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ARTICLE

Microflora Dynamics of Mullaperiyar Reservoir, Idukki

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Abstract

Periyar Lake situated inside the Periyar Tiger Reserve, a major international tourist centre in Kerala, was studied for one year inorder to explore the phytoplantkton status of the oldest manmade freshwater Lake in Kerala. A total of 59 taxa of phytoplanktons of three different habitats (plankton, benthos and periphyton) were identified in the Lake. Among the total microflora, Melosira granulata of Bacillariophyceae dominated in the Lake waters during all the seasons. The Lake was found to be oligotrophic, but certain trends of eutrophication was observed at the tourism zone. In the waters of the boat landing site (P-1), indicator species like *Euglena acus*, *Microsystis aeruginosa* were observed, where the anthropogenic influence in comparatively larger.

Keywords: Microflora Dynamics, Periyar Lake, phytoplantkton

Introduction

Fresh water Lakes/Reservoirs situated in the Western Ghats region of India are little explored for their Phytoplankton. Periyar Lake in the Idukki District is the largest (26km^2 area) and oldest (built in 1895) reservoir –Lake constructed in Kerala to irrigate the plains of Tamil Nadu. The Mullaperiyar dam was constructed near the confluence of Periyar (244km) and Mullayar. This study was designed to understand the micro-flora of the Lake, which was not yet explored, and will give information about the biology of the freshwater bodies in the Western Ghats region (one of the biodiversity hotspots of the World), majority of them are parts of International tourist centers.

Materials and Methods

The Lake is situated at the centre of PTR (core environment of the precious wildlife of the Project Tiger Reservoir and Project Elephant Sanctuary), and it lies between 09'16' and 09'40'N latitude, and 76'55' and 77'26'E longitude, and an altitude of 1525m above mean sea level. Three stations were fixed in the Lake. They were P-1 (Boat landing), P-2(Mullaperiyar Dam site), and P-3 (confluence zone of Mullayar and Periyar). The stations were sampled between January 2011 and December 2012. Free floating Plankton, Benthic algae and Periphyton were collected and examined. Samples for free floating plankton were collected from surface water (1-2cm) in 1L, clean wide mouthed plastic jars and were centrifuged to concentrate the planktonic organisms, before counting. Epiphytes were gathered by collecting the micro-algae colonized on angiosperm plants along the shorelines of the Lake, and were kept in 100mL distilled water in clean plastic bottles. Benthic algae were collected from the surface sediments using 50ml (2cm wide) syringe from the shorelines. Two representative samples (having 50mL) for Benthos analysis were collected from each location (50mLx50mL=100mL). All the samples were fixed in Lugol's iodine solution immediately after collection (1mL:10mL). The phytoplanktons were enumerated by Lackey's drop method APHA (1980), in the laboratory using an electric microscope, having 45x magnifications and were identified using the standard keys provided by Reynolds (1984), and Subrahmanyam (1946).

Results and Discussion

A total of 59 taxa of micro-flora were identified from different representative samples. Among them 54 were identified up to Species level and 5 were identified up to the Genus level (Table-1).

Plankton assemblage

Among the total planktons identified 60 per cent were Diatoms, 30 per cent were Desmids and 10 per cent were Blue-green algae. Major species among Diatoms noticed was Melosira granulata, which dominated the whole year in the Lake. The filament integration of this centric Diatom varied with season. During rainy season with increased water level, Melosira showed 6 to 8 celled, and large sized filaments. While during other seasons filament size and cell numbers decreased (3 to 4). The second most abundant

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A COMPARATIVE STUDY OF PHYTOCHEMICALS AND LARVAL LETHALITY OF THREE MOSQUITO REPELLENT PLANTS IN LAMIACEAE

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Abstract: *Mosquito menace is a big concern to the human World. Many of the diseases caused by mosquito are life threatening if not treated on time. Mosquito completes its life cycle in water. Hence a suitable herbal application needs to be identified to eliminate mosquitoes in water itself. The aim of the study was to identify plants suitable for such an herbal application and from within the families of such plants three varieties were selected and the most suitable one was identified. The investigation mainly based on the application of lower concentrations of leaf extract and thus yielding higher lethality rate of mosquito larva especially Aedes species within a short duration. The mosquito repellent ability of the three plants belonging to Lamiaceae family - Leucas aspera, Anisomeles malabarica and Mentha piperita was conducted. The dried methanolic extract of Mentha piperita gave maximum percent lethality of larva of mosquito Aedes aegypti. A combination of fresh methanolic extract of Leucas aspera, Anisomeles malabarica and Mentha piperita showed maximum mortality rate of larva. All the combination extract at different concentrations of both aqueous and methanolic extract exhibited an average of* LD_{40}. *The fresh aqueous extract of Leucas aspera showed mortality rate lesser than that of combination extract. The fresh methanolic extract of Leucas aspera and Mentha piperita also showed good mortality rate of mosquito larvae.*

Keywords: *Aedes aegypti,, Lamiaceae, Leucas aspera, Anisomeles malabarica and Mentha piperita*

INTRODUCTION

Plants play crucial role in maintaining a sustainable environment. Nowadays, Plant Kingdom is a very interesting area of research for deriving consistent and eco-friendly products. The world is gradually turning to herbal formulations which are effective against a wide range of diseases and ailments. The Lamiaceae plant family is one of the largest families among the dicotyledons, many species belonging to the family being highly aromatic, due to the presence of external glandular structures that produce volatile oil.

In the present day scenario, our planet is undergoing the threat of global warming and climate change in a

drastic way. The global average surface temperature had risen to 0.6 - 0.9ºC between 1906 and 2005 and the rate of temperature increase has nearly doubled in the last 50 years. This has resulted in the increased transmission of mosquitoes and other insect pests leading to their extended spread over diverse geographic ranges. The climate change has also contributed the spreading of diseases like Malaria, Yellow fever, Dengue fever, Chikunguniya etc. To prevent proliferation of mosquito borne diseases and to improve quality of environment and public health, mosquito control is essential.

Aedes aegypti is a so-called holometabolous insect. This means that the insect goes through a complete metamorphosis with an egg, larvae, pupae, and adult stage. The adult life span can range from two weeks to a month depending on environmental conditions. The life cycle of *Aedes aegypti* can be completed within one-and-a-half to three weeks. After taking a blood meal, female *Aedes aegypti* mosquitoes produce eggs and are laid on damp surfaces in areas likely to temporarily flood, such as tree holes and man-made containers like barrels, drums, jars, pots, buckets, flower vases, plant saucers, tanks, discarded bottles, tins, tyres, water cooler, etc. and a lot more places where rain-water collects or is stored.

The major tool in mosquito control operation is the application of synthetic insecticides such as organochlorine and organophosphate compounds. . Chemicals larvicides could be carcinogenic, mutagenic and teratogenic for humans. Natural products, including plant extracts could be suitable candidates for such alternative approaches.

Hence in the present study, an attempt has been made to screen and evaluate the larvicidal properties of medicinal plants: *Leucas aspera, Anisomeles malabarica* and *Mentha piperita*. Extracts from plant sources have demonstrated promising potential as insecticidal or larvicidal agents. The use of plant parts for insect control has several appealing features, as these are generally more biodegradable, less hazardous, and rich storehouse of chemicals of diverse biological activity (Mudrigal, R. V. et al., 1979). In view of

an increasing interest in developing plant origin insecticides as an alternative to chemical insecticide, this study was undertaken to assess the larvicidal potential of the extracts from three medicinal plants.

MATERIALS AND METHODS

Materials: Studies were conducted in three different medicinally important and mosquito repellent plants *Leucas aspera*, *Anisomeles malabarica* and *Mentha piperita*, belonging to Lamiaceae family and larvae of mosquito *Aedes aegypti*.

Methods: Three different plants were cultivated in the same environmental conditions (*in vivo*) through vegetative propagation. Stem cuttings of *Anisomeles malabarica* and *Mentha piperita* were propagated in separate pots. Seedlings of *Leucas aspera* were also planted. All the three plants were watered twice daily and the growth was observed regularly.

Phytochemical studies: Phytochemical screening of extracts of the three mosquito repellent plants were carried out by the standard methods in order to identify the diverse secondary metabolites present in the leaf extracts of three plants. Qualitative assay of Phenols, Tannins, Flavanoids, Saponins and Alkaloids were conducted.

Test for Phenols (sodium hydroxide test): Five milligram of each leaf extract was dissolved in 0.5 ml. 20% sulphuric acid solutions. Followed by addition of few drops of aqueous sodium hydroxide solution, it turns blue which indicates the presence of phenols.

Test for Tannins: Ten millilitres of freshly prepared 10% KOH was added to 1 ml. of each of the leaf extract and observed for dirty white precipitate. Two drops of 5% $FeCl_3$ was added to 1 ml. extracts and observed for green precipitate.

Test for Flavanoids: One millilitre of NaOH was added to 3 ml. of each leaf extracts and observed for yellow colouration.

