \setminus \{v\}$. Suppose then that there is a component W of $G-v$ that is not a clique, so that there are vertices w_1, w_2, w_3 in W such that w_1, w_2, w_3 is a path, but $w_1 \not\sim w_3$. However, this implies that w_2 and w_3 cannot both belong to a largest w-position set S_{w_1}, which is a contradiction, since $S_{w_1} = V(G) \setminus \{w_1, v\}$. Hence the graph must be the join of K_1 with a disjoint union of cliques, which is easily verified to have the correct vertex position numbers. ∎

5. Computational complexity

Given a graph G, in this section we show that the vertex position number $p_x(G)$ can be computed in polynomial time for any vertex $x \in V(G)$. In particular, we will show that $p_x(G)$, for each $x \in V(G)$, can be computed as an independent set calculated on a graph obtained as a transformation of G. To this aim we need the following definitions.

Definition 5.1. *A graph is a* comparability graph *if the edges connect pairs of elements that are comparable to each other in a partial order.*

Definition 5.2. *Given a graph G and a vertex $x \in V(G)$, the* reduced *graph $\widetilde{G}_x$ is the graph on the same vertices $V(G)$ obtained from G by removing all the edges connecting vertices at the same distance from x.*

Definition 5.3. *Given a graph G and a vertex $x \in V(G)$, the graph G^*_x is the graph on the same vertices $V(G)$ obtained from the reduced graph $\widetilde{G}_x$ by adding an edge between any two vertices of any geodesic to x.*

See Figure 5.1 for a visualisation of $\widetilde{G}_x$ and G^*_x, starting from a graph G and a vertex x.

Lemma 5.4. *Given a graph G and a vertex $x \in V(G)$, G^*_x is a comparability graph.*

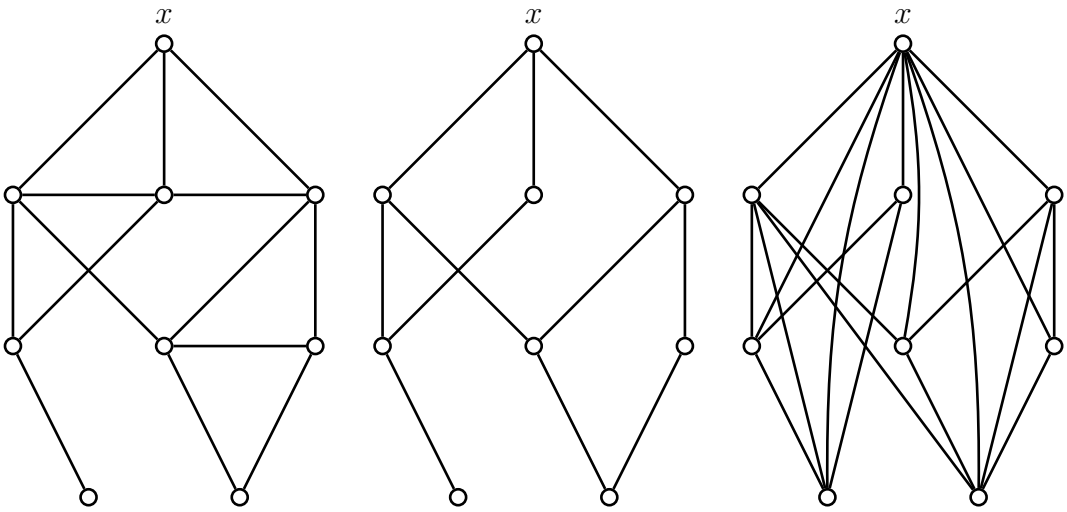

Figure 5.1: From left to right: a graph G with a vertex x, the graph $\widetilde{G}_x$, and the graph G_x^*. The graphs G and $\widetilde{G}_x$ are drawn by placing the vertices at the same distance from x on a common horizontal level.

Proof. The partial order underlying the graph G_x^* consists of its vertices and, by definition, two vertices $u, v \in V(G_x^*)$ are such that $u < v$ if u and v are on the same geodesic to x and $d(u,x) < d(v,x)$. Since G_x^* has been built from $\widetilde{G}_x$ by adding an edge between every pair of vertices on each geodesic to x, then any two comparable vertices are adjacent and hence G_x^* is a comparability graph. ∎

Lemma 5.5. *Given a graph G and a vertex $x \in V(G)$, S_x is an x-position set of G if and only if S_x is an x-position set for $\widetilde{G}_x$. Then $p_x(G) = p_x(\widetilde{G}_x)$.*

Proof. Note that any geodesic to x in G is also a geodesic to x in $\widetilde{G}_x$. Then S_x is a x-position set for G if and only if there are no two vertices on the same geodesic to x in G, that is, if and only if there are no two vertices on the same geodesic to x in $\widetilde{G}_x$. Hence, if and only if S_x is a x-position set for $\widetilde{G}_x$. As consequence, any maximum vertex position set of G_x is a maximum vertex position set for $\widetilde{G}_x$. Then $p_x(G) = p_x(\widetilde{G}_x)$. ∎

Given a graph G, let us denote the graph induced by vertices in $V(G)\backslash\{x\}$ as $G - x$.

Lemma 5.6. *Given a graph G and a vertex $x \in V(G)$, S_x is an x-position set of G if and only if S_x is an independent set of $G_x^* - x$. Then $p_x(G) = \alpha(G_x^* - x)$.*

Proof. Let S_x an x-position set in G. By Lemma 5.5, S_x is also a x-position set in $\widetilde{G}_x$. Assume that S_x is not an independent set in $G_x^* - x$. Then there are two adjacent vertices $u, v \in V(G_x^* - x) \cap S_x$. By definition of G_x^*, u and v are on the same geodesic to x in $\widetilde{G}_x$ and then in G, a contradiction.

Assume now that S_x is an independent set of $G_x^* - x$. Let $u \in S_x$ and let P be any $u - x$ geodesic in G. Then it follows from the construction of G_x^* that u is adjacent to all the vertices of $V(P - u)$ in G_x^*. This immediately shows that $V(P) \cap S_x = \{u\}$. Consequently, S_x is a x-position set in G and hence $p_x(G) = \alpha(G_x^* - x)$. ∎

Theorem 5.7. *Given a graph G and a vertex $x \in V(G)$, a maximum x-position set can be computed in $O(nm \log(n^2/m))$ time, where $n = |V(G_x^*)|$ and $m = |E(G_x^*)|$.*

Proof. Algorithm A in Figure 5.2 compute the distances of each vertex $v \in V(G)$ from x at Line 1. This requires $O(n + m)$ time. With the loop at Line 2, $\widetilde{G}_x$ is computed from G by removing edges between vertices at the same distance from x. This requires $O(m)$ time. The loop at Line 5 add edges to the graph in order to build G_x^*. This requires $O(n^2 + nm)$ time since Lines from 6 to 14 codifies for a breadth-first visit of the vertices on a geodesic to x passing through a vertex u. This visit, based on a queue Q and a set R of the visited vertices, requires $O(n + m)$ time and since it is repeated for each vertex u in $V(G-x)$, the total time is $O(n^2+nm)$. Finally, at Line 15 an independent set S of the resulting comparability graph $G^* - x$ is computed. According to [12], the computation of an independent set for a comparability graph requires $O(nm \log(n^2/m))$. The last step determines the computational time of the whole algorithm. By Lemma 5.6, the set S is also a x-position set of G, then Algorithm A correctly returns S and its order. ∎

Corollary 5.8. *Given a graph G, $\mathrm{vp}^-(G)$ and $\mathrm{vp}(G)$ can be computed in $O(n^4 \log(n))$ time, where $n = V(G)$.*

Proof. Given a graph G, by calling Algorithm A for each vertex x of G, $\mathrm{vp}^-(G)$ and $\mathrm{vp}(G)$ can be easily computed. Since by Theorem 5.7 each call

Algorithm A:
Input: A connected graph G, a vertex $x \in V(G)$
Output: A maximum x-position set S_x, and $p_x(G)$

```
1  Let D[u] := d(u, x), for each u ∈ V(G);
2  for each uv ∈ E(G) do
3      if D[u] = D[v] then
4          remove uv from E(G);
5  for each u ∈ V(G − x) do
6      Let Q be a queue and R := {u};
7      Q.enqueue(u);
8      while Q is not empty do
9          v := Q.dequeue();
10         for each w in N_G(v) \ R such that D[w] > D[v] do
11             Q.enqueue(w);
12             R := R ∪ {w};
13             if D[w] > D[u] + 1 then
14                 add uv to E(G);
15 Let S a maximum independent set of G − x;
16 return S, |S|
```

Figure 5.2: Algorithm A to compute a maximum x-position set S_x of a graph G and $p_x(G)$, for a given $x \in V(G)$.

requires $O(nm\log(n^2/m))$, where $n = |V(G_x^*)|$ and $m = |E(G_x^*)|$. Considering that $n = |V(G_x^*)| = |V(G)|$ and $m = O(n^2)$, each call requires $O(n^3\log(n))$ time, for a total of $O(n^4\log(n))$ time. ∎

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Computational and structural aspects of the geodetic and the hull numbers of shadow graphs ☆

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Abstract

Given a set $X \subseteq V(G)$, let $[X]_G$ denote the set of all vertices of G lying on some shortest path between two vertices of X. If $[X]_G = X$, then X is a convex set of G. The convex hull of X, denoted by $\langle X \rangle_G$, is the smallest convex set containing X. We say that X is a hull set of G if $\langle X \rangle_G = V(G)$ and that X is a geodetic set of G if $[X]_G = V(G)$. The hull number $h(G)$ of G is the minimum cardinality of a hull set of G; and the geodetic number $g(G)$ of G is the minimum cardinality of a geodetic set of G. The shadow graph of G, denoted by $S(G)$, is the graph obtained from G by adding a new vertex v' for each vertex v of G and joining v' to the neighbors of v in G. In this paper, we present sharp bounds for the geodetic and the hull numbers of shadow graphs. We characterize the classes of graphs for which some of these bounds are attained. We also prove for a fixed integer k, that the problem of deciding whether $g(S(G)) \leq n - k$ is NP-complete even if the diameter of G is 2; and that the problem of deciding whether $h(S(G)) \leq n - 1$ belongs to P.

Introduction

We consider finite, simple and undirected graphs. In the graph convexity induced by the shortest paths of a graph G, the *interval* of a set $X \subseteq V(G)$ is formed by the vertices lying on some shortest path between two vertices of X. Sometimes, it will be useful to write $[u, v]_G$ standing for $[\{u, v\}]_G$. Set X is *(geodesically) convex* if $[X]_G = X$. We say that X is a *geodetic set of* G if $[X]_G = V(G)$. The *geodetic number* of G, denoted by $g(G)$, is the cardinality of a minimum geodetic set of G. The *convex hull* $\langle X \rangle_G$ of X is the smallest convex set that contains X, and X is a *hull set* of G if $\langle X \rangle_G = V(G)$. The cardinality of a smallest hull set of G is the *hull number* $h(G)$ of G. Since every geodetic set is also a hull set, it holds that $h(G) \leq g(G)$. An extensive survey on this graph convexity can be found in[20] and on abstract convexities in[25]. We also refer[13], [15] for other (hyper)graph convexities and parameters. The geodetic number of a graph was introduced in [1], [2], [6], [8], [9], [18], [20], [22] contain numerous results and references concerning geodetic sets and the geodetic number. The hull number of a graph was introduced by Everett and Seidman in[14]. See[2], [7], [12], [20] for recent developments on the hull sets and the hull number of a graph. The hull number of composition, Cartesian product and strong product of graphs were studied in [3], [4], [5], [23].

One of the most studied parameters associated with graphs is the chromatic number. The *chromatic number* $\chi(G)$ of G is the minimum number of colors that can be assigned to the vertices of G so that adjacent vertices are colored differently. It is clear that $\chi(G) \geq \omega(G)$, where $\omega(G)$ is the cardinality of a largest clique in G. However, a graph G may have arbitrarily large chromatic

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A note on the convexity number of the complementary prisms of trees

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Abstract

A set of vertices S of a graph G is a (geodesically) convex set, if S contains all the vertices belonging to any shortest path connecting two vertices of S. The cardinality of a maximum proper convex set of G is called the convexity number, $\mathbf{con}(G)$, of G. The complementary prism $G\overline{G}$ of G is obtained from the disjoint union of G and its complement $\overline{G}$ by adding the edges of a perfect matching between them. In this work, we examine the convex sets of the complementary prism of a tree and derive formulas for the convexity numbers of the complementary prisms of all trees.

Introduction

A *finite convexity space* is a pair $(V, \mathscr{C})$ consisting of a non-empty finite set V and a collection $\mathscr{C}$ of subsets of V such that $\emptyset \in \mathscr{C}$, $V \in \mathscr{C}$ and $\mathscr{C}$ is closed under intersections. The elements of $\mathscr{C}$ are called *convex sets*. An extensive survey of abstract convexity and related combinatorial geometry can be found in[12], [13], [21]. Different convexities associated with the vertex set of a graph are well-known. The most natural convexities in graphs are path convexities defined by a family of paths $\mathscr{P}$, in a way that a set T of vertices of G is *convex* if and only if each vertex that lie on a (u, v)-path of $\mathscr{P}$ belongs to T. An extensive survey of different types of path convexities can be found in[20].

In this paper, we consider the geodesic convexity in graphs. In this convexity, $\mathscr{P}$ is the family of geodesics (shortest paths) of the graph. A set of vertices S of a graph G is a (*geodesically*) *convex set*, if S contains all the vertices belonging to any shortest path connecting two vertices of S. The cardinality of a maximum proper convex set of G is called the *convexity number*, $\mathbf{con}(G)$, of G.

Let us briefly recall the progress on the convexity number so far. The convexity number of a graph was introduced by G. Chartrand, C. E. Wall and P. Zhang in[7]. In[14], it is proved that the decision problem associated with the convexity number is NP-complete. The convex sets and the convexity number of a graph have been further investigated in a sequence of papers[10], [12], [13], [17]. The convexity numbers of join, Cartesian products and lexicographic products have been further studied in[1], [4].

If G is a graph and $\overline{G}$ its complement, then the *complementary prism* $G\overline{G}$ of G is the graph formed from the disjoint union of G and $\overline{G}$ by adding the edges of a perfect matching between the corresponding vertices of G and $\overline{G}$[16]. For example, $C_5\overline{C}_5$ is the Petersen graph. Solely from this particular reason, but also from many additional ones, complementary prisms were studied from different perspectives. Since the Petersen graph is a key example in the theory of edge colourings, it is no surprise that the chromatic index of complementary prisms was studied in[22]. Other topics studied on complementary prisms include domination[15], cycle structure[18], complexity properties[11], spectral properties[5], hull number[9], b-chromatic number[2] and general position number[19].

The convexity number of complementary prisms has been investigated in [6]. In [6], $\mathbf{con}\left(G\overline{G}\right)$ is determined when G or $\overline{G}$ is disconnected and it is proved that the decision problem related associated to the convexity number is NP-complete even restricted to

The general position achievement game played on graphs

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Abstract

A general position set of a graph G is a set of vertices S in G such that no three vertices from S lie on a common shortest path. In this paper we introduce and study the general position achievement game. The game is played on a graph G by players A and B who alternatively pick vertices of G. A selection of a vertex is legal if has not been selected before and the set of vertices selected so far forms a general position set of G. The player who selects the last vertex wins the game. Playable vertices at each step of the game are described, and sufficient conditions for each of the players to win is given. The game is studied on Cartesian and lexicographic products. Among other results it is proved that A wins the game on $K_n \,\square\, K_m$ if and only if both n and m are odd, and that B wins the game on $G \circ K_n$ if and only if either B wins on G or n is even.

Key words: general position set; achievement game; Cartesian product of graphs; lexicographic product of graphs

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1 Introduction

The general position problem for graphs was independently introduced and researched in [17, 27], but should be noted that in the case of hypercubes, it has been studied much earlier by Körner [15]. Among motives for introducing the problem is the more than a century old no-three-in-line problem of Dudeney [5], see also [16, 19, 23]. For the related general position subset selection problem in computational geometry see [6, 22].

A *general position set* of a graph $G = (V(G), E(G))$ is a set of vertices $S \subseteq V(G)$ such that no three vertices from S lie on a common shortest path of G. The general position problem asks for the largest possible size of a general position set of G; this number is denoted by $\mathrm{gp}(G)$. Immediately after its introduction, the concept received a great response [2, 7, 11–13, 18, 21, 24–26, 28]. Furthermore, in [14] general position sets have been extended to general d-position sets, while in [10] the Steiner general position problem was studied.

In this paper we study the achievement game associated with general position sets. Achievement games have already been studied in different contexts. For instance, in a finite group two players in turn select previously unselected elements of the group, and the player who is the first to achieve a generating set from the jointly selected elements wins the game [1,3]. Similarly, and closer to our game, two players in turn select vertices of a finite graph, and the player who first plays such a vertex that the union of the intervals between the vertices played contains all the vertices wins the game [4, 9, 20].

Let G be a graph. Then the *general position achievement game* (*gp achievement game* for short) is played by two players, *player A* and *player B*. The first player A chooses a vertex v_1. The second player B then chooses a vertex $v_2 \neq v_1$. Next A picks a vertex $v_3 \in V(G) \setminus \{v_1, v_2\}$ such that the set $\{v_1, v_2, v_3\}$ is a general position set in G. The game then proceeds along the same way and ends when there is no more vertex to be played, that is, there exists no vertex such that the general position set consisting of the already played vertices could be enlarged. The player who has played the last vertex wins the game.

We proceed as follows. In the rest of this section, additional definitions and notation needed are recalled. In the next section we give some general results and provide several examples. Among other results we observe that A wins the gp achievement game on a bipartite graph G if and only if the number of isolated vertices in G is odd. In Section 3 we study the game on Cartesian products, while in Section 4 we prove that B wins the game on the lexicographic product $G \circ K_n$ if and only if either B wins on G or n is even. At the end several concluding remarks are given, among which a closely related avoidance game is commented.

All graphs considered are finite, simple, and without loops or multiple edges.

The *distance* $d_G(u,v)$ between vertices u and v of G is the length of a shortest u,v-path. A u,v-path of minimum length is also called an u,v-*geodesic*. The *interval* $I_G[u,v]$ between u and v is the set of vertices that lie on some u,v-geodesic of G. For $S \subseteq V(G)$, we set $I_G[S] = \bigcup_{u,v \in S} I_G[u,v]$. A subgraph H of a graph G is *convex* if for every $u,v \in V(G)$, every u,v-geodesic in G lies completely in H.

2 Some general results and examples

The sequence of vertices played in the achievement game on a graph G will be denoted by $a_1, b_1, a_2, b_2, \ldots$, that is, the vertices played by A are $a_1, a_2, \ldots$, and the vertices played by B are $b_1, b_2, \ldots$ For instance, we may say that A starts the game by playing $a_1 = x$, where $x \in V(G)$. Suppose that $x_1, \ldots, x_j$ are vertices played so far on the graph G. Then we say that $y \in V(G)$ is a *playable vertex* if $y \notin \{x_1, \ldots, x_j\}$ and $\{x_1, \ldots, x_j\} \cup \{y\}$ is a general position set of G. Let $\mathrm{Pl}_G(x_1, \ldots, x_j)$ be the set of all playable vertices after the vertices $x_1, \ldots, x_j$ have already been played; we may sometimes simplify the notation $\mathrm{Pl}_G(x_1, \ldots, x_j)$ to $\mathrm{Pl}_G(\ldots x_j)$. For instance, if x and y are arbitrary vertices of a path P, then $\mathrm{Pl}_P(x) = V(P) \setminus \{x\}$ and $\mathrm{Pl}_P(x,y) = \emptyset$. Denoting by S the set of vertices $\{x_1, \ldots, x_j\}$ played so far, we may also write $\mathrm{Pl}_G(S)$ for $\mathrm{Pl}_G(x_1, \ldots, x_j)$. In the sequel we will implicitly but frequently use the following description of playable vertices.

Lemma 2.1 *Let S be the sequence of played vertices so far in a gp achievement game on a graph G. Then $x \in \mathrm{Pl}_G(S)$ if and only if the following two conditions hold:*

(i) if $u,v \in S$, then $x \notin I[u,v]$, and

(ii) if $u \in S$, then $I[x,u] \cap S = \{u\}$.

Proof. By definition, $x \in \mathrm{Pl}_G(S)$ if and only if $S \cup \{x\}$ is a general position set. Since S is a general position set by the assumption of the game, deciding whether $S \cup \{x\}$ is a general position set reduces to checking the conditions (i) and (ii). □

Let us next look at some examples. Since in a complete graph every vertex subset is a general position set, A wins the gp achievement game on the complete graph K_n if and only if n is odd. In the course of the gp achievement game on a graph G of order at least 2, at least two vertices will be played. Hence B wins the game on graphs G with $\mathrm{gp}(G) = 2$. As proved in [27], the only graphs with $\mathrm{gp}(G) = 2$ are paths and C_4. On the other hand, the class of graphs G with $\mathrm{gp}(G) = 3$ has not yet been characterized. If $\mathrm{gp}(G) = 3$, then gp achievement game will take either two or three moves. In fact, if $\mathrm{gp}(G) = 3$ then B wins the gp achievement game if only only

if every vertex of G lies in a maximal general position set of order 2. Applying this observation to cycles we infer that B wins the gp achievement game on the cycle C_n, $n \geq 3$, if and only if n is even.

The following result is simple but at the same time quite useful.

Theorem 2.2 *Let G be a graph. Then the following holds.*

(i) If A has a strategy such that after the vertex a_k, $k \geq 1$, is played, the set $\mathrm{Pl}_G(\ldots a_k) \cup \{a_1, b_1, \ldots, a_k\}$ is a general position set and $|\mathrm{Pl}_G(\ldots a_k)|$ is even, then A wins the gp achievement game.

(ii) If B has a strategy such that after the vertex b_k, $k \geq 1$, is played, the set $\mathrm{Pl}_G(\ldots b_k) \cup \{a_1, b_1, \ldots, b_k\}$ is a general position set and $|\mathrm{Pl}_G(\ldots b_k)|$ is even, then B wins the gp achievement game.

Proof. (i) Suppose that A has a strategy such that after A plays a_k, the set $\mathrm{Pl}_G(\ldots a_k) \cup \{a_1, b_1, \ldots, a_k\}$ is a general position set. By definition, in the rest of the game only vertices from $\mathrm{Pl}_G(\ldots a_k)$ are playable. Moreover, each of these vertices will actually be played because $\mathrm{Pl}_G(\ldots a_k) \cup \{a_1, b_1, \ldots, a_k\}$ is a general position set. Just after this will be done, the game will be finished. Since $|\mathrm{Pl}_G(\ldots a_k)|$ is assumed to be even, this means that A will be the last player to select a vertex.