Test for Saponins (Foam Test): 0.5 mg. of leaf extract was diluted with 20 ml. distilled water and shaken well in a graduated cylinder for 15 minutes. The formation of foam to a length of 1 cm. indicated the presence of saponins and steroids.

Test for Alkaloids: One millilitre of HCl was added to 3 ml. of each extract in a test tube. The mixture was heated for 20 minutes, cooled and filtered. Two drops of Wagner's reagent was added to1 cm^3 of the filtrate and observed for reddish brown precipitate.

Quantitative Test for Phenols: The test was conducted using Folin-Ciocalteau reagent.

Pilot experiment: The preliminary study was conducted in mosquito repellent ability of the three selected medicinally important plant leaf extracts by directly applying into small plastic containing mosquito larvae. The observations were carried out in 1 hr., 3 hrs., 6 hrs., 12 hrs. and 24 hrs.

Treatments: The aqueous and methanolic leaf extracts of *Leucas aspera*, *Anisomeles malabarica* and *Mentha piperita* were prepared. Both fresh and sun dried leaf extracts at different concentrations and combinations were added to wide-mouthed beakers containing mosquito larva. The percentage lethality of mosquito larva in each beakers were analysed on the basis of Probit Analysis (Finney, 1952).

Fresh methanolic leaf extracts of *Leucas aspera*, *Anisomeles malabarica* and *Mentha piperita* were prepared. The leaves were washed thoroughly with running water. One gram of each fresh and sun dried samples were extracted with distilled water and methanol solvents in Soxhlet apparatus. The extract was kept in containers in cool dry conditions at 32± 1º C. The experiment designed in the following method by applying the codes given below.

Solvent System	***Leucas aspera***	***Anisomeles malabarica***	***Mentha piperita***	**Combination**
Fresh leaf in Aqueous	L_{FA}	A_{FA}	M_{FA}	LAM_{FA}
Dried leaf in Aqueous	L_{DA}	A_{DA}	M_{DA}	LAM_{DA}
Fresh leaf in Methanol	L_{FM}	A_{FM}	M_{FM}	LAM_{FM}

Dried leaf in Methanol	L_{DM}	A_{DM}	M_{DM}	LAM_{DM}

Burning ability: The author got the inspiration to study the burning ability of leaves of *Anisomeles malabarica* from an article published in a magazine. In the three selected varieties, the author tested the burning ability of the other two plant leaves also.

RESULTS AND DISCUSSION

As an alternative, the use of plants as insect repellents dates back more than 2000 years, and a wide range of plants have been used to repel mosquitoes (C. F. Curtis *et al.*, 1990).

Phytochemicals in three medicinally potent plants of Lamiaceae – *Leucas aspera* (L.), *Anisomeles malabarica* (L.) and *Mentha piperita* (L.) had shown differences - both, qualitatively and quantitatively.

Phytochemical studies: Qualitative tests for Phenols, Tannins, Flavanoids, Saponins and Alkaloids in three different mosquito repellent plants in three different solvents revealed the presence of those phytochemicals in them. The results observed are represented in Table 1.

Table 1: Expression of Phytochemicals in Different Solvents

Sl. No.	**Tests**	**Solvent (Extracts)**	***Leucas aspera* (L.)**	***Anisomeles malabarica* (L.)**	***Mentha piperita* (L.)**
1	Phenols	Aqueous	++	++	++
2		Methanol	+++	+++	+++
3		Ethanol	++	+++	++
4	Tannins	Aqueous	+	+	+
5		Methanol	++	++	+++

6		Ethanol	++	++	++
7	Flavanoids	Aqueous	+	+	+
8		Methanol	++	+	+++
9		Ethanol	++	++	++
10	Saponins	Aqueous	+	+	+
11		Methanol	++	+	+++
12		Ethanol	+	-	+
13	Alkaloids	Aqueous	+	+	++
14		Methanol	++	++	+++
15		Ethanol	-	+++	++

Number of '+' indicates the presence and strength of phytochmicals

Estimation of Phenols: Due to the peculiar aroma of stem and leaves, the members of Lamiaceae is considered as a group containing valuable phytochemicals. The aqueous, methanolic and ethanolic leaf extracts were analysed for identifying the presence of Phenols, Tannins, Flavanoids, Saponins and Alkaloids. *Anisomeles malabarica* is estimated to have high phenolic content. Over the past few years, investigations for phenolics compounds in medicinal herbs have gained importance due to their high antioxidative properties (Zhu *et al*., 2004).

Phenol estimation from the fresh leaves of three different mosquito repellent plants revealed that the phenol content was higher in *Leucas aspera* (17.2 µg/100 gm.) compared to others (Table 2). In all the three the highest values observed in methanolic extract.

Table 2: Phenol Content (µg/100 gm.)

Sl. No.	**Solvent (Extracts)**	***Leucas aspera* (L.)**	***Anisomeles malabarica* (L.)**	***Mentha piperita* (L.)**
1	Aqueous	17.2	4.84	4.82
2	Methanol	55.68	41.20	17.32

3	Ethanol	34.92	29.16	9.20

Mosquito repellent capacity: Mosquito Aedes sps. are responsible for different diseases. Their life cycle is completed through water only. So, the author conducted the experiments to destroy the larvae through the mosquito repellent plants.

Pilot experiment: In the preliminary studies conducted, *Leucas aspera* had shown high mortality rate in the first hour itself (60.32%) and in 24 hours, the mortality rate was 100% (Table 3). *Anisomeles malabarica* had shown low mortality rate compared to the other to plants in the initial period. Nearly hundred percent mortality was observed in *Mentha piperita* (99.62%) and *Anisomeles malabarica* (97.13%) after 24 hours.

Table 3: Percentage of Mosquito Larvae Mortality

Duration	***Leucas aspera* (L.)**	***Anisomeles malabarica* (L.)**	***Mentha piperita* (L.)**
1 hr.	60.32	10.73	55.27
3 hrs.	79.54	24.36	62.71
6 hrs.	85.07	45.82	74.54
12 hrs.	92.41	64.13	87.83
24 hrs.	100.00	97.13	99.62

Both fresh and sun dried leaf extracts of the three different plants at different concentrations and combinations revealed significant variations in the percentage of mortality. Alone and combination of fresh and dried leaves of the different plants in two different solvents – aqueous and methanol – in different concentrations (0, 0.5%, 1%, 1.5%, 2%, 2.5% and 3%) had expressed a dose dependent, duration dependent variation in percentage of mosquito larvae mortality.

The percentage of mortality in fresh leaves in aqueous extract had shown great variations among the treatments along with the control. The highest percentage of 40% observed in 3%

aqueous in *Leucas aspera* within three hours. The lowest value 0 observed in control.

The percentage of mortality in dried leaves in aqueous extract had shown a great variations among the treatments along with the control. The highest percentage of 25% observed in 3% aqueous in *Leucas aspera* and *Mentha piperita* within three hours. The lowest value 0 observed in control.

The percentage of mortality in fresh leaves in methanol extract had shown great variations among the treatments along with the control. The highest percentage of 75% observed in 3% methanol in *Mentha piperita* within three hours. The lowest value 0 observed in control.

The percentage of mortality in dried leaves in methanol extract had shown great variations among the treatments along with the control. The highest percentage of 100% observed in 2.5 % and 3% methanol in *Mentha piperita* within three hours. The lowest value 0 observed in control.

Mentha piperita exhibits greater flavanoid content and *Anisomeles malabarica* the least. Flavonoids exhibit inhibition of mutagenicity induced by chemical mutagens and have anticarcinogenic, antioxidant and anti-inflammatory activities (Miyazawa *et al.*, 2000). The methanolic extractof *Mentha piperita* showed higher rate of Saponin content whereas *Anisomeles malabarica* and *Leucas aspera* showed medium appearance.

The percentage of mortality in combination of selected leaves both fresh dried leaves in aqueous and methanol extract shad shown great variations among the treatments along with the control. The highest percentage of 100% observed in 2.5% and 3% methanol in combination of fresh leaves within three hours. The lowest value 0 observed in control.

Mosquito repellent capacity of three plants was conducted both in aqueous and methanolic medium. The experiments were conducted at 32 ± 1º C. Plant products have been used traditionally to repel and kill mosquitoes in many parts of the world. Thousands of plants

have been tested as potential sources of insect repellents (King, 1954; Jacobson,

1990). Repellent properties are reported in *Mentha piperita* against Anopheles annularis, *Anopheles culicifacies* and *Culex quinquefasciatus* (Ansari *et al.*, 2000).