(ii) Follows by a parallel argument. □

For the first application of Theorem 2.2 consider the Petersen graph P. Suppose that after A plays some vertex a_1 of P, B plays a vertex b_1 adjacent to a_1. Then $\mathrm{Pl}_P(a_1, b_1)$ consists of four vertices which, together with a_1 and b_1, form a general position set of P. Hence Theorem 2.2(ii) implies that B wins the gp achievement game on the Petersen graph. As another application of Theorem 2.2 we have the following result.

Proposition 2.3 *Let G be the complete multipartite graph $K_{n_1,\ldots,n_k}$, where $k \geq 2$ and $n_i \geq 2$ for $i \in [k]$. Then A wins the gp achievement game on G if and only if k is odd and at least one n_i is odd.*

Proof. Suppose first that n_i is even for all $i \in [k]$. Let X be the partition set of G in which the first move a_1 has been played by A. Then B replies by playing a vertex $b_1 \neq a_1$ from X. Note that $\mathrm{Pl}_G(a_1, b_1) = X \setminus \{a_1, b_1\}$. Since X is a general position set of G, Theorem 2.2(ii) applies and B wins the gp achievement game on G.

Hence, the only possibility for A to win the game is that at least one n_i is odd and that the first move a_1 is from an odd partition set X. Now, if B would reply by playing a vertex in X, then by the argument of the previous paragraph and with Theorem 2.2(i) in hand, A would win. So it is better for B to play a vertex b_1 which lies in a partition set $Y \neq X$. Since $\mathrm{Pl}_G(a_1, b_1) = V(G) \setminus (X \cup Y)$, the vertex

a_2 must lie in a partition set Z different from both X and Y. Continuing in this manner, each of the subsequent played vertices belongs to its private partition set. In conclusion, if some n_i is odd, then A will win if and only if k is odd. □

In view of Theorem 2.2(ii) we easily infer that B wins the gp achievement game on an arbitrary connected, bipartite graph of order at least two. This observation generalizes to arbitrary bipartite graphs as stated in the next theorem, for which we need the following fact that was observed for the first time in the proof of [2, Theorem 5.1].

Lemma 2.4 *Let G be a connected, bipartite graph. If S is a general position set of G with $|S| \geq 3$, then S is an independent set.*

Theorem 2.5 *Let G be a bipartite graph. Then A wins the gp achievement game on G if and only if the number of isolated vertices in G is odd.*

Proof. Let k be the number of isolated vertices of G.

First suppose that $k \geq 0$ is even and consider the following strategy of B. Whenever A selects a vertex v in some component of G of order at least 2, B replies with a move on a neighbor of v. And whenever A plays an isolated vertex, B replies by playing another isolated vertex. Note that after two adjacent vertices of a component H of G are played, Lemma 2.4 implies that no additional vertex from H will be played in the rest of the game. Moreover, since k is even, whenever A plays an isolated vertex, there exists at least one isolated vertex which was not played yet, hence B can follow the described strategy. It follows that the game will finish when all the isolated vertices and precisely two (adjacent) vertices from each component will be played. So the number of played vertices will be even, hence B wins the gp achievement game.

Second, let $k \geq 1$ be odd. Then A has the following strategy to win the gp achievement game. The first vertex played will be an isolated vertex. After that, the strategy of A is just as the described strategy of B in the above paragraph: whenever B plays a vertex v in some component of G of order at least 2, A replies with a move on a neighbor of v, and if B plays an isolated vertex, A replies by playing another isolated vertex. Using parallel arguments as above, the total number of vertices played will be odd, which in turn implies that A wins the game. □

3 The game played on Cartesian products

The *Cartesian product* $G \,\square\, H$ of graphs G and H has the vertex set $V(G) \times V(H)$, the vertices $(g_1, h_1), (g_2, h_2)$ being adjacent in $G \,\square\, H$ if either $g_1g_2 \in E(G)$ and

$h_1 = h_2$, or $g_1 = g_2$ and $h_1h_2 \in E(H)$. If $g \in V(G)$, then the subgraph of $G \,\square\, H$ induced by the vertex set $\{(g,h) \mid h \in v(H)\}$ is an *H-layer ${}^gH$*. *G-layers G^h* are defined analogously. If $S \subseteq V(G \,\square\, H)$, then the *projection* $\pi_G(S)$ of S on G is the set $\{g \in V(G) :\ (g,h) \in \text{ for some } h \in V(H)\}$. The projection $\pi_H(S)$ of S on H is defined analogously.

Throughout this section we will use the following basic fact about the distance function in the Cartesian product. If G and H are connected graphs and $(g,h),(g',h') \in V(G \,\square\, H)$, then the *distance formula* holds:

$$d_{G \,\square\, H}((g,h),(g',h')) = d_G(g,g') + d_H(h,h')\,. \tag{1}$$

Moreover, if P is a $(g,h),(g',h')$-geodesic in $G \,\square\, H$, then $\pi_G(P)$ induces a g,g'-geodesic in G and $\pi_H(P)$ induces a h,h'-geodesic in H. The distance formula (1) implies that

$$I_{G \,\square\, H}[(g,h),(g',h')] = I_G[g,g'] \times I_H[h,h']\,. \tag{2}$$

For these results and more on the Cartesian product operation see the standard book on product graphs [8]. We will also need the following known result.

Lemma 3.1 [26, Lemma 2.4] *Let G and H be connected graphs and let R be a general position set of $G \,\square\, H$. If $u = (g,h) \in R$, then $V({}^gH) \cap R = \{u\}$ or $V(G^h) \cap R = \{u\}$.*

We next prove two additional lemmas on general position sets in Cartesian products.

Lemma 3.2 *Let G and H be connected graphs and let $R \subseteq V(G \,\square\, H)$ has the following two properties.*

(i) If $(g,h) \in R$, then $V({}^gH) \cap R = \{(g,h)\}$ or $V(G^h) \cap R = \{(g,h)\}$.

(ii) $\pi_G(R)$ and $\pi_H(R)$ are general position sets of G and H, respectively.

Then R is a general position set of $G \,\square\, H$.

Proof. Suppose on the contrary that R contains three vertices $x_1 = (u_1,v_1)$, $x_2 = (u_2,v_2)$, and $x_3 = (u_3,v_3)$ such that $x_2 \in I_{G \,\square\, H}[x_1,x_3]$. Applying the distance formula (1) and the triangle inequality we can estimate as follows:

$$\begin{aligned} d_{G \,\square\, H}(x_1,x_3) &= d_{G \,\square\, H}(x_1,x_2) + d_{G \,\square\, H}(x_2,x_3) \\ &= (d_G(u_1,u_2) + d_H(v_1,v_2)) + (d_G(u_2,u_3) + d_H(v_2,v_3)) \\ &= (d_G(u_1,u_2) + d_G(u_2,u_3)) + (d_H(v_1,v_2) + d_H(v_2,v_3)) \\ &\geq d_G(u_1,u_3) + d_H(v_1,v_3) \\ &= d_{G \,\square\, H}(x_1,x_3)\,. \end{aligned}$$

It follows that $d_G(u_1, u_3) = d_G(u_1, u_2) + d_G(u_2, u_3)$ and $d_H(v_1, v_3) = d_H(v_1, v_2) + d_H(v_2, v_3)$.

Suppose first that x_1 and x_3 lie in a common G-layer or in a common H-layer. By the commutativity of the Cartesian product we may without loss of generality assume that they lie in a common H-layer, that is, $u_1 = u_3$. Since ${}^{u_1}H$ is a convex subgraph of $G \,\square\, H$ (see [8] again), it follows that $u_1 = u_2 = u_3$. Hence the vertices v_1, v_2, v_3 are pairwise different, and so the fact $d_H(v_1, v_3) = d_H(v_1, v_2) + d_H(v_2, v_3)$ yields a contradiction with the assumption that $\pi_H(R)$ is a general position set of H.

Assume second that x_1 and x_3 lie neither in a common G-layer nor in a common H-layer. Then $u_1 \neq u_3$ and $v_1 \neq v_3$. Assumption (i) then implies that $(u_2, v_2) \notin \{(u_1, v_3), (u_3, v_1)\}$. As a consequence, at least one of the sets $\{u_1, u_2, u_3\}$ and $\{v_1, v_2, v_3\}$ is of cardinality 3. But then we have a contradiction for one of these sets just as in the previous paragraph. □

The converse of Lemma 3.2 does not hold. As an example consider the path P_3 on vertices $1, 2, 3$, and the Cartesian product $P_3 \,\square\, P_3$. Then $\{(1, 2), (2, 1), (2, 3), (3, 2)\}$ is a general position set of $P_3 \,\square\, P_3$, but neither its projection onto the first factor not the projection onto the second factor is a general position set.

If each H-layer contains at most one vertex from R, then the conditions of Lemma 3.2 simplify as follows.

Lemma 3.3 *Let G and H be connected graphs and let $R \subseteq V(G \,\square\, H)$. If $\pi_G(R)$ is a general position set in G and $\pi_G(R) = |R|$, then R is a general position set of $G \,\square\, H$.*

The proof of Lemma 3.3 proceeds along the same lines as the proof of Lemma 3.2 and is hence omitted. That the converse of Lemma 3.3 again does not hold, consider again the Cartesian product $P_3 \,\square\, P_3$. Then $\{(1, 1), (2, 2), (3, 1)\}$ is a general position set of $P_3 \,\square\, P_3$ with exactly one vertex in each of the layers with respect to the first factor, but its projection onto the first factor is not a general position set.

Lemma 3.4 *Let G and H be connected graphs. If for every $u \in V(G)$ there exists a vertex v such that $\mathrm{Pl}_G(u, v) \cup \{u, v\}$ is a clique of even order, then B wins the gp achievement game on $G \,\square\, H$.*

Proof. Consider the gp achievement game on $G \,\square\, H$. Let $a_1 = (u_1, v_1)$. Then there exists a vertex $u_2 \in V(G)$ such that $\mathrm{Pl}_G(u_1, u_2) \cup \{u_1, u_2\}$ is a clique of even order. The initial strategy of B is to play $b_1 = (u_2, v_1)$. Suppose that A next plays $a_2 = (u_3, v_3)$. By Lemma 3.1, $\mathrm{Pl}_{G \,\square\, H}(a_1, b_1) \subseteq V(G \,\square\, H) \backslash ({}^{u_1}H \cup {}^{u_2}H)$, hence $u_3 \notin \{u_1, u_2\}$. We claim that $\{u_1, u_2, u_3\}$ is a general position set of G. If not, then,

since $u_1u_2 \in V(G)$, we may without loss of generality assume that $u_2 \in I_G[u_1, u_3]$. But then the distance formula implies that $(u_2, v_1) \in I_{G\,\square\, H}[(u_1, v_1), (u_3, v_3)]$. Hence the claim, which in turn implies that $u_3 \in \mathrm{Pl}_G(u_1, u_2)$. Since $|\,\mathrm{Pl}_G(u_1, u_2)|$ is even and $\mathrm{Pl}_G(u_1, u_2, u_3) = \mathrm{Pl}_G(u_1, u_2)\backslash\{u_3\}$, player B can continue the game by choosing the vertex (u_4, v_3), where $u_4 \in \mathrm{Pl}_G(u_1, u_2, u_3)$. By Lemma 3.3, the set $S_4 = \{(u_1, v_1), (u_2, v_1), (u_3, v_3), (u_4, v_3)\}$ is a general position set of $G\,\square\, H$. Player B then continues this strategy and by repeatedly applying Lemma 3.3, we can see that each set S_n is a general position set of $G\,\square\, H$. Also since B wins on G, at each stage of the game $|\,\mathrm{Pl}_{G\,\square\, H}(\ldots b_k)|$ is even. Hence by Theorem 2.2(ii), B wins on $G\,\square\, H$. $\square$

Since in a connected, bipartite graph, every pair of adjacent vertices is a maximal general position set, the following theorem follows directly from Lemma 3.4.

Theorem 3.5 *Let G be a connected graph and let H be a connected bipartite graph with at least one edge. Then B wins the gp achievement game on $G\,\square\, H$ after his first move.*

Theorem 3.5 should be compared with the main result from [26] which asserts that if T and T' are trees, then $\mathrm{gp}(T\,\square\, T') = \ell(T) + \ell(T')$, where $\ell(G)$ is the number of leaves of a graph G.

We next resolve the gp achievement on Hamming graphs.

Theorem 3.6 *If $n, m \geq 2$, then A wins the gp achievement game on $K_n\,\square\, K_m$ if and only if both n and m are odd.*

Proof. Let $V(K_n) = \{u_1, \ldots, u_n\}$, $V(K_m) = \{v_1, \ldots, v_m\}$, and set $G = K_n\,\square\, K_m$ for the rest of the proof. If one of n and m is even, then B wins the gp achievement game on G by Lemma 3.4.

In the rest assume that both n and m are odd. We need to prove that in this case A wins the gp achievement game. The strategy of A is to achieve the following goal. After each move a_i, $i \geq 1$, we have that

$$|\,\mathrm{Pl}_G(\ldots a_i) \cap V(K_n^{v_k})| \text{ is even and } |\,\mathrm{Pl}_G(\ldots a_i) \cap V({}^{u_j}K_m)| \text{ is even} \qquad (3)$$

for all layers $K_n^{v_k}$ and all layers ${}^{u_j}K_m$ in which at least one vertex has already been played.

By the vertex-transitivity of G we may assume that $a_1 = (u_1, v_1)$. Note that (3) holds true after this move. For the first move $b_1 = (u_i, v_j)$ of B we may, again using the symmetry of G, without loss of generality assume that $i = 2$ and $j \in [2]$.

Suppose first that $b_1 = (u_2, v_1)$. Then A selects $a_2 = (u_3, v_1)$. Since by Lemma 3.1, $\mathrm{Pl}_G(a_1, b_1, a_2) \subseteq V(G)\backslash({}^{u_1}H \cup {}^{u_2}H \cup {}^{u_3}H)$, the condition (3) is fulfilled

after the move a_2. The next move of B must be in a new K_m-layer, say $b_2 = (u_4, v_j)$. Then A replies by the vertex $a_3 = (u_5, v_j)$. This is a legal move since n is odd and because Lemma 3.3 guarantees that the so far selected vertices form a general position set of G. The game then continues in this manner, that is, whenever it is B's turn, he must select a vertex x from some new K_m-layer, and then A replies with a playable neighbor of x in the corresponding K_n-layer. As n is odd, A will play the last vertex.

Suppose second that $b_1 = (u_2, v_2)$. In this case A replies by picking $a_2 = (u_3, v_3)$. Then $\mathrm{Pl}_G(a_1, b_1, a_2) = V(G) \setminus (\{u_1, u_2, u_3\} \times \{v_1, v_2, v_3\})$ and (3) is fulfilled after the move a_2. In the sequel of the game, if B plays a vertex such that it is the first vertex played in the two layers in which it lies, then A replies with another such vertex. Note that this is possible as both n and m are odd. After each such move of A, the conditions (3) remain fulfilled. Suppose now that at some point of the game, B selects a vertex in a K_n-layer in which at least one vertex has been played earlier. Because before this move (3) holds, A can reply by playing a vertex from the same K_n-layer. Now, in this K_n-layer exactly two less vertices are playable, so the number of playable vertices in the layer is even (possibly zero). Moreover, in the two K_m-layers, in which the last two moves were played, no vertex is now playable, hence (3) holds also for these two layers. In the case when at some point of the game, B selects a vertex in a K_m-layer in which at least one vertex has been played earlier, A proceeds analogously, that is, he plays next a vertex from the same K_m-layer. Following this strategy, A wins the game. □

Lemma 3.4 immediately implies the following.

Corollary 3.7 *If n is even and G is a connected graph, then B wins the gp achievement game on $K_n \,\square\, G$.*

On the other hand, if n is odd and G is a connected graph, the the outcome of the gp achievement game on $K_n \,\square\, G$ appears more involved. This statement is in part justified by the following result.

Theorem 3.8 *If $m \geq 3$, then A wins the gp achievement game on $K_3 \,\square\, C_m$ if and only if $m \in \{3, 5\}$.*

Proof. Let $V(K_3) = \{u_1, u_2, u_3\}$ and let $V(C_m) = \{v_1, \ldots, v_{2k+1}\}$, where the edges are in natural order. Set $G = K_3 \,\square\, C_m$ for the rest of the proof.

If m is even, then Theorem 3.5 implies that B wins the gp achievement game on G. If $m = 3$, then by Theorem 3.6 we know that A wins the game. Consider next the case $m = 5$. We are going to prove that A wins the game by considering all possibilities (up to symmetry). Let A start the game with $a_1 = (u_1, v_1)$. Then,

up to the symmetry of G and having in mind that each vertex of G is at distance at most 3 from a_1, we need to consider the following replies of B: (u_1, v_2), (u_1, v_3), (u_2, v_1), (u_2, v_2), and (u_2, v_3). If $b_1 = (u_1, v_2)$, then A selects $a_2 = (u_1, v_4)$ and wins the game. If $b_1 = (u_1, v_3)$, then A selects $a_2 = (u_1, v_5)$ and wins the game. If $b_1 = (u_2, v_1)$, then the move $a_2 = (u_3, v_1)$ finishes the game. If $b_1 = (u_2, v_2)$, then A replies by $a_2 = (u_3, v_3)$. Then we have three subcases: if $b_2 = (u_1, v_4)$, then A plays $a_3 = (u_2, v_5)$; if $b_2 = (u_2, v_4)$, then A plays $a_3 = (u_3, v_5)$; and if $b_2 = (u_3, v_4)$, then A plays $a_3 = (u_2, v_5)$. In each of the subcases, A wins. Finally, if $b_1 = (u_2, v_3)$, then A selects $a_2 = (u_3, v_2)$. Similarly as in the second case we now see that B cannot win with the move b_2, while afterwards A wins with his third move.

It remains to prove that B wins on G when $m \geq 7$ is odd. By the vertex-transitivity of G we may assume that A starts with the vertex (u_1, v_1). Then B picks the vertex $b_1 = (u_2, v_2)$. From here on, we distinguish two cases.

Case 1: $a_2 = (u_3, v_i)$, where $i > 2$.
We may without loss of generality assume that $i \leq k+1$. By Lemma 2.1 and by (2), the move $b_2 = (u_3, v_s)$, where $s \geq k + 2$, is a legal move of B. Let $a_3 = (u_r, v_l)$. If $r = 1$ and $l > k + 2$, then $a_1 \in I_G[a_3, b_1]$, and if $r = 2$ and $l \leq k + 1$, then $b_1 \in I_G[a_1, a_3]$. If $r = 3$, then either $\{a_1, a_2, a_3\}$ or $\{a_1, b_2, a_3\}$ is not a general position set of G. These cases imply that

$$\mathrm{Pl}_G(a_1, b_1, a_2, b_2) \subseteq (u_1 \times \{v_1, \ldots, v_{k+2}\}) \cup (u_2 \times \{v_{k+2}, \ldots, v_{2k+1}\}) . \qquad (4)$$

We can without loss of generality assume that A continues by playing $a_3 = (u_2, v_j)$, where $j > k + 1$. Since $m \geq 7$, B can choose $b_3 = (u_1, v_t)$ with $2 < t \leq k + 2$ and $i \neq t \neq j$. Again by Lemma 2.1 and (2), $S = \{a_1, b_1, a_2, b_2, a_3, b_3\}$ is a general position set of G. We claim that S is a maximal general position set. Suppose on the contrary that $a_4 = (u_g, v_h)$ is a legal move. Then by (4), $g \neq 3$. If $g = 1$, then applying (4) again, $h \leq k + 2$. But then by (2), $\{b_1, b_3, a_4\}$ is not be a general position set of G. And if $g = 2$, then again by (4), $h > k + 1$. If $h = k + 2$ or $j = k + 2$, then $\{a_1, a_3, a_4\}$ is not be a general position set. And if $h > k + 2$ and $j > k + 2$, then $\{b_1, a_3, a_4\}$ is not be a general position set in G. This proves the claim which in turn finishes th argument for Case 1.

Case 2: $a_2 = (u_i, v_j)$, $i \in [2]$ or $j \in [2]$.
First suppose that $i \in [2]$, say $i = 1$. Then clearly $j \neq 2$. If $j > k + 2$, then $a_1 \in I_G[a_2, b_1]$. Hence $2 < j \leq k+2$. Set $b_2 = (u_3, v_2)$. By Lemma 2.1 and (2), the set $\{a_1, b_1, a_2, b_2\}$ is a general position set. Using Lemma 3.1, we get $\mathrm{Pl}_G(a_1, b_1, a_2, b_2) \subseteq {}^{u_1}C_m$. If A can choose $a_3 = (u_1, v_r)$, then, as mentioned above, $r \leq k + 2$. But then by (2), $\{b_1, a_2, a_3\}$ is not be a general position set. Hence B wins the game. Suppose second that $j \in [2]$, say $j = 2$. Then clearly $i = 3$. Hence by Lemma 3.1, $\mathrm{Pl}(a_1, b_1, a_2) \subseteq {}^{u_1}C_m$. Now B can choose $b_2 = (u_1, v_s)$ with $2 < s \leq k + 2$. Then as in the case $i = 1$, B wins the gp achievement game on G. □

4 The game played on lexicographic products

The *lexicographic product* $G \circ H$ of graphs G and H has the vertex set $V(G) \times V(H)$, vertices (g, h) and (g', h') being adjacent if either $gg' \in E(G)$, or $g = g'$ and $hh' \in E(H)$. Layers and projections are defined for the lexicographic product in the same way as they are defined for the Cartesian product. The distances in lexicographic products can be computed as follows, see [8, Proposition 5.12].

Proposition 4.1 *If (g, h) and (g', h') are two vertices of $G \circ H$, then*

$$d_{G\circ H}((g,h),(g',h')) = \begin{cases} d_G(g,g'); & g \neq g', \\ d_H(h,h'); & g = g', \deg_G(g) = 0, \\ \min\{d_H(h,h'), 2\}; & g = g', \deg_G(g) \neq 0. \end{cases}$$

Lemma 4.2 *If G and H are connected graphs, and S is a general position set of $G \circ H$, then $\pi_G(S)$ is a general position set of G.*

Proof. Let S be a general position set of $G \circ H$, and suppose on the contrary that $\pi_G(S)$ is not a general position set of G. Then there exist vertices (u_1, v_1), (u_2, v_2), and (u_3, v_3) from S such that $u_2 \in I_G[u_1, u_3]$. Since u_1,u_2, and u_3 are pairwise distinct, Proposition 4.1 yields

$$\begin{aligned} d_{G\circ H}((u_1,v_1),(u_3,v_3)) &= d_G(u_1,u_3) = d_G(u_1,u_2) + d_G(u_2,u_3) \\ &= d_{G\circ H}((u_1,v_1),(u_2,v_2)) + d_{G\circ H}((u_2,v_2),(u_3,v_3)), \end{aligned}$$

which is not possible as S is a general position set of $G \circ H$. □

Theorem 4.3 *If G is a connected graph, then B wins the gp achievement game on $G \circ K_n$ if and only if either B wins on G or n is even.*

Proof. We first claim that $S \subseteq V(G \circ H)$ is a maximal general position set of $G \circ K_n$ if and only if $S = S_G \times V(K_n)$, where S_G is a maximal general position set of G. Proposition 4.1 and Lemma 4.2 imply that if S_G is a maximal general position set of G, then $S_G \times K_n$ is a maximal general position set of $G \circ K_n$. On the other hand, let S be a maximal general position set of $G \circ K_n$. The maximality implies that if $(u, v) \in S$, then $V({}^uK_n) \subseteq S$. Hence $S = \pi_G(S) \times V(K_n)$, and clearly, $\pi_G(S)$ is a maximal general position set in G. This proves the claim.