Percentage of mortality was observed at different concentrations of leaf extracts taken in methanolic and aqueous medium. Methanolic medium was taken because maximum extraction of phytochemicals was observed in methanol extract. Combinations of the three leaves were also conducted. Maximum effect was observed for dried methanolic extract of *Mentha piperita* and in fresh methanolic extract of combination of the three samples. It showed a Probit value of 8.09. Dried methanolic extract of combination of three samples showed a Probit value of 5.39. Dried methanolic extract of *Anisomeles malabarica* showed a value 5.00. Thus, we can infer that methanolic extracts has given maximum lethality of mosquito larva both in fresh and dried leaves.85% lethality was shown by *Mentha piperita* in the midst of 12 hours. Within 24 hours, maximum mortality rate was achieved. The dried aqueous extracts of *Mentha piperita* and *Leucas aspera* exhibited 20% and 15% lethality. This refers that as dosage increased, mortality rate also increased. The dosage criteria is completely time dependent. As dosage is increased, time required for attaining maximum efficiency decreases. Extracts of several plants - neem (*Azadirachta indica*), basil (*Ocimum basilicum*), mint (*Mentha piperita*) and lemon eucalyptus (*Corymbia citriodora*) - have been studied as possible mosquito repellents and have demonstrated good efficacy against some mosquito species (Sharma *et al.*, 1993; Ansari *et al.*, 2000 ; Trigg and Hill, 1996).

The average larval mortality data were subjected to probit analysis for calculating LC50, LC90, and other statistics at 95 per cent fiducial limits of upper confidence limit and lower confidence limit (Reddy *et al.*, 1992).

The rate of mortality of mosquito larva in aqueous medium is high for *Leucas aspera* at a concentration of 2.5% and 3.0%. In the case of dried leaves extract in aqueous medium, both *Leucas aspera* and *Mentha piperita* exhibit maximum mortality rate at 2.5% and 3.0% concentrations. The highest percentage of 75% mortality was

observed in 3% methanolic extract of *Mentha piperita* within three hours. Maximum efficiency of lethality was observed in a dosage of 2.5% and 3.0% in dried methanolic extracts of *Mentha piperita*.

The highest percentage of 100% observed in 2.5% and 3% methanol in combination of fresh leaves within one hour. Fresh methanolic extracts of combination of selected plant leaves provide greater mortality within a short time compared to dried methanolic extracts. The larvicidal activity was assessed by the procedure of WHO (World Health Organization).

Burning ability: Among the three selected varieties, the *Anisomeles malabarica* had shown the burning ability of leaf of leaf until the oil burns out in a lamp. The other two just burned only for few minutes.

CONCLUSION

The comparative studies were conducted on phytochemical and mosquito repellent activity of three medicinally potent plants - *Leucas aspera, Anisomeles malabarica and Mentha piperita* belonging to the family Lamiaceae.

The members of Lamiaceae are known for their aromatic peculiarities. The presence of different phytochemicals is responsible for this. The presence of these phytochemicals was studied. Qualitative assay of Phenols, Tannins, Flavanoids, Saponins and Alkaloids were conducted. *Leucas aspera, Anisomeles malabarica and Mentha piperita* exhibited higher amount of Phenolic compounds. The aqueous, methanolic and ethanolic extracts responded to phenolic test. The presence of Tannins was tested and *Mentha piperita* showed higher rate of tannins and *Anisomeles malabarica* the least. *Mentha piperita* has maximum flavanoid content whereas *Leucas aspera and Anisomeles malabarica have* flavanoid content less than that of *Mentha piperita. Anisomeles malabarica* showed least Saponin content, *Leucas aspera* showed good responses but *Mentha piperita* had maximum saponin content. *Anisomeles malabarica exhibited* more alkaloid content than *Leucas aspera* but *Mentha piperita* had maximum alkaloid content.

The quantitative estimation of phenols was conducted. Phenols are compounds known for repelling insects and pests. *Leucas aspera and Anisomeles malabarica* had higher phenolic content than that of *Mentha piperita.*

The mosquito repellent ability of the three plants was conducted. The dried methanolic extract of *Mentha piperita* gave maximum percent lethality of mosquito larva. A combination of fresh methanolic extract of *Leucas aspera, Anisomeles malabarica* and *Mentha piperita* showed maximum mortality rate of larva. All the combination extract at different concentrations of both aqueous and methanolic extract exhibited an average of $LD_{40.}$ The fresh aqueous extract of *Leucas aspera* showed mortality rate lesser than that of combination extract. The fresh methanolic extract of *Leucas aspera* and *Mentha piperita* also showed good mortality rate of larva.

Time is a criterion in analysing the mortality rate of mosquito larva. The dried methanolic extract of *Leucas aspera, Anisomeles malabarica* and *Mentha piperita* attained faster mortality rate. The aqueous extract of combinations also showed average probit values. Because of these reasons, the author concluded that methanolic extract of combinations and *Mentha piperita* are suitable for repelling mosquitoes even at their larval stages.

Thus, the author suggests that herbal products are the clean method for controlling mosquitoes. These leaf extract are proved to repel mosquitoes at lower concentration itself. So, it is said to be eco-friendly. This ability can be exploited in a wide spectrum for controlling insect pests by establishing herbal based products like incense sticks, joss sticks, and benzoin resin etc. The smoke from these products is effective in repelling mosquitoes. Also, the burning ability of fresh leaves of *Anisomeles malabarica* can be exploited for making mosquito coils with lesser chemicals. This is beneficial not only for man but also the whole environment itself

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Floristic Diversity of a Sacred Grove in Pandalam

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ABSTRACT

Objective: The objective was to study the species diversity of plants in the sacred grove of Kadakadu Devi temple with special reference to the taxonomic enumeration of the Rare, Endangered and Threatened Plants (RET) present there. **Methodology**: Regular field visits, collection and enumeration of plants were carried out. **Results**: A total of 150 plants were identified, 94% of the plants were Angiosperms, 1.4% were Gymnosperms, 3% were Pteridophytes and the remaining 1.4% were Bryophytes. Among the total plants identified, 7 plant species belonged to the RET category. Among the 7 RET plants, 1 is critically endangered, 3 were Vulnerable and 3 were in least concern category. **Inference:** The study revealed that Sacred groves act as a gene pool and they holds many rare endemic endangered and threatened and ethno botanically important flora.

Keywords: *Floristic diversity, Temple Sacred Groves, Rare, Endangered, Threatened, Pathanamthitta District*

INTRODUCTION

Harmonious living with nature has been an integral part of Indian culture. Sacred groves or forests preserved with reverence have been part of Hindu and Buddhist culture. In Christianity as well as in Islam, conservation of the environment is based on the principle that nature and its components are created by God, and humans are entrusted with the responsibility of protecting it. Many religions and moral philosophies have professed the unity of all life on Earth and the obligation of human beings to care for them. For the people of India, environmental conservation is not a new concept. Some of the fundamental principles of ecology-the interrelationship and interdependence of all life-were conceptualized in the Indian ethos and reflected in the ancient scriptural text, the *Isopanishad*, over 2000 years ago.

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Preliminary Study on the Antibacterial Activity of Six Medicinal Plants against Two Naso-Pharyngeal Pathogens—*Streptococccus pyogenes* and *Pseudomonas aeruginosa*

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Abstract

Objective: The objective is to study the antibacterial activity of six medicinal plants against two naso-pharyngeal pathogens and determination of total phenol contents in ethanol extracts of those plants. Methods: Different serial concentrations (0.05 g/mL, 0.1 g/mL, 0.2 g/mL, 0.4 g/mL) of ethanolic and acetone extracts of *Piper nigrum* L. (*Piperaceae*), *Ocimum sanctum* Linn., *Plectranthus amboinicus* L. (*Lamiaceae*), *Ayapana triplinervis* M.Vahl. (*Asteraceae*), *Cinnamomum zeylanicum* L. (*Lauraceae*), *Allium schoenoprasum* Linn. (*Liliaceace*) were evaluated for the antibacterial activity using disc diffusion method against gram positive *Streptococcus pyogenes* and gram negative *Pseudomonas aeruginosa*. The extracts were prepared from different parts of the plants. The total phenol content was estimated using folin-ciocaltau reagent in catechol equivalents. Results: Majority of the extracts had inhibitory effect against the tested bacteria at different concentrations. In ethanol extracts, *Plectranthus amboinicus* exhibited the maximum zone of inhibition (14 mm) at 0.05 g/mL concentration against *Streptococcus pyogenes*, and *Ocimum sanctum* showed highest zone of bacterial inhibition (19 mm) at 0.05 g concentration against *Pseudomonas aeruginosa*. In acetone extracts, *Piper nigrum* had the maximum zone of bacterial inhibition (17 mm) in 0.4 g/mL concentration against *Streptococcus pyogenes* and *Cinnamomum zeylanicum* and *Allium schoenoprasum* exhibited the highest zone of bacterial inhibition (0.4 g/mL) against *Pseudomonas aeruginosa*. The ethanol extract of *Plectranthus amboinicus* contained the highest amount of phenol (0.8 mg/mL) and *Allium schoenoprasum* contained the lowest amount (0.62 mg/mL). In acetone, *Cinnamomum zeylanicum* contained highest phenol content (0.78 mg/mL). Conclusion: All these investigations pave way to the molecular modeling of the lead phyto compounds present in the