Suppose that n is odd and that A wins the game on G. We will show that then A wins also on $G \circ H$. The strategy of A is the following. First he selects a vertex (u, v), where u is an optimal start vertex in the game played on G and v is an arbitrary vertex of K_n. After that, A replies to moves of B in the following way. Whenever B

selects a vertex b_i from a K_n-layer, from which no vertex was played earlier, A replies with a vertex a_{i+1} such that $\pi_G(a_{i+1})$ is an optimal reply of A to the move $\pi_G(b_i)$ of B played in G. On the other hand, whenever b_i belongs to a previously visited K_n-layer, A replies by choosing a vertex a_{i+1} such that $\pi_G(a_{i+1}) = \pi_G(b_i)$. Note that this is possible since n is odd. Because A wins on G, the described strategy implies that vertices from an odd number of K_n-layers will be played during the game. In addition, the above claim implies that all the vertices from these K_n-layers will be played, hence in total odd number vertices will be played. We conclude that A wins the game on $G \circ H$ when n is odd and A wins the game on G.

It remains to prove that in the other cases B has a winning strategy. If n is even, then the claim implies that an even number of vertices will be played during the game. This means that B wins. And if B has a winning strategy on G, then B follows a similar strategy as A in the previous paragraph. Whenever A plays in some new K_n-layer, B replies optimally (with respect to the projected game on G) in a new K_n-layer, and whenever A plays in an already visited K_n-layer, B plays in some other already visited K_n-layer in which not all vertices has been played yet. In this way an even number of K_n-layer will be visited during the game and then the claim implies that B wins the game. □

5 Concluding remarks

The main message of this paper is the following. If at an early stage of the gp achievement game played on G, one of the players has a possibility to play a vertex that significantly reduces the number of playable vertices during the rest of the game, then it is often easier to analyze the gp achievement game on G than the general position number of G. On the other hand, we have also seen that many challenging problems concerning the gp achievement game remain open.

In parallel to achievement games one can also consider avoidance games. In our particular case of the gp achievement game, the gp avoidance game is defined analogously, the only difference is that in the general position avoidance game the player who has played the last vertex loses the game. So the gp achievement game and the gp avoidance game are much similar, however, they are in general independent. For instance, one can check that player B wins both games on the cycle C_6. Hence it would be interesting to investigate also the gp avoidance game and to compare it with the gp achievement game.

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INVASIVE EXOTIC PLANT SPECIES AND THEIR INFLUENCE ON THE ENVIRONMENT, ECOSYSTEM SERVICES, ECONOMY AND HEALTH: A SEARCH

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ABSTRACT

Invasive exotic plant species (IEPS) is recognized as threat to the native biodiversity and leads to the loss of habitat for the indigenous species on the earth. Invasions not only tear down the native plant species but have adverse impacts on economy and human health. Many documented records from Western countries connected with alien species revealed altered ecosystem services and socio-economic conditions via diverse mode of actions. Even though, the ecological impacts of alien species were documented, there is a dearth of analysis regarding their economic quantification, livelihood considerations, biotechnological aspects and human health risk assessments are the need of the hour. The noxious exotic invasive plants in India were *Ageratum conyzoides*, *Eupatorium adenophorum, Parthenium hysterophorus, Lantana camara, Mikania micrantha, Argemone mexicana* and *Eichhornia crassipes*. In this context, an attempt was made to enlist the alien species of Kerala and a review to account the impacts of invasive exotic plant species on various aspects of the environment globally. Results regarding the alien species search revealed the following species such as *Chromolaena odorata, Senna spectabilis, Hypoestes sanguinolenta, Maesopsis eminii, Eupatorium cannabinum, Mikania micrantha, Sphagneticola trilobata* and *Acacia mearnsii* were intruded in to various ecosystems of Kerala after the repeated floods. They directly affect the germination and survival of local species, damage the quality of soil and affect ground water availability. Nearly 80 species were noted as alien species in Kerala by many state level surveys. Research in the direction of impact of alien species on socio-economic cultural aspects of life and derailment of ecosystem is not yet seriously carried from Kerala. Further, there is a paucity of the ecological models/indicators to establish interrelationship among global environmental changes, biodiversity and health, warranting future researches.

Keywords: Alien species, Ecological impacts, Ecosystem, Invasion, Native species, Biodiversity.

1. INTRODUCTION

Invasive exotic plant species (IEPS) are considered to be the major direct driving force of loss of biodiversity across the earth. Management of invasive exotic plant species seems to be a challenge in the field of conservation of biological diversity. The alien species threatens the ecosystems, degrade the habitats and create issues to other indigenous species through invasion. It is treated as the second largest factor of species endangerment and extinction of biodiversity in an area. The ecological cost is often irrecoverable via loss of native species and ecosystems. It also causes high loss of economy, in terms of reduced crop yield and production of livestock, declined natural biodiversity, increased production costs and so on. Biodiversity has become one of the hottest areas at local, national and global scale. Biodiversity includes all forms of biological entities inhabiting the earth including microbes, wild plants and animals, domesticated animals and cultivated species and even genetic material like seeds and germplasm etc [1]. Invasive exotic plant species are species, native to one area or region, that have been introduced into an area outside their normal distribution, either by accidental or for on usage and

which latter gets colonized or invaded their new habitats, threatening the native biodiversity, ecosystems and habitats, and human wellbeing. Alien species invasion globally threatens biological diversity, ecosystem dynamics, resource availability, economy of an area and human health [2]. The spread of these species is considered as one of the high risk factor to the ecosystem. Accidental introductions happened via trade or travel across continents and import of various items such as timber, food grains, fodder etc.

Currently, the human centered landscapes are typically featured by intensive land-use pattern and increased scale of habitat destruction, often results in to contrasted mosaics of habitat. Fragmentation of the existing habitat is a major threat to biological diversity and ecosystem functioning. Decreasing existing habitat size and increasing isolation of habitat patches results in to decline in species richness and abundance, also changes in community structure. This process of habitat fragmentation and destruction may greatly change the landscape architecture and local ecosystem functioning. After habitat fragmentation, the surviving plant communities become more prone to invasion by non-native plant species. Many studies documented that floristic changes emerge after habitat fragmentation, which may be due to invasion by an alien weed. Forest study of Costa Rica reported that fragmented tropical dry forest were prone to invasion by weedy generalist plant species. When changes in community occur either through habitat alteration or through the invasion of alien species, local decline, and even extinction of native species may occur. The effect of fragmentation on species loss is now becoming well known in many parts of the earth. However, limited studies have viewed at the effects of fragmentation on the success of invaders and the subsequent effects of the invader on the native species resident in fragments. In this scenario, the objective of the review is to report the alien invasion of species threating to various aspects on the environment including health and economy. Further, a check list of exotic species was also prepared in this context from Kerala.

2. MATERIAL AND METHODS

Intensive floristic survey reports were screened in different areas of Kerala in such a way that each location could be studied in every season of the year. A comprehensive list of invasive exotic plant species and the information regarding the various issues of invasive exotic plant species of the area was prepared. The nativity, sources and mode of introduction of these alien invasive plants were noted from the available literatures. The native ranges of the species were recorded from published literatures. Plants were categorized according to their life forms as herb, undershrub, shrub, climber and tree. The studied habitats were wasteland, cultivated field, riverbank, pond bank, home garden, forest, roadside etc.

3. RESULTS AND DISCUSSION

3.1. Invasions of species by anthropogenic activities and natural means

The introduced invasive exotic plant species (IEPS) by human beings threaten the ecosystems, biodiversity and replaced many economically unique native plant species and thereby creating issues in agriculture and silviculture practices, upsetting the vegetation dynamics and nutrient recycling. Introductions of alien plants by human activities in the native habitats are the major reason for the drastic changes recorded within the indigenous native plant communities of the area [3]. Trade connected with commerce (especially imports) and extensive travel by people magnified the intensity of invasive alien species across the world. Current scenarios of transport have directly/indirectly increased the inadvertent migration of species, often resulted in to disastrous consequences [4]. Introduced or indirectly carried species reports like *Eucalyptus citriodora*, *Lantana camara, Acacia auriculiformis* and *Senna spectabilis* were the examples substantiating the degradation of natural ecosystems [5].

The natural invasion mainly depends upon the dispersal ability of the invading species. The time scale for natural invasion usually ranges from few to many years. Birds, animals, water and wind forms the agents for natural invasion. *Ageratum conyzoides* and *Parthenium hysterophorus* were examples for natural invasion [6]. After migration of an exotic plant species, there is a lag phase before an exponential phase of its fast spread. The species like *P. hysterophorus* that at a given period may seems to be non-invasive but suddenly spread vigorously.

3.2. Various types of environmental impacts by the invasive exotic plant species (IEPS)

3.2.1. Impacts of exotic species invasions on indigenous species

Study reports of past introduced plants illustrated that the impacts of invasive species are complex and may permanently alter the vegetation and community structures. Invasive exotic plant species inducts more

stress especially where communities are disturbed. Limited data was available on alien plant species threatened the undisturbed local indigenous plant communities. In Kerala, *Chromolaena odorata*, *Senna spectabilis*, *Hypoestes sanguinolenta, Maesopsis eminii, Eupatorium cannabinum, Mikania micrantha, Sphagneticola trilobata* and *Acacia mearnsii* were well recognized alien invaders which posed threat to indigenous plant communities including the protected areas under conservation and also the habitats from planes to hilly tracts (Table 1).

Table 1: List of alien invaders which posed threat to indigenous plant communities in Kerala

Sl. No	Plant name	Family, habit & origin	Threatens
1.	*Chromolaena odorata* (L.) R.M. King & H. Rob	Asteraceae, Climber South America and Central America	Threatens the species like *Sida cordifolia*
2.	*Senna spectabilis* (DC.) Irwin & Barneby	Caesalpinioideae, Tree, South and Central America	Intruded in to wildlife sanctuaries as well as in plantations
3.	*Hypoestes sanguinolenta* Hook.	Acanthaceae, Herb, Madagascar	High risk species to native plants
4.	*Maesopsis eminii* Engl.	Tree, Rhamnaceae, Africa	Inhibits the undergrowth of native species
5.	*Eupatorium cannabinum* L.	Herb, Asteraceae, Europe to Central Asia	High nuisance value around water ways
6.	*Mikania micrantha* Kunth.	Asteraceae, Climber, America	Herbivores face food scarcity as the native plant species
7.	*Sphagneticola trilobata* (L.) Pruski	Asteraceae, Runner, Mexico	Garden plant threatened
8.	*Acacia mearnsii* De Wild	Mimosoideae, Tree, south-eastern Australia	Ground water threatened

Disturbed and unattended habitats are more prone to the invasion when compared to the well-managed ecosystems and habitats. The habitats which have more diverse plant communities were highly competitive and resist invasion. Schmitz et al., [7] reported that the invasive trees of Florida such as *Schinus terebinthifolius*, *Melaleuca quinquenrvia* and *Casuarina* spp resulted in to major threats to the native vegetation. Similarly, the introduced different pine species created issues to natural habitats in Australia, New Zealand, and South Africa. It was reported that in Christmas Island at Australia 52.70% species have been found to be exotic like *Leucaena leucocephala, Muntingia calabura, Ricinis communis, Carica papaya* and *Psidium guajava* and most of them were confined to disturbed regions such as minefields, overburden dumps, and road sides [8].

The alien terrestrial species introduced in to the natural habitats are responsible for the extensive and unpredictable irreversible changes in those areas (Table 2). Many countries initiated techniques to utilize the exotic tree species for commercial, economic uses and for ornamental landscapes which further intensified more noxious invaders growth. These tree species have impacted the natural above-ground herbal and other native vegetation. Sometimes, under the alien conditions or in new invaded ecosystems, such type of species become naturalized and expands over other native ecosystems. Richardson et al., [9] reported that introduced pines in the Southern Hemisphere have affected large areas of natural grasses and thickets. It brought a lot of change in the dominant annual and perennial herbals and decreased the species composition and modified vegetation patterns and the nutrient cycles. The disturbed forest understories are more prone to invasion as compared to the undisturbed zones. Dogra et al., [10] reviewed that there are many species such as *Alliaria petiolata*, *Acer platanoides*, *Lonicera bella, Rhamnus cathartica* and *Berberies thunbergii* that established and dominated the low light forest understories in the Northwestern USA. The invasive species survive under the shade because rapid growth takes place in the microhabitats than exposed conditions.

3.3. Impact on the soil structure and its dynamics

Invasion by exotic plant species affects the dynamics and structure of the soil on a holistic scale and have immense impact on ecosystem functions like soil-mineral recycling. Since these effects result from differences in the mode of behavioural patterns between the exotic and native species, novel physiological characters such as nitrogen, phosphorus cycling may cause maximal alterations in the ecosystem function [11].

Table 2: List of Invasive Alien plant species in India

Plant species	Family, Habit & origin	Impacts
Acacia mearnsii De Wild.	Mimosoideae, Tree, South-eastern Australia	It rapidly grows to forms dense thickets and destroys the grazing lands.
Acanthospermum hispidum DC.	Asteraceae, Herb, Brazil	Troublesome annual weed of annual and perennial crops.
Aerva javanica (Burm.f.) Juss. ex Schult.	Amaranthaceae, Herb, Trop. America	It has only recently come to be regarded as a serious environmental weed.
Ageratum conyzoides L.	Asteraceae, Herb, Trop. America	Allelopathic, highly invasive, threat to croplands
Alternanthera tenella Colla.	Amaranthaceae, Herb, Trop. America	Rapid colonizer and harmful to forest ecosystem.
Alternanthera philoxeroides Mart.) Griseb	Amaranthaceae, Herb South America	By forming dense mats of interwoven stems over water or land, this invasive weed may threaten the native flora and fauna, reduce crops yields, block ships, and promote flooding
Argemone mexicana L.	Papaveraceae, Herb, Trop. Central & South America	Harm native flora through allelopathy
Asclepias curassavica L.	Asclepiadaceae, Herb, Trop. America	It is prolific in disturbed sites and competes with agricultural crops and indigenous species. This plant contaminates crop seed.
Blainvillea acmella (L.) Philipson.	Asteraceae, Herb, Trop. America	It is a common weed in cultivated fields, degraded forests.
Bidens pilosa L.	Asteraceae, Herb, Trop. America	The plant is thought to produce allelopathic toxins that affect a number of crops.
Blumea obliqua (L.) Druce	Asteraceae, Herb, Trop. America	The extinction of native species and has negative impact on crop production
Calotropis procera (Ait.) R.Br.	Asclepiadaceae, Shrub, Trop. Africa	It is noxious weed; hence it is controlled within the area. Establishing the weed has been advocated for environmental protection and as a nurse crop for more valuable species
Cardamine hirsuta L.	Brassicaceae, Herb, Trop. America	It is a fast-growing herb that often behaves as a weed in both disturbed and undisturbed sites
Cassia alata L.	Caesalpiniaceae, Shrub, West Indies	Introduced as an ornamental and became threat to local flora
Celosia argentea L	Amaranthaceae, Herb, Trop. Africa	It is a common weed of cultivated fields and scrub lands.
Chromolaena odorata (L.) King & Robinson	Asteraceae, Herb, Trop. America	Its foliage is reportedly flammable (contains essential oils), making it a threat to indigenous coastal forest patches, which are not resilient to fire.
Cleome viscosa L.	Cleomaceae, Herb, Trop. America	This species produces large numbers of sticky seeds that can be easily dispersed by wind and has the potential to spread much further into new habitats.
Chrozophora rottleri (Geis.) Spreng.	Euphorbiaceae, Herb, Trop. Africa	This plant species act as the main cause for threat to the native biological diversity.
Cleome gynandra L.	Cleomaceae, Herb, Trop. America	It is aggressive colonizer and is weed of village wastelands, dumping grounds, crop lands
Crotalaria retusa L.	Papilionaceae, Herb, Trop. America	The risk of new introductions as well as the probability of escape from cultivation is high
Croton bonplandianum Boil.	Euphorbiaceae, Herb, Temperate South America	Became threat to endemic flora and gradually destroys.
Cryptostegia grandiflora R.Br.	Asclepiadaceae, Herb, Madagascar	A threat to native biodiversity.
Cuscuta chinensis Lam.	Cuscutaceae, Herb, Mediterranean	It has proved locally invasive and damaging to fruit and ornamental trees.

Cytisus scoparius (L.) Link	Papilionaceae, Herb, Europe	It displaces native understorey vegetation and grasses, finally forming monospecific stands.
Crassocephalum crepidioides (Benth) S. Moore	Asteraceae, Herb, Africa	The plants pose a serious threat to flora and fauna.
Datura innoxia Mill.	Solanaceae, Shrub, Trop. America	It has the capacity to invade natural habitats and can be considered as potential threat for natural biodiversity.
Digera muricata (L.) Mart.	Amaranthaceae, Herb, SW Asia	Common weed of irrigated dry cultivated fields.
Echinops echinatus Roxb.	Asteraceae, Herb, Afghanistan	Serious aquatic weed, allelopathic in nature, causes hindrance in navigation, reduces water quality and algal growth
Eclipta prostrata (L.) Mant.	Asteraceae, Herb, Trop. America	It has never been reported as a serious weed but it is troublesome in several crops.
Eupatorium cannabinum L.	Asteraceae, Herb, Europe to Central Asia	Allelopatic effect causes serious threats to native flora
Euphorbia heterophylla L.	Convolvulaceae,:Herb, Trop. America	It is reported as an emerging weed in cotton and processing tomato.
Evolvulus nummularius (L.) L.	Convolvulaceae, Herb, Trop. America	It is found both in agricultural land and waste and fallow lands mainly as noxious weeds.
Gomphrena serrata L.	Amaranthaceae, Herb, Trop. America	Occasional weed of cultivated fields, habitation and forest openings.
Gnaphalium polycaulon Pers.	Asteraceae, Herb, Trop. America	It is a noxious species found in tanks, ditches and margins of river banks.
Hyptis suaveolens (L.) Poit.	Lamiaceae, Herb, Trop. South America	It is a major threat to native biodiversity, ecosystems and livelihoods.
Hypoestes sanguinolenta Hook.	Acanthaceae, Herb, Madagascar	It competes with the native flora and reduces its population.
Indigofera linifolia (L.f.) Retz.	Papilionaceae, Herb Trop. America	Invasion of the species threat natural habitat
Ipomoea carnea Jacq.	Convolvulaceae, Shrub Trop. America	The invasions of the species cause ecological disturbances that threaten native biodiversity.
Ipomoea obscura (L.) Ker.-Gawl.	Convolvulaceae, Herb Trop. Africa	Common weed in moist places of degraded forests and hedges.
Lantana camara L.	Verbenaceae, Herb Trop. America	Strongly allelopathic, serious threat to medicinal plants, responsible for forest fire
Lagascea mollis Cav.	Asteraceae, Herb, Trop. Central America	Common weed of forests, plantations, habitation, waste lands and scrub lands
Leucaena leucocephala (Lam.) de Wit	Mimosacceae, Herb, Trop. America	Runs wild in waste lands, scrub lands and fringes of plantations.
Macroptilium atropupureum (DC.) Urban	Papilionaceae, Climber, Trop. America	It is a weed species quite common but often scarce in crops.
Maesopsis eminii Engl.	Rhamnaceae, Tree, Africa	A threat to tropical forest conservation.
Malvastrum coromandelianum (L.) Garcke	Malvaceae, Herb, Trop. America	Common weed of cultivated fields, forest openings and habitation.
Merremia aegyptia (L.) Urban.	Convolvulaceae, Herb, Trop. America	A very good website detailing weed species
Melochia corchorifolia L.	Sterculiaceae, Herb, Trop. America	Common weed of moist places.
Mikania micrantha Kunth.	Asteraceae, Climber, Trop. America	Known for its allelopathic potential, highly invaded forest areas
Mimosa pigra L.	Mimosacceae, Shrub, Trop. North America	It has the potential to harm a wide number and variety of different types of primary production
Ocimum americanum L.	Lamiaceae, Herb, Trop. America	Common weed of waste lands and scrub lands.
Ocimum gratissimum L.	Lamiaceae, Herb, Africa	Species prefers wet and fertile conditions, but can tolerate drought after flowering and influence the natural habitat.
Oxalis corniculata L.	Oxalidaceae, Herb, Europe	Common winter season weed.
Parthenium hysterophorus L.	Asteraceae, Herb, Trop. North	Aggressive colonizer, highly allelopathic,