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SEASONAL TROPHIC STATUS OF MULLAPERIYAR LAKE IN THE WESTERN GHATS OF KERALA, INDIA

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Absratct

Periyar lake, situated inside the Periyar Tiger Reserve (PTR) and Wildlife Sanctuary, a major international tourist centre in Kerala, was studied for a year (January to December 2013), in order to explore the nutrient status and associated phytoplankton growth. This oldest manmade freshwater reservoir/Lake in the Western Ghats of Kerala, is getting more attention now a days due to the dispute between Kerala State and Tamil Nadu (TN) State for the ownership of the Mullaperiyar Dam. Moreover, it is situated inside India's prime Tiger reserve in its quantity, area and quality. Total nitrogen and inorganic phosphorus of the waters were studied every month and the data were grouped into three different seasons and analyzed the seasonal fluctuation if any, moreover, water samples from different parts of the entire lake were also analyzed to account any spatial variation due the increasing anthropogenic influence in and around the lake related with tourism. From the study, it was revealed that nitrogen and phosphorus concentration of the lake was at an alarming rate during premonsoon and northeast monsoon in stations-1 and 5 (2400 to 3000 µg/L), with maximum human influence and sewage entry. While the inlets zones (station-4) showed minimum N and P contents (1500 µg/L). The density of phytoplankton showed a positive correlation with the nutrients in almost all seasons. The highest plankton density (490 no./L) was recorded during premonsoon at station-5 and the lowest was at station-4 (253 no./L) during northeast monsoon. From this study, it was clear that the nutrient and phytoplankton of the lake is dependent on the seasonal fluctuations in the environment as well influenced by the increased anthropogenic activities in and around the lake. Strict measures should be taken to monitor the water quality of this pristine water body within the sanctuary because this is the source of drinking water for 4 districts of Tamil Nadu.

Key words : Nutrients, nitrogen, phosphorus, tropical, high altitude, freshwater, Western Ghats.

Introduction

The PTR is one of the most fascinating wildlife sanctuaries of the world, a major site of tourist attraction for the last fifty years. It is designated by the Department of Environment as a major wetland site of the Country. Mullaperiyar Lake located in the Idukki District of Kerala is the largest (26km^2 area) and oldest (built in 1986) reservoir/lake constructed in the state to irrigate the plains of TN. Mullaperiyar Dam was constructed near the confluence of Mullayar and Periyar (the largest river in Kerala with a length of 244 km). It lies between 09'16 and 09'40N latitude and 76'55 and 77'26E longitude and an altitude of 1525m above mean sea level (Govt. Report, 1986).

This study was designed to understand the nutrient status of the freshwater system, which was not explored and will give information about the general trend in nutrient load of the water bodies in the Western Ghats (one of the 25 biodiversity hotspots of the world) region of India, majority of them are under explored. This will help to understand the present nutrient condition of the water body on behalf of the fast developing tourism based on the Lake/Sanctuary system.

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Materials and Methods

Collection of water samples

Five stations were fixed in the lake (fig. 1) based on the maximum and minimum anthropogenic influence to different locations. They were PLS (Periyar Lake Station)-1 (boat landing for tourists), PLS-2 (Mullaperiyar Dam site), PLS-3 (confluence zone of Mullayar to the lake), PLS-4 (confluence zone of Periyar the lake), PLS-5 (open water tunnel to TN from the lake, where the

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INVESTIGATION ON THE IMPACT OF MONOCROPPING ACTIVITES ON THE FLORA DYNAMICS OF AN ECOLOGICALLY SENSITIVE AREA IN THE WESTERN GHATS REGION OF KERALA

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ABSTRACT:

From this investigation it was clear that Nilamel, especially the Campus of this College is having a peculiar type of vegetation with rich biodiversity. This is transitional vegetation between the Western Ghats and the Coastal plains of the District. Many rare, endangered and medicinal plants of this locality indicate the importance of its protection and conservation. This study also highlights the rich soil in this locality and stresses the importance of investigation of this soil. Moreover the remnant of Western Ghats vegetation prevails here. This should be studied in detail to get more significant knowledge of this vegetation.

KEY WORD: Monocropping activities, Flora dynamics, Ecologically sensitive area, Kerala.

INTRODUCTION:

Biodiversity is degrading day by day. Many of the wild plants having high medicinal value are now a day's disappearing or they are in a vulnerable state of existence due to habitat destruction by humans. Ordinary people are not much aware of the importance of protection of these plants and the high value they are contributing to the wellbeing of the ecosystem. This study was undertaken due to such a human interference into pristine

RESEARCH ARTICLE

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INVESTIGATION ON THE MICRO ALGAE OF MANIMALA RIVER AT PATHANAMTHITTA DISTRICT

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Abstract: *Algae (in different form-plankton, benthos, periphyton, lithophytes) of water bodies play an important role in determining the prevailing status of that water body. The study of such organisms in the fluctuating physico-chemical environment is very relevant. Biodiversity of such groups of algae significantly varies in different water bodies according to seasonal changes as well as the specific environment. Manimala is one among the major Rivers in Kerala originating from the Muthavara hills in the Western Ghats and flowing through Pathanamthitta and Kottayam Districts till it joins with Pampa in Alappuzha District. This study is an attempt to understand the biodiversity of microalgae of the River in different locations in Pathanamthitta District, which is a major contributor of drinking and irrigation water resource for the people of the District. The diversity of algal flora is estimated by direct microscopic analysis followed by standard methods. A total of thirty six (different forms-plankton, benthos, epiphytes and lithophytes) algal species belonging to three major classes, Chlorophyceae (22), Euglenophyceae (3) Cyanophyceae (4), and Bacillariophyceae (7) were identified. Among Chlorophyceae a significant number of flagellates were observed. This indicates the increased anthropogenic nutrient enrichment in and around the study area. This preliminary investigation revealed the fact that river Manimala is a rich treasure house of algal flora. The role of our precious water bodies in preserving the biodiversity is highly evident and these resources should be properly utilized for conserving such a diverse ecosystem.*

Keywords: *Algal flora, anthropogenic influence, fresh water, Western Ghats, Pathanamthitta District*

INTRODUCTION

Rivers originating from the Western Ghats are precious water ecosystems with many diverse and unexplored flora and fauna. Many of the West flowing rivers of Kerala are studied for the physico-chemical parameters, but the phytoplankton flora of these rivers is little explored. Manimala is one of the major Rivers of Kerala originating from the Muthavara hills near Peermade in Idukki District. The river passes through the Districts of Kottayam, Pathanamthitta and finally joins with Pampa at Muttar in Alappuzha District. It has a length of 92km. This study was designed to understand the algal community (in different forms- plankton, epiphytes, benthos, lithophytes etc) structure of the River in Pathanamthitta District, which was not yet explored.

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A Comparitive Investigation to Distinguish Two Closely Resembling Families of Gamopetalae, In Some Selected Genera – An Anatomical Overview

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ABSTRACT

The aim of present study was to distinguish two gamopetalous families namely Lamiaceae and Verbenaceae by investigating the anatomical characteristics of total ten selected members, five from each family. The anatomical parameters selected include stomatal types, stomatal intensity, trichome types and trichome intensity. The significance of this study lies in the fact that, some of the Verbenacean members based on Bentham and Hooker system of classification are now found to be shifted to Lamiaceae, according to APG system of classification. This is analogous to the present anatomical study result, which point out the fact that anatomical features of leaf, petiole, stem etc have found application in systematics, particularly for resolving controversial taxonomic problems.

Key words *Gamopetalae, Verbenaceae, Lamiaceae, Trichome, Stomata*

From ancient times, plants have been classified differently at different times. Common four major system of classification are practical, artificial, natural and phylogenetic system of classification. In 1998 a classification of the angiosperms namely Angiosperm Phylogeny Group (APG) system was introduced based on molecular phylogenetics. Now a day's molecular techniques such as molecular markers are used to classify plants. These methods are very costly. So a simple way is needed to differentiate a genus between plants. Anatomical data help to study the ranges of variability of characters in same genus or different genus. It has been successfully employed for the elucidation of phylogenetic relationship. In the present study the characteristic traits used to solve the comparison between Lamiaceae and Verbenaceae includes length and width of stomata, guard cell, subsidiary cell, trichomes and stomatal index. Also stomatal and trichome type were considered.

Major difference between Verbenaceae and Lamiaceae

- Verbenaceae has terminal style where as Lamiaceae has gynobasic style.
- Verbenaceae has racemose inflorescence where as Lamiaceae has racemose as well as cymose arrangements.
- Verbenaceae traditionally include woody, shrubby plants while Lamiaceae consist of mostly herbaceous plants.

There is only a little difference between these families. Also several genera from Verbenaceae were transferred to Lamiaceae in 1990s on the basis of phlylogenetic studies of DNA sequences. So, based on these aspects, the main objective of the present study is to evaluate the anatomical characteristics of selected plant species and identify the plant family through these anatomical characters.

Objectives of the study include the comparison of anatomical characters between Verbenaceae and Lamiaceae, such as study of trichome variability, intensity and type, stomatal type and stomatal index study, compare length and width of guard cell and subsidiary cells.

MATERIALS AND METHODS

Sample materials of ten plants comprising five genera from both Verbenaceae and Lamiaceae families respectively, based on Bentham and Hooker's system of classification have been investigated in the study. Plants were collected from the localities of Pandalam, Pathanamthitta. The genera selected for the study are listed below.

VERBENACEAE MEMBERS : 1. *Lantana camara*, **2.** *Vitex negundo*, **3.** *Clerodendrum thomsoniae*, **4.** *Duranta repens*, **5.** *Stachytarpheta indica*

LAMIACEAE MEMBERS : 6. *Ocimum sanctum*, **7.** *Leucas aspera*, **8.** *Hyptis suaveolens*, **9.** *Coleus aromaticus*, **10.** *Mentha spicata*

The stem, petiole and leaf anatomical characteristics were investigated in cross sections taken in laboratory conditions. The cross section of

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Phytorepellency and Mortality Effect of Five Selected Plants Against Rice Weevil, *Sitophilus oryzae*

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ABSTRACT

The present study was conducted to evaluate the phytorepellency and mortality effects of five plants which possess aromaticity and belong to different families, against the stored food grain insect pest namely *Sitophilus oryzae* which inhabit stored rice grain. The selected plants are *Azadirachta indica*, *Ocimum sanctum*, *Aegle marmelos*, *Lantana camara* and *Eupatorium rugosum*. The study conducted in two steps. Crushed leaves, leaf extract and powdered leaf of five aromatic plant species were tested for their insecticidal activities against *Sitophilus oryzae*. Responses varied with plant material and exposure time. The first step was repellency test, insect showed highest repellency against *A. indica*, followed by other selected genera. The same plant itself showed the highest mortality percentage. Significance of the present study is traditionally it's possible to avoid the damaging effects of *S. oryzae* using plants without going for any chemical products.

Key words Phytorepellency, *S. oryzae*, *O. sativa*, *A. indica*, *O. sanctum*, *A. marmelos*, *L. camara*, *E. rugosum*

Rice, wheat and maize are the world's three leading food crops. Among these three major crops, rice is by far the most important food crop for people. Also it is the most important and staple food of the world's population. Every year cereals such as wheat, rice etc suffers heavy losses during the storage due to insect pest infection. Most of the world's harvested food is destroyed annually by insect and rodent pests. *Sitophilus oryzae* is a common rice weevil and it is one of the most important storage pests, which causes severe damage to raw cereals throughout the world. One pair of *Sitophilus oryzae* can reproduce about one million of its species within a period of three months under favorable conditions (Thomas *et.al.* 2002) and the adults are internal feeders and cause serious quantity and qualitative losses to the grains.

However, due to lack of good and efficient storage facilities, most rice grains are still being stored traditionally in granaries (Odeyemi *et al.*, 2010). Control of stored-product insect populations is primarily dependent upon continued applications of liquid and gaseous insecticides. Although effective, their repeated use for several decades has disrupted biological control system by natural enemies and lead to outbreaks of insect pests. (Champ and Dyte, 1977).

Many plant secondary metabolites play an important role in plant insect interactions and therefore are used in many parts of the world since ancient days. Plant materials that are safe for human consumption and have the ability to retain their insecticidal potency overtime should be recommended to farmers. There is a need to look for an alternative method that is easy, less poisonous and less detriment for pest control. However, very little research has been performed on the development of affordable organic pesticides which offer same control levels as synthetic, to weevil. Hence the present study aimed to examine the effect of five locally available plants for its repellency and mortality effect against *Sitophilus oryzae*.

Objectives of the study include Control *Sitophilus oryzae* in stored rice and analyse the repellency and mortality effect of the five selected plants against *Sitophilus oryzae*.

MATERIALS AND METHODS

Selected plants are used in three forms in this study, crushed leaves, leaf extract in water and dried powdered leaf. Water extract is obtained by grinding the leaves with motor and pestle. Powdered form is obtained by shade drying the selected plants for some days and finely powdered within a blender.

INSECTS TESTED

Live rice weevils were collected from the storage area of the rice trader. Cultures of *S. oryzae* were maintained in the laboratory without exposure to any insecticide on rice grain, in plastic containers. Figure 5 shows the habit as well as habitat of *Sitophilous oryzae*.

PLANTS SELECTED

Five aromatic plant species were selected and collected from Pandalam NSS College campus. The plants selected in this study were *Azardirachta indica*, *Ocimum sanctum*, *Eupatorium rugosum*, *Lantana camara* and *Aegle marmelos*. The leaves of plants

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FREE-RADICAL SCAVENGING ACTIVITY OF LEAVES OF *BIDENS BITERNATA* (LOUR.) MERR. & SHERIFF

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ABSTRACT

Bidens biternata commonly known as "Thunilotti / Alenchappu", in Malayalam language, is a common green leafy vegetable of Western Ghats regions of Kerala state. The leaves of this plant are traditionally used for curing hepatitis, cold, asthma, cough, dysentery and also used as a vegetable by Paniya, Chetti, Kani and Kattunaayika tribes of Waynadu districts. The aim of this work is to evaluate antioxidant potentials of leaves of Bidens biternata by evaluating DPPH, hydroxyl radicals (OH.), nitric oxide (NO.), superoxide (O_2.-) scavenging activity and ferric reducing power activity. Present analysis revealed that this wild leafy plant Bidens biternata possess high free-radical scavenging properties and has potential to destroy the free radicals that damage the cells. This plant extract could be explored as therapeutic agent in future.

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Keywords- *Bidens biternata, Alenchappu, Western Ghats, DPPH free-radical scavenging activity etc.*

INTRODUCTION

A large number of plant sources including many green leafy vegetables and fruits have been reported to have high antioxidant activities, for example mushrooms, cabbage, cauliflowers, garlic, broccoli, beet, corn etc. [Yang *et al.*, 2002]. In traditional societies, nutrition and health care are strongly interconnected and many plants have been consumed as food and also for medicinal purposes [Pieroni, 2000].

The protective action of green leafy vegetables has been attributed to the presence of antioxidants, especially antioxidant vitamins including ascorbic acid, α- tocopherol and β-carotene [Cao *et al.*, 1998]. However, numerous studies have conclusively shown that the majority of the antioxidant activity may be from compounds such as flavonoids, isoflavone, flavones, anthocyanin, catechin and isocatechin rather than from vitamins C, E and β-carotene [Chu *et al.*, 2002]. The consumption of food and beverages rich in phenolics contents can reduce the risk of heart disease by slowing the progression of

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Swapna T. S et al.(2015) Vol.5 Issue.2 Pg:1246-1250
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In vitro Hepatoprotective activity of a wild medicinal plant from Western Ghats - *Bidens Biternata* (lour.) Merr. & Sheriff

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ABSTRACT

Bidens biternata(Lour.)Merr.& Sheriff, belongs to the family Asteraceae, is a wide spread weed of cultivated areas, in Western Ghats regions of Kerala state. It is used as a leafy vegetable by Paniya, Chetti, Kani and Kattunaayika tribes of Waynadu Districts in Kerala. It is also used to cure hepatitis, cold, cough, dysentery, asthma etc. In the present study, the *in vitro* hepatoprotective activity was analysed in crude methanol extract of *B. biternata* leaves. Hepatoprotective effect of plant extracts were determined *in vitro* using cultured Chang liver cells. In MTT assay for evaluation of hepatoprotective activity, cells which are exposed with toxicant CCL_4 showed a percentage cell viability of 19.05%. Cells which are treated with methanol extracts showed an increase in percentage viability ranged from 38.12-85.35% and this cell viability was compared to the standard at the same concentrations (90.52%). The results revealed that the crude methanol extracts of *B.biternata* possessed high hepatoprotective activity, so could be used as an effective therapeutic agent against hepatic diseases of modern society.

Keywords: *Bidens biternata*, Western Ghats, Chang liver cells, CCL_4, MTT assay.

INTRODUCTION

The liver performs hundreds of critical functions to maintain homeostasis and health, includes detoxification of foreign and naturally occurring chemicals, production of serum proteins and hormones, glucose and lipid metabolism and so on. Liver diseases severely affect health and can be life threatening. There are four major types of liver diseases, cirrhosis, fatty liver, hepatitis and liver cancer, with the latter two being among the most serious global public health problems[1].

Hepatitis means 'inflammation of the liver' and the most common symptoms when infected by viruses hepatitis A, B, C, D and E[2]. All of these viruses can cause acute disease with symptoms lasting several weeks. It is estimated that 3 to 4 million people are newly infected each year, with 70% of them develop chronic hepatitis[3]. Both HBV (Hepatitis-B virus) and HCV (Hepatitis-C virus) chronically infected individuals are at high risk of death from cirrhosis, disease that kills about 1 million people each year[3].

Herbal medicines are cheaper, easily available and their method of preparation is also simple and above all it suits the social and culture needs of peoples. Some of the herbal medicines used for the treatment of hepatitis by the tribal people are *Phyllanthus niruri* (Euphorbiaceae), *Azadirachta indica* (Meliaceae), *Boerhaavia diffusa* (Nyctaginaceae), *Allium cepa* (Liliaceae), *Justicia adhothoda* (Acanthaceae),*Emblica officinalis* (Euphorbiaceae), *Cassia fistula* (Caesalpiniaceae), *Terminalia bellarica* (Combretaceae) etc[4].

B. biternata is a medicinal herb found throughout India, especially in Western Ghats of Kerala. This plant medicinally used to treat cough, dysentery, inflammation, asthma etc. And antioxidant potential has already been reported by Pradeesh *et al.*[5] Though the plant and its extracts have been extensively used in the folklore medicine, information from published literature does not provide evidence for its hepatoprotective activities[5]. So the present study aimed to investigate the *in vitro* hepatoprotective effects of methanolic extracts of leaves of *B.biternata*, in CCl_4treated Chang liver cells.

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HPLC AND GC-MS ANALYSIS OF *BIDENS BITERNATA* (LOUR.) MERR AND SHERIFF A WILD ETHNO MEDICINAL PLANT

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ABSTRACT

Bidens biternata (Lour.) Merr and Sheriff, belongs to the family Asteraceae, is a wide spread weed in Waynadu district of Kerala state. It is used as a leafy vegetable by Paniya, Chetti, Kani and Kattunaayika tribes of Waynadu Districts in Kerala and also to cure inflammation, hepatitis, fever, cough, dysentery, bronchitis etc. In the present study crude methanolic leaves extract of *B. biternata* was investigated using HPLC and GC-MS. Presence of bioactive molecules like quercetin, gallic acid, luteolin, ferrulic acid and rutin, were identified using HPLC. Quercetin was found in higher quantities among them. GC-MS analysis of crude methanolic extract showed the presence of four important compounds.

KEYWORDS

Bidens biternata, Western Ghats, HPLC and GC-MS.

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INTRODUCTION

Plants used for traditional medicine contain a wide range of compounds that can be used to treat chronic as well as infectious diseases[1]. Due to the development of adverse effects and microbial resistance to the chemically synthesized drugs, men turned to ethnopharmacognosy[2]. They found literally thousands of phytochemicals from plants as safe and broadly effective alternatives with less adverse effect. Many beneficial biological activity such as anticancer, antimicrobial, antioxidant, anti-inflammatory, analgesic and wound healing activity were reported. In many cases the people claim the good benefit of

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Stress Induced Elicitation of Flavanoids in the Suspension Culture of *Diplazium esculentum* (Retz.)Sw - A Wild Edible Fern of Western Ghats

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ABSTRACT

Diplazium esculentum (Athyriaceae) an edible fern of Western Ghats has many medicinal properties and phytochemical profiling showed the presence of alkaloids, flavonoids, glycosides, alkaloids, steroids and saponins in the extracts of *Diplazium esculentum*. The presence of flavonoids in all extracts (methanol, acetone, petroleum ether, chloroform and distilled water extract) of D. esculentum indicated possible medicinal properties of this leafy vegetable. So, flavonoids were elicited in the cell suspension culture of *Diplazium esculentum* (Retz.) Sw. in 50 ml ½MS media supplemented with 2, 4-D: BAP (1.0:0.5 mg/l), treated with elicitors for 24, 48 and 72 hours under in *vitro* condition. Quantitative analysis of total flavonoids accumulation was done by aluminium nitrate colorimetric method. The results obtained reveal that chitosan at concentration of 20 mg is most effective in eliciting flavonoid production (134.41µg/g) when treated for 24 hrs. The result obtained on elicitation revealed that the studied elicitor trigger the synthesis of flavanoids in *D. esculentum* at in vitro level.

Keywords: Distiled, pahytochemical, accomulation

The pteridophytes are long known for their medicinal and therapeutical utility. Recently enormous efforts have been made to determine the potential of pteridophytes in relation to their chemical composition and other aspects. These plants are distinct in having many primary as well as secondary metabolites like glycosides, flavonoids, terpenoids and alkaloids (Manickam and Irudayaraj 1992). Polyphenolic compounds display a remarkable spectrum of biological activities including antiallergic, anti-inflammatory, antioxidant, antimutagenic, anticarcinogenic, and modulation of enzymatic activities (Craig 1999, Middleton *et al.* 2000, Galati *et al.* 2000, Yang *et al.* 2001). They may, therefore, have beneficial health effects and could be considered as possible chemopreventive or therapeutic agents against cancer (Birt *et al.* 2001, Wang 2000).

Secondary metabolites are produced by the plants when they are under stress conditions like environmental alteration and pathogen attack. Moreover, their production also depends on the

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Research Article

ANTIOXIDANT ACTIVITY IN LEAVES OF *SESBANIA GRANDIFLORA* (L.) PERS.

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ABSTRACT

Objective: The main aim of this study was to evaluate the antioxidants present in *Sesbania grandiflora* (L.) Pers. belongs to the family Fabaceae.

Methods: Fresh samples were used for the analysis of antioxidants such as total phenol, carotenoids, Vitamin-A, Vitamin-C, Vitamin-E, peroxidase (POD), catalase (CAT), superoxide dismutase (SOD), ascorbate peroxidase, monodehydroascorbate reductase, and glutathione reductase by standard estimation methods.

Results: Present studies revealed that this wild leafy plant has numerous antioxidant factors that destroying the free radicals that damage the cells.

Conclusion: *S. grandiflora* contain many enzymatic and non-enzymatic antioxidants and could be a good source of dietary antioxidants which play an important role in the prevention of diseases associated with oxidative stress.

Keywords: Total phenol, Vitamin C, Vitamin E, Peroxidase, Superoxide dismutase, Ascorbate peroxidase, Catalase, Monodehydroascorbate reductase, Glutathione reductase.

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INTRODUCTION

The protective action of vegetables has been attributed to the presence of antioxidants, especially antioxidant vitamins including ascorbic acid, α-tocopherol, and β-carotene [1]. However, numerous studies have conclusively shown that the majority of the antioxidant activity may be from compounds such as flavonoids, isoflavone, flavones, anthocyanin, catechin and isocatechin rather than from Vitamin C, E, and β-carotene [2]. The consumption of food and beverages rich in phenolics contents can reduce the risk of heart disease by slowing the progression of arteriosclerosis by acting as antioxidants toward low-density lipoproteins [3]. The antioxidant activity of phenolics is mainly because of their redox properties, which allow them to act as reducing agents, hydrogen donors, singlet oxygen quenchers, and metal chelators [4]. A large number of plant sources including many vegetables and fruits have been reported to have high antioxidant activities, for example, mushrooms, cabbage, cauliflowers, garlic, broccoli, pinto beans, beans, beet, and corn. Other vegetables such as kale, spinach, brussel sprouts, alfalfas sprouts, red bell pepper, onion, eggplants, and cucumber are also rich sources of antioxidants [5].

In traditional societies, nutrition and health care are strongly interconnected, and many plants have been consumed both as food and for medicinal purposes [6]. Free radicals are highly reactive compounds. They are chemical species associated with an odd or unpaired electron and can be formed when oxygen interacts with certain molecules. They are neutral, short-lived, unstable and highly reactive to pair with the odd electron and finally achieve a stable configuration. Once formed these highly reactive radicals can initiate a chain reaction they are capable of attacking the healthy cells of the body, causing them to lose their structure and function. Cells may function poorly or die if this occurs [7]. Antioxidant is a molecule capable of slowing or preventing the oxidation of other molecules and thereby reduces the possibility of cancer and other diseases. The major action of antioxidants in cells is to prevent damage due to the action of reactive oxygen species (ROS). Studies have indicated that antioxidant supplements have benefits for health. All living organisms contain complex systems of antioxidant enzymes and chemicals, some to combat oxidative damage to cellular components and others to regulate and sustain natural cellular processes such as oxidative phosphorylation and the formation of disulfide bonds [8].

Oxidative stress has been implicated in a variety of diseases such as cardiovascular diseases and cancer [9]. ROS, which induces the oxidative stress, are produced by the reaction of oxygen with radiation, various environmental chemicals, or produced in the course of metabolism by one-electron transfers to an unstable oxygen molecule. ROS respond to most of the biological molecules and damage membranes, enzymes and genes [10]. Since the generation of ROS cannot control, antioxidants and radical scavengers are important to suppress the oxidative stress [11]. Many herbal diets contain antioxidative components such as phenolics, terpenoids, and tocopherols [1]. The production of ROS, such as singlet oxygen ($^1O_2$), superoxide radical (O_2^-), and hydrogen peroxide (H_2O_2), intrinsically accompanies photosynthesis [12]. Hydrogen peroxide (H_2O_2) is generated by the glycolate oxidase reaction in the process of photorespiration [13]. Thus, the consumption of fruits and vegetables could reduce the risk of chronic diseases.

Therefore, in the present investigation, an attempt has been made to understand the antioxidant properties of the wild leafy edible plant *Sesbania grandiflora*, which possess numerous medicinal properties and are consumed by the common peoples of Kerala in India. Studies on the antioxidant value of wild plants are of considerable significance since it may help to identify forgotten medicinal resources.

MATERIALS AND METHODS

Plant material collection and sample preparation

S. grandiflora were collected from different localities of Thiruvananthapuram district of Kerala state in India. Fresh samples were used for the antioxidant analysis and experiments were repeated thrice to confirm the result.

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Functional group analysis of *Cleome viscosa* L. and *C. burmanni* W. & A. (Cleomaceae) extracts by FT-IR

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ABSTRACT

The present study attempts to establish the FT-IR profile and identify the functional components of the methanol extracts of two species of *Cleome*, *C. viscosa* and *C. burmanni*. Similar absorption peaks were exhibited by the two species at different transmission percentages. Also, most of the functional groups observed as per their peaks are similar in the two species with a difference only in their wave numbers. An effort was made to link the observed bands to the probable components in the samples. The two species could be distinguished based on the presence of certain marker compounds. Aromatic amines and alkynes were observed only in *C. viscosa* while *C. burmanni* contained phenols. The possible bioactive properties of the detected compounds are also discussed.

Keywords: FT-IR, spectroscopy, *Cleome viscosa*, *Cleome burmanni*, wavenumbers, amines, alkynes, phenols

1. Introduction

The present generation is witnessing an unanticipated revival in the popularity of natural foods and medicines. The non-availability of data regarding the qualitative and quantitative phytochemical content and scientific validation studies however, prevents the use of herbal drugs among the educated public.

In nature, plants are bestowed with chemical compounds to help provide defense against predators. However, some of the secondary metabolites in plants have also been identified to act as pharmaceutical intermediates or drug precursors which may be utilized for the production of the more potent synthetic drugs. Plant natural product chemistry has played an active role in generating a significant number of candidate compounds in drug discovery programs [1]. However, the climate and other ecological conditions may affect secondary metabolite production in medicinal plants and need to be incessantly monitored to maintain the potency of the plant drugs [2].

Fingerprinting (marker compound analysis) by chemical and validated chromatographic and spectroscopic techniques are gaining importance for standardization in the herbal medicinal formulations. The evaluation of an herbal product by metabolomic fingerprinting can be accomplished by appropriate methods, including HPLC with UV (DAD), ELSD, GC-MS, HPTLC, FT-IR, NIR, NMR or a combination of these techniques [3-5]. Such techniques also provide useful information about qualitative and quantitative composition of herbal medicines and their pattern recognition by chemometry [6].

It is well known that medicinal materials comprise hundreds of components, and produce their curative effects through mutual effects of many ingredients, so the limited number of specific components cannot availably reflect the real qualities of herbal medicines. Therefore, an inexpensive and effective method to entirely monitor all the constituents of the medicinal materials and their corresponding extract products is required [7].

Infrared spectroscopy (IR) has the potential to provide biochemical information without disturbing the biological sample. It is a powerful method for the study of molecular structure and intermolecular interaction in samples. Fourier transform infrared spectrometers, with their high signal-to-noise ratio and high precision in absorbance and wave number measurements have caused a resurgence of interest in the use of infrared spectra for identification of biomolecules [8].

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IN-VITRO ANTI-INFLAMMATORY STUDIES IN *CLEOME VISCOSA L.* AND *CLEOME BURMANNI* W. & A. (CLEOMACEAE)

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Keywords:

Cleome viscosa, *Cleome burmanni*, albumin denaturation, proteinase, hyaluronidase, phytochemicals

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ABSTRACT: The present study evaluates the anti-inflammatory potential of the methanol and chloroform extracts of *Cleome viscosa* and *C. burmanni* by *in-vitro* methods. The anti-inflammatory property of the extracts was assessed using albumin denaturation assay, proteinase inhibitory activity and hyaluronidase inhibition assay and the results compared against reference drugs such as Aspirin and Indomethacin. The present findings exhibited a concentration dependent inhibition of albumin denaturation and hyaluronidase enzyme by the extracts of both plants. Proteinase activity was also significantly inhibited by both plant extracts. The methanol extract was more effective than chloroform extract and was comparable to the standards. From the present study, it can be concluded that the extracts of *C. viscosa* and *C. burmanni* possessed marked *in- vitro* anti-inflammatory activity and the effect could be due to the presence of various phytochemicals present in the plants.

INTRODUCTION: There is a growing interest in the pharmacological evaluation of various plants used in Indian traditional systems of medicines. Traditional medicines are sources of easily available, effective healing agents to the people. It is in this context, that the people consume several plants or plant derived preparations to cure different diseases. Therefore, traditional medicines are being re-evaluated and extensive research involving different plant species and their active therapeutic principles is being carried out. Screening of plants for their biological activity is done on the basis of either their ethnobotanical knowledge or the results of chemotaxonomic investigation.

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Purified natural compounds from plants can serve as template for the synthesis of new generation drugs with low toxicity and higher therapeutic value [1]. Thus it is expected that natural products would play a significant role in human health in relation to the prevention and treatment of disease conditions [2].

An uncontrolled and persistent inflammation may act as an etiologic factor for many of the chronic illnesses [3]. Inflammation is a primary physiologic defense mechanism that helps the animal body to protect itself against infection, burns, toxic chemicals, allergens or other noxious stimuli in order to eliminate or limit the spread of injurious agents. It is a local response of living mammalian tissues to foreign substances such as bacteria, trauma chemicals and heat. It is characterized by pain, swelling and redness which are brought about by various inflammogens like histamines, bradykinins, prostaglandins, leukotrienes. By inhibiting these mediators, the inflammatory response could be suppressed [4]. Although it is a

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Molecular docking studies using Sinigrin and Tamoxifen

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Abstract
Drug design is a process which involves the identification of a compound that displays a biological profile and ends when the biological profile and chemical synthesis of the new chemical entity are optimized. The present work deals with a comparative *in silico* docking analysis using sinigrin, an aliphatic glucosinolate and tamoxifen, the commonly used oral anticancer drug. Protein-ligand docking studies were performed to explore the anti-cancer property of sinigrin. The results revealed that Libdock scores were high for sinigrin when compared to tamoxifen. The protein, iNOS docked with sinigrin possessed a high Libdock score. Sinigrin and tamoxifen passed the Lipinski's rule of five which evaluates the drug-likeness of plant derived compounds. The suitability of sinigrin as a lead candidate for the drug industry was revealed by ADMET and TOPKAT studies.

Keywords: sinigrin, tamoxifen, libdock, ADMET, TOPKAT, lipinski

Introduction
Drug discovery and designing is an expensive process due to the high costs involved in Research & Development (R&D) and the final release of a useful drug. While drug development involves the identification of targets and suitable soluble candidates that block or activate the target; drug design involves the actual designing of small molecules, exhibiting pharmacological interactions with biological receptors [1]. Computer assisted drug design (CADD) involves all the computer-assisted techniques used to design, discover and optimize biologically active compounds [2].
Traditionally it is difficult to select the best chemical moiety of compound that plays an effective role in treating diseases, so computational strategies including molecular docking, ADMET and virtual toxicity studies are essential for identifying potential protein targets of various phytochemicals.
Obviously, *in silico* technique is inexpensive and shortens the time required for testing drug efficacy. The present study is concerned with sinigrin and its potential, relative to the synthetic drug, tamoxifen as an anticancer agent. Sinigrin is an aliphatic glucosinolate and is the precursor of the anticancer compound, allyl isothiocyanate [3]. Tamoxifen is a drug, taken orally as a tablet, which interferes with the activity of estrogen [4]. For the molecular docking studies, eight cancer protein receptors were selected and tested for their interactions with sinigrin as well as tamoxifen along with evaluation of Lipinski's rule of five, ADMET and TOPKAT properties.

Materials and Methods
Ligand preparation
The compound sinigrin (compound ID: 23682211) and the synthetic drug tamoxifen (compound ID: 2733526) were used in the present study. The structure of the compounds was retrieved from the PubChem database (http//pubchem.ncbi.nlm.nih.gov/) as .sdf files. The .sdf files were then converted to .pdb files using smiles online translator.

Protein preparation
The proteins with their PDB ID were retrieved from RCSB protein data bank (www.rcsb.org), crystallographic water molecules were removed from the proteins and the chemistry of the proteins was corrected for missing hydrogen. The eight proteins used in the study along with their PDB ID were 1. α-β tubulin (1JFF), 2. iNOS (1M9K), 3. PTP1B (1Q1M), 4. hppARγ (3VI8), 5. VEGF (1FLT), 6. VEGF2 (2X1X), 7. VEGFR2 (1Y6A) and 8. PIGF-1 (1FZV).
All the analyses were conducted using the facilities available in Accelrys Discovery Studio 4.0 (Ligandfit - docking, Lipinski's drug filter - Lipinski' rule of five, ADMET descriptors-ADMET properties, TOPKAT parameters – virtual toxicity)

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QUANTIFICATION OF SINIGRIN IN TWO SPECIES OF CLEOME L. (CLEOMACEAE) USING HPLC

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ABSTRACT

The genus *Cleome* belongs to the family Cleomaceae. Most of the species of the genus are considered to be weeds but some are reported to possess nutritional and medicinal properties. The present investigation deals with the quantification of sinigrin, in the methanol extracts of two species of *Cleome*, *Cleome viscosa* L. and *C. burmanni* W. & A. using HPLC. Sinigrin is reported to be the precursor of the anticancer compound, allylisothiocyanate and possesses antimicrobial property. HPLC analysis confirmed the presence of sinigrin in both the species. *Cleome viscosa* contained higher amounts of sinigrin (21.35mg/g extract) than *C. burmanni* (17.02mg/g extract). Eventhough, sinigrin has been subjected to extensive research in recent years, isolation protocols have not yet been standardised for sinigrin. The two species of *Cleome* can serve as alternative sources for the isolation of sinigrin due to their abundance and availability.

Keywords: Cleome viscosa, Cleome burmanni, sinigrin, HPLC

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Evaluation of the growth sustaining attributes of *Sonneratia alba* Sm. for strategic afforestation protocols

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Abstract

Mangrove afforestation programs primarily require unswerving information on the growth requirements of the targeted mangrove species. The present investigation was carried out to evaluate the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species *Sonneratia alba* Sm. in pursuit of their afforestation practices. Estimation of the physicochemical characteristics of water and soil / sediment along with climatological attributes from three heterogeneous habitats falling in the coastal environments of Kerala was monitored monthly for a period of one year for deriving conclusions regarding the growth requirements of *S. alba* Statistical analysis revealed the most vital attributes of water which influence the growth of *S. alba* are water turbidity, TSS, nitrogen, potassium and sedimentological attributes such as moisture %, sand, silt, clay %, organic carbon and potassium without any significant variation. The study as a whole reported the capability of *S. alba* to cope up with different hydrological and sedimentological conditions in terms of tolerance or augmented range, which will form a basis for future afforestation initiatives.

Key words: Climatology, Growth sustaining conditions, Sediment quality, *Sonneratia alba* Sm., Water quality.

Introduction

Restoration or afforestation endeavor on mangroves primarily requires reliable information on ecology, hydrology and sedimentology that control the successful growth of the targeted mangrove species. Among all such vital attributes, water and sediment quality are known to have supreme influence on the growth of mangroves (Thom, 1967). In light of this, the present investigation was carried out with the objective of evaluating the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species *S. alba* in pursuit of their utilization for species specific afforestation practices.

Materials and Methods

Sonneratia alba is a widespread and common species found in the low-intertidal zone. It is intolerant of long periods of freshwater, and prefers high salinity. It is a pioneering species that is fast growing, but has low seed-viability. Three heterogeneous natural habitats confining to the coastal environments of Kerala (Fig. 1) have been fixed for assessing the growth sustaining conditions of the mangrove species *S. alba* (Table 1). Location 1 (Kadalundi 1) and Location 2 (Kadalundi 2) was falling in Malappuram district and Location 3 (Thekkumbad) in Kannur district.

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Growth Sustaining Aspects of *Excoecaria Agallocha* L. for Strategic Afforestation Protocols

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Abstract- Restoration/ afforestation initiatives on mangroves primarily require reliable information on the growth requirements of the targeted mangrove species. The present investigation was carried out to evaluate the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species *Excoecaria agallocha* L. in pursuit of their afforestation practices. Assessment of the physicochemical characteristics of water and soil / sediment along with climatological attributes from three heterogeneous habitats falling in the coastal environments of Kerala was monitored monthly for a period of one year for deriving conclusions regarding the growth requirements of *E. agallocha*. Statistical analysis revealed the most vital attributes of water which influence the growth of *E. agallocha* are water pH, turbidity, total suspended solids, resistivity, acidity, alkalinity, phosphorous and potassium and also the sedimentological characteristics such as pH, moisture %, sand, silt, clay %, organic carbon, nitrogen, potassium and sodium. The study as a whole reported the capability of *E. agallocha* to cope up with different hydrological and sedimentological conditions in terms of tolerance or augmented range, which will form a basis for future afforestation initiatives.

Keywords- *Excoecaria agallocha,* growth sustaining conditions, water quality, sediment quality, climatology

I. Introduction

Any afforestation or restoration endeavor on mangroves primarily requires reliable information on ecology, hydrology and sedimentology that control the successful growth of the targeted mangrove species. Among all such vital attributes, water and sediment quality are known to have supreme influence on the growth of mangroves [1]. In light of this, the present investigation was carried out with the objective of evaluating the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species *E. agallocha* in pursuit of their utilization for species specific afforestation practices.

II. Materials and Methods

Excoecaria agallocha L. is a small to medium sized back mangrove species and often exploits open areas along with some marine and coastal protected regions. Three heterogeneous natural habitats confining to the coastal environments of Kerala (Fig. 1) have been fixed for assessing the growth sustaining conditions of the mangrove species *E. agallocha* (Table 1). Location 1 (Ayiramthengu) was falling in Kollam district. Location 2 (Kumbalam) of Ernakulam District was 102 km far from Location 1 and Location 3 (Thekkumbad) was in Kannur district, which was 294 km from location 2.

Table 1. Study Area

Sl. No:	Location	District	Latitude	Longitude
1	Ayiramthengu	Kollam	9°07'28.71"N	76°28'38.89"E
2	Kumbalam	Ernakulam	9°54'15.02"N	76°18'45.49"E
3	Thekkumbad	Kannur	11°58'00.71"N	75°17'49.79"E

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Standardization of the growth sustaining attributes of *Avicennia officinalis* L. for strategic afforestation protocols

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Abstract

Any afforestation / restoration initiatives on mangroves primarily require reliable information on the ecology, hydrology and sedimentology of the targeted mangrove species. The present investigation was carried out to evaluate the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species *Avicennia officinalis* L. in pursuit of their afforestation practices.

Evaluation of the physicochemical characteristics of water and soil / sediment along with climatological attributes from three heterogeneous habitats falling in the coastal environments of Kerala was monitored monthly for a period of one year for deriving conclusions regarding the growth requirements of *A. officinalis*. Statistical analysis revealed the most vital attributes of water which influence the growth of *A. officinalis* are pH, total suspended solids, resistivity, alkalinity and nutrients like nitrogen, phosphorous and potassium. Similarly sedimentological parameters include pH, moisture percentage, organic carbon, nitrogen, potassium, sodium and relative percentage of sand, silt and clay. The study as a whole reported the capability of *A. officinalis* to cope up with different hydrological and sedimentological conditions in terms of tolerance or augmented range, which will form a basis for future afforestation initiatives.

Key words: *Avicennia officinalis, growth sustaining conditions, water quality, sediment quality, climatology.*

1. Introduction

Basically, any afforestation or restoration endeavor on mangroves primarily requires reliable information on ecology, hydrology and sedimentology that control the successful growth of the targeted mangrove species. Among all such vital attributes, water and sediment quality are known to have supreme influence on the growth of mangroves (Thom, 1967). In light of this, the present investigation was carried out with the objective of evaluating the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species *Avicennia officinalis* L. in pursuit of their utilization for species specific afforestation practices.

2. Materials and Methods

Avicennia officinalis L. is a fast growing shrub / tree, mostly found in the lower intertidal estuarine zones. It is a shade intolerant species, grows on soft, recently consolidated mud banks. Three heterogeneous natural habitats confining to the coastal environments of Kerala (Fig. 1) have been fixed for assessing the growth sustaining conditions of the mangrove species *A. officinalis* L. (Table 1). Location 1 (Kumbalam) was falling in Ernakulam district. Location 2 (Kadalundi) of Malappuram District was 165 km far from Location 1 and Location 3 (Thekkumbad) was in Kannur district, which was 130 km from location 2.

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Evaluation of the growth sustaining attributes of *Rhizophora mucronata* Lam. for strategic afforestation protocols

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ABSTRACT

Afforestation program on mangroves primarily require reliable information on the growth requirements of the targeted mangrove species. The present investigation was carried out to evaluate the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species *Rhizophora mucronata* Lam. in pursuit of their afforestation practices.

Estimation of the physicochemical characteristics of water and soil / sediment along with climatological attributes from three heterogeneous habitats falling in the coastal environments of Kerala was monitored monthly for a period of one year for deriving conclusions regarding the growth requirements of R. *mucronata* Lam. Statistical analysis revealed the most vital attributes of water which influence the growth of R. *mucronata* are water pH, TSS, resistivity, alkalinity and potassium and also in sedimentological characteristics such as silt %, organic carbon, nitrogen, potassium and sodium without any significant variation. The study as a whole reported the capability of R. *mucronata* to cope up with different hydrological and sedimentological conditions