	America	allergic to animals and human being, threat cause to crops and other native flora
Passiflora foetida L.	Passifloraceae, Herb, Trop. South America	Common weed of forest fringes and bunds of cultivated fields.
Pedalium murex L.	Pedaliaceae, Herb, Trop. America	Occasional weed of waste lands, road sides and cultivated fields.
Pennisetum purpureum Schum.	Poaceae, Herb Trop. America	Posing a threat to the native species
Peristrophe paniculata (Forssk.) Brummitt	Acanthaceae, Herb, Trop. America	The native flora is facing severe threats from this species.
Peperomia pellucida (L.) Kunth.	Piperaceae, Herb, Trop. South America	Common winter season weed in gardens and on moist rocks near by habitation.
Pilea microphylla (L.) Liebm.	Urticaceae, Herb, Trop. South America	Pilea microphylla also known as rockweed, common weed of gardens and often as a pot weed.
Physalis pruinosa L..	Solanaceae, Herb, Trop. America	This alien invasive species is a serious threat to indigenous flora.
Portulaca oleracea L..	Portulacaceae, Herb, Trop. South America	Weed of moist fields and gardens.
Prosopis juliflora (Sw.) DC.	Mimosacceae, Shrub, Mexico	Aggressive and has not only successfully invaded several habitats but has also caused substratum degradation in these by causing loss of finer soil particles
Rhynchelytrum repens (Willd.) C.E. Hubb.	Poaceae, Herb, Trop. America	Occasional weed of disturbed places.
Senna spectabilis (DC.) Irwin & Barneby	Caesalpinioideae, Tree, South and Central America	The plant is posing a threat to wildlife and indigenous plants in the forest areas.
Sesbania bispinosa (Jacq.) Wight	Papilionaceae, Shrub, Trop. America	It has a tendency to naturalize and thus poses a threat of local dispersal.
Solanum americanum Mill.	Solanaceae, Herb, Trop. America	Occasional weed of cultivated fields and often found in forest fringes.
Sida acuta Burm.f.	Malvaceae, Herb, Trop. America	This plant has a pantropical distribution and is considered a weed.
Solanum torvum Sw.	Solanaceae, Shrub, West Indies	It is considered to be a serious threat to the productivity and sustainability of pasture.
Solanum seaforthianum Andrews.	Solanaceae, Climber, Brazil	This species is an aggressive invasive vine that has been widely cultivated as an ornamental.
Spermacoce hispida L.	Rubiaceae, Herb, Trop. America	Common weed of degraded forests, scrub and cultivated fields.
Spilanthes radicans Jacq.	Asteraceae, Herb, Trop. South America	Common weed of gardens and occasionally found in cultivated fields and forest fringes.
Sphagneticola trilobata (L.) Pruski	Asteraceae, Runner, Mexico	Plant is belongs to the top 100 of most alien invasive species in the world, which seriously threatens the biodiversity of its indigenous congener.
Stachytarpheta cayennensis (Rich) Vahl.	Verbenaceae, Herb, America	According to a risk assessment this species is regarded as being highly invasive and is a casual weed, a "garden thug", with effects on the local plant.
Synedrella nodiflora (L.) Gaertn.	Asteraceae, Herb, West Indies	Common weed of waste lands and gardens.
Tridax procumbens L.	Asteraceae, Herb, Trop. Central America	Common weed, along railway tracks, road sides, in cultivated fields and degraded forests.
Tribulus terrestris L.	Zygophyllaceae, Herb, Trop. America	Plants invade roadsides, pastures, fields, grasslands and degraded forests.
Triumfetta rhomboidea Jacq.	Tiliaceae, Herb, Trop. America	Common weed of forest openings, scrub and waste lands.
Turnera ulmifolia L.	Turneraceae Herb, Trop. America	Occasional weed of habitation and disturbed lands.
Urena lobata L.	Malvaceae, Shrub, Trop. Africa	It invades disturbed areas, pastures, eroded areas, and perennial crop plantations.

		Tolerates salt spray but does not grow in saturated soils.
Ulex europaeus L.	Papilionaceae, Shrub, Western Europe	It is an invasive shrub deemed as one of the most invasive species in the world.
Waltheria indica L.	Sterculiaceae, Herb, Trop. America	Abundant along railway tracks, road sides and in degraded forests.
Xanthium strumarium L.	Asteraceae, Herb, Trop. America	Occasional weed of cultivated fields and scrub lands.
Youngia japonica (L.) DC	Asteraceae Herb, Trop. South America	Occasional weed of cultivated fields and scrub lands.

(Source:C. Sudhakar Reddy, G. Bagyanarayana, K.N. Reddy & Vatsavaya S. Raju. 2008. Invasive Alien Flora of India. National Biological Information Infrastructure, Usgs, USA)

Kourtev et al., [12] studied the differences in earthworm densities and nitrogen dynamics in soils under exotic and native plant species. The invasion of *Berberis thunbergii* and *Microstegium vimineum* in hardwood forests of New Jersey, Europe has showed significant increase of pH in soils under the invasive plants when compared to soils under native shrubs (*Vaccinium* spp.). In addition, the available nitrate and net potential nitrification were remarkably higher in soils under the two exotic species. Sharma and Dakshini [13] reported the integration of plant and soil features and the ecological success of *Prosopis* species. The introduced *P. juliflora* was fast growing, highly aggressive and invasive, and causes substratum degradation in the semi-arid and arid areas of North and North-west India as compared to native species *P. cineraria*. This lack of integration amongst plant and soil characteristics and the ability to meet its nutrient requirements in all situations could be the basis of the phenomenal spread of *P. juliflora* across varying environmental conditions, in contrast to *P. cineraria* [13]. Correlations between habitats with contrasting levels of soil resource availabilities suggest that an increase in resource availability tends to increase invasion of non-native grassland communities than native plants. For example, nutrient enrichment has been consistently shown to increase the abundance of alien plant species and decrease the abundance of native ones.

3.4. Impact on economy due to invasion

Many introduced alien species for human welfare around the world are known to create environmental and economic havoc [14]. Therefore, people's views about alien spp. and their local ecological knowledge can be an effective mode to classify the exotic impacts. For example, *Acacia mangium*, an exotic species in northern Brazilian Amazon, is noted for its harmful effects to economy, environment and indigenous people through alteration of the water quality [14]. Similar reports were also noticed from India.

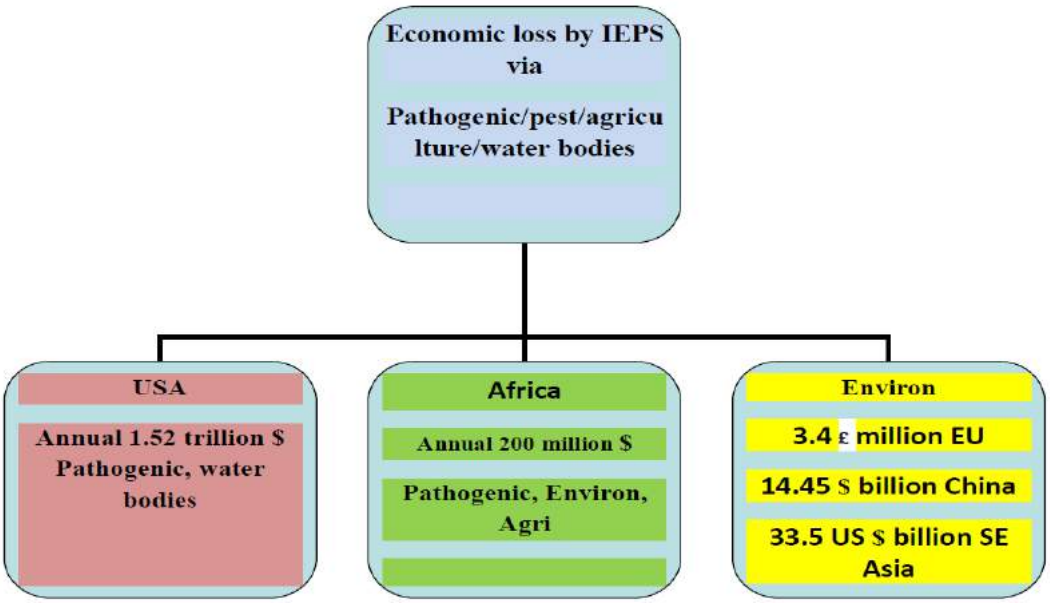
The invasion of aquatic species like *Eichhornia crassipes* in Lake Victoria has become a disaster for human welfare as it reduces fish growth and eco-tourism of the area [15]. Furthermore, the ecological niche models, and Global Climate Models have predicted a shift of water hyacinth, under climate change regime, towards European and Mediterranean regions indicating the serious economic implications of such invasion. Farming in Kuttanad depends on the entry of water into the fields. It has become routine for us to remove water hyacinth, locally known as *pola* or *kulavazha,* before preparing the fields for cultivation. The removal of weeds is labour and cost-intensive. The government provides us Rs. 4,880, but sometimes it is too meager an amount given the degree of infestation. The farmers also face difficulty in transporting machineries and harvested grains in boats through the weed-infested water channels in Kainakary. The plant chokes the life out of the freshwater ecosystem by preventing penetration of sunlight, required for the survival of underwater fauna. It also provides a breeding ground for mosquitoes, insects and disease pathogens. In Alappuzha, its overgrowth in Vembanad Lake, a designated Ramsar site, has affected the movement of passenger boats and houseboats. It causes damage to boats' engine. Fishing is another sector hit hard with large swathes of water bodies remaining carpeted with the plant. Efforts to remove the weeds from water bodies using various methods including physical, mechanical, chemical and biological have so far failed. In fact, the problem has virtually multiplied over the years. A sum of Rs. 30 crore earmarked under the first Kuttanad Package was "wasted" owing to the unscientific approach adopted. The locals in the area meet the major part of this expense by utilizing these weeds for making value-added products and thereby generating employment. Kottapuram, a village in

Thrissur district of Kerala, residents has found an innovative way to use the water weed to create jobs for poor underprivileged women.

In USA, the invaded *Tamarix ramosissima* plants has resulted in huge loss of water (1.4-3.0 billion cubic meters worth US$ 26.3-67.8 million) that deprives various human needs [15]. Similarly, *Melaleuca quinquenervia* in Florida, and *Eucalyptus* species in California, with their deep tap roots, use a huge quantity of the ground water.

In Southeast Asian context, human health sector alone suffered economic loss of US $1.85 bill ion from disease-spreading alien invaders. Negi et al., [16] attempted a long-term ecological monitoring on forest ecosystems in Indian Himalayan Region. The agriculture and health sectors together suffered an economic loss of US$33.5 billion due to the invasive species. Thus economic loss due to invaders was more pronounced in agriculture (approximately 90 % of monetary loss) than human health sector.

Shackleton et al., [17] documented in African region related with the alien species as high risk i.e. *Opuntia stricta*, was evaluated to cause the economic loss of US$ 500–1000 per household per year through participatory rural appraisal technique. Further, Sileshi et al., [18] reported that in the agriculture sector of African countries, alien invaders were evaluated to result in an economic annual loss of US$ 1 billion by causing damage to agriculture crops. Pejchar and Mooney, [15] evaluated *Myriophyllum spicatum*, an aquatic plant, in Lake Tahoe of Sierra Nevada (US), caused a recreational loss by 1%, which in monetary terms amounts to US$500 000 annually. Similarly, *Euphorbia esula* and pathogenic *Xanthomonas campestris* (citus canker) were known to cause economic loss of nearly US $200 million dollar annually [1]. It has been estimated that about US $ 600 million goes to minimize the loss caused by alien species to environment and agriculture (Fig.1).



Source [(Office of Technology Assessment.

Fig. 1: Quantification of alien species impacts in terms of economic loss driven by environmental alterations in terms of socio-ecological/economic aspects of human wellbeing of different countries - United states, China, Africa European Union, South East (SE) Asia

3.5. Impacts on the ecosystem services

Many alien/introduced exotic species are well known for their impacts on ecosystem services *viz,* aesthetic, recreational, cultural and regulatory [15]. Eiswerth et al., [19] recorded the adverse effect of alien species such as obstruction of the water navigation, they by the recreation and tourism services. Restrictions on trade of ornamental exotic species to avoid their harmful effects on environment have been reported to impact the aesthetic services of ecosystems [15]. Many alien species are also known to impact the regulatory ecosystem services i.e., hazards mitigation (e.g. landslide), water

treatment, pest management, pollination, climate change, etc., which are inextricably linked with agriculture and forestry [15].

The invasion of *Opuntia stricta* in African region adversely affected the environment and economy. It has also affected the livelihood of local people through reduction in fodder and livestock health [17]. Since the cultural values are confined to a specific community, their economic quantification is difficult [15]. The cultivation of multi-purpose trees and shrubs is encouraged widely in order to boost bioenergy and industrial sectors [20]. Although, multi-purpose plants provide several benefits to humans, the introduction of alien species as a multipurpose species like *Prosopis* sp. (mesquite) in South Africa can profoundly affect the ecosystem services [21].

3.6. Impact on invasion in diverse environment, protected areas and diversity hotspots

Hughes and Convey [22] reviewed the possible mechanism of protection of Antarctic terrestrial ecosystems from inter- and intra-continental transfer of non-indigenous species by human activities. Alien invasion of microbes, plants and animals may be occurred due to scientific explorations, industrial activities, tourism and cargo oriented travel of people [23]. Frenot et al., [24] reported the biological invasions in the Antarctic area and its impacts and implications. The red quinine tree was introduced in the treeless ecosystems of Galapagos highland, but recently it turned as invasive; thereby reduced the incoming solar radiation which in turn affected the endemic herbaceous species more adversely than non-endemic native species [25].

Foxcroft et al., [26] assumed that the well-managed protected areas, particularly those located on mountain hotspots, are resistant to plant invasion as evident from Kruger Natonal Park of South Africa. Now there is growing literature which reveals that the plant invasion is a major threat to forest biodiversity in protected areas also as is demonstrated in Gros Morne National Park in boreal Canada [26]. Najar et al., [27] analyzed the shola tree regeneration is lower under *Lantana camara* thickets in the upper Nilgiris plateau. Kannan et al., [28] warned on playing with the forest:invasive alien plant species, policy and protected areas in India.

Ecosystem functioning is derailed due to alien species to a greater extent in the geographically isolated islands than in the main lands [29]. It has been documented that such species affect the ecosystem functioning through (a) reduction in the diversity of native species and animals, (b) remarkable changes in physico-chemical soil features (mostly through allelopathy), and (c) enhancement in ecosystems response towards altered fire regimes [29]. Schindler et al., [30] and Heshmati et al., [31] documented the impacts of alien species to reduce the biodiversity of native plants, which may have adverse implications for environment functioning, ecosystem services and global climate change.

However, their proposed role in extinction was argued by invasion biologists and in order to invalidate it or ascertain it uniform dataset across the diverse habitats especially in the isolated islands are needed. Arya et al., [32] documented the ecological impact of planting indigenous plants instead of exotic Acacia trees in Anchal. Jones [33] studied the changes in cropping patterns, resilience and invasive plants of the home gardens of Kerala. Mangla et al., [34], recorded the impacts of exotic invasive plant accumulates native soil pathogens which inhibit native plants growth.

Competition between alien species vs native flora for resources regulating ecosystem functioning may lead to the invasion melt down. Simberloff and Von Holle, [35] meltdown hypothesis states that the establishment of one invasive species in a new environment makes it easier for other nonnative species to invade. The first impact of alien species is the reduction in biodiversity is common across the earth. Alien invaders are also affect the wildlife for example, Gan et al., [36] reported that the alien species *Spartina alterniflora* replaces native *Phragmites australis* and *Scirpus mariqueter* in wetlands of China, which eventually leads to the decline in avian populations due to the movement and feeding restrictions.

Eutrophication in the oligotrophic water bodies leads to intensify the strength of alien species. Similarly, alien species tend to spread at a faster rate, consequent upon the expansion of natural fire regime, which may also have adverse impacts on the ecosystem functioning. Pejchar and Mooney, [15] recorded that many alien species were found to alter the fire regimes in several terrestrial ecosystems that result in a huge socio-economic loss.

3.7. Impacts of the alien species on human health

Biodiversity and its changes are inextricably linked with the human health, both in positive and negative sense like malaria transmission, positive health effects of diversity in nature and green spaces etc [37, 2]. Positive

implications include their applications in vector borne control and ethno-medicinal uses. For instance, a mosquito repellent was extracted from *Lantana camara* [37]. *Ambrosia artemisiifolia, Parthenium hysterophorus, Ailanthus altissima, Acacia, Acer, Casuarina, Eucalyptus, Helianthus, Platanus and Xanthium* were some of the alien species which cause allergy in human beings.

Lake et al., [38] tried to prioritize the impacts of alien species on human health, through direct exposure, as vectors or through transfer of toxins in edibles. *Lantana camara* provides a favourable habitat to tse-tse fly which causes sleeping sickness. Likewise, brush tail possum transmits bovine tuberculosis to live-stock and deer in New Zealand, affecting human health indirectly through food-chain; whereas *Parthenium hysterophorus* serves as a vector of Malaria. Similarly, *Ixodes scapularis* is a vector of *Borrelia burgdorferi*, which causes the Lyme disease in humans.

The prominent aquatic alien species like *Phragmites australis* and *Typha* assist in the colonization and multiplication of vector-borne pathogens, particularly West Nile virus [39]. *Eichhornia crassipes* is a high risk alien species, helping in the spread of schistosomiasis [37]. *Arundo donax* another top ranked alien species posing severe threats to the global environment and health. Trade of such aquatic plants facilitates the spread of disease causing vectors and increases the health risks from vector borne diseases [37]. Water blooms like cyanobacteria that release the cyano-toxins like microcystin, hepatotoxins, saxitoxins, lynbyatoxin and anatoxins are teratogenic (embryotoxic), carcinogenic, and promote tumours. These bio-toxins enter into food chain through the edible species of aquatic ecosystems like water chestnut, fishes etc. Besides the bacterial invaders, there are several other alien species which release diverse chemical toxins for example, grayanotoxins of *Rhododendron ponticum*, which contaminates honey with hazardous toxins. Similarly, the sap of *Ailanthus altissima* upon direct contact effectuates myocarditis, glochids of *Opuntia stricta* cause the eye irritations, retrorsine, an alkaloid of pyrrolizidine group from *Senecio inaequidens, Cortaderia selloana*, *Spartina anglica*, *Caesalpinia decapetala,* and *Rosa rugosa* causes skin cuts and injuries owing to their sharp edge and silicate crystal depositions on leaves. Several ornamental alien species also pose health issues as they emit toxins in the environment. For example, Allergen-specific immunotherapy is considered the most effective tool for managing human health issues due to such allergic species, whereas the adoption of ecological breeding measures like cross-breeding, and understanding the invasion biology of the may be useful for reducing their health impacts. However, species specific focused studies are needed to provide an insight of health hazards, emanating from the exposure alien species for developing better mitigation strategies [40].

3.8. Invasion is it a nuisance? The quest of management implications

Biologists in the field of invasion of alien species are now realizing that not all the alien species impose threats to environment [41]. Pejchar and Mooney [15] reported that 99% of the selected alien species were used globally as food crops directly or indirectly. Even, certain species like *Lantana camara* and *Ageratum conyzoides* were reported to have some ethno medicinal roles in primary health care [20].

IUCN's (2003) clearly states that management of alien species is a priority issue and must be mainstreamed into all aspects of managements of forests and protected areas. Both positive as well as negative ecosystem services must be clearly identified to elucidate their cost-benefit to guide the stakeholders and policy makers [17]. In biodiversity conservation, identifying/ prioritizing alien species has been given the top priority. In this respect, 10% of coastal/ marine areas and 17% of terrestrial and inland water areas are conserved through the diverse targets/action plans. Further, attention is needed for the management of global protected areas, which cover the 14.9 %, of the terrestrial realm.

4. CONCLUSION

The invasion of exotic species is the major concern throughout the earth and has adverse impact on vegetation and agricultural system. There are multiple features which influence the invasion process of alien species. Various mechanisms of invasion of alien species have been proposed. Studies highlighted that antibiosis has major role in establishment and rapid invasion of alien species. Studies documented that the allelochemicals leached from the exotic species are the major factor to compete them with habitat and environment for successful invasion. Similarly, different strategies have been also discussed regarding control of the invasive plant species including biological, cultural and chemical practices. The consequences of invasion are, diverse across the states. Public awareness related to environmental change and biodiversity loss related to alien invasion is mandatory. Sustainable utilization of

land and to counter the invasive species on the native flora and biodiversity is to be designed. The rate of spread of alien species in each of the climatic zones is different. There is also a need to give adequate resources and strategies through which ideal management can be done to control the invasion process in future.

Conflict of interest

The authors report no conflict of interest

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Oxidation reactions of carbaryl in aqueous solutions

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Abstract

Hydroxyl radical induced oxidation of carbaryl has been studied using steady state photolysis followed by high-resolution mass spectrometry (LC-Q-TOF-MS), pulse radiolysis, and theoretical (DFT) calculations. The reaction of •OH with carbaryl resulted in a number of hydroxylated adduct radicals (λ_{max} - 330 nm and 390 nm; k_2 - 1.2×10^{10} dm^3 mol^{-1} s^{-1}). The DFT calculations and results obtained from LC-Q-TOF-MS analysis shows the possible addition of •OH at C1 (energetically most stable) and C7 positions of carbaryl leading to the generation of resonance stabilized hydroxycyclohexadienyl-type radicals as the immediate intermediates, which eventually converted into naphthol and a hydroxylated naphthols. LC-Q-TOF-MS results also revealed the formation of other hydroxylated derivatives and naphthoquinones that are most likely originated from the consecutive •OH attack on the initially formed

products. Naphthoquinones are found to undergo ring opening and the corresponding products are identified. The reaction of $SO_4^{\bullet-}$ with carbaryl, on the other hand, results the radical cation of parent molecule (λ_{max} - 320 nm and 390 nm) which exhibits reasonable stability in the pulse radiolysis timescale. Total organic carbon (TOC) analysis after H_2O_2/UV photolysis revealed that nearly 70% of the organic content is mineralized after 35 min of irradiation, which demonstrates the potential application of oxidative methods towards the degradation of carbaryl.

Introduction

Carbaryl belongs to the carbamate insecticide class which is used for pest control in more than 120 different varieties of crops [1]. It is often used in the cultivation fields and also as a garden insecticide. Recently, it is used as a replacement for persistent organochlorine insecticides [2], [3]. In India, it is commonly used against pests in agricultural fields and its consumption rate is very near to benzene hexachloride [4].This compound is also widely detected in surface water and it stands the second position among the detected insecticides in that medium [3], [5].

Similar to all carbamates, carbaryl also inhibits the enzyme acetylcholine esterase at nerve endings. This can result in an increased level of acetylcholine in the body, which lead to paralysis and uncontrolled movement [6], [7].The massive use of carbaryl is mainly attributed to its low level of mammalian toxicity and comparatively lesser half-life in the environment [2]. The base hydrolysis of carbaryl produces α-naphthol and the hydrolysis rate will be increased at high temperatures [8], [9]. Unlike other aromatic esters and carbamates, carbaryl is not reported to show photo-Fries rearrangement and its photolysis rate is reported to be 100 times smaller than the corresponding naphthyl ester [10]. The in-cage recombination of naphthoxyl and methyl carbamyl radicals (photo dissociated radicals) can give back carbaryl and results in the lower photolysis rates compared to naphthyl esters [10].

Advanced oxidation processes (AOPs) for the degradation of carbamate pesticides using reactive oxygen species are reported [11], [12]. Hydroxyl radicals ($^{\bullet}OH$) are the main oxidant in majority of the AOPs like H_2O_2/UV photolysis, Fenton, photo-Fenton, sonolysis, TiO_2photocatalysis etc [13], [14], [15], [16], [17], [18]. The capability of AOPs to achieve nearly complete mineralization is well documented in the case of a variety of pollutants [11], [12], [19]. In certain cases, it is also probable that a number of intermediate products/end-products, which are even more toxic and persistent, can be formed in the system [20], [21], [22], [23]. Consequently, a detailed investigation of the transformation mechanism is utmost important in the case of any degradation protocol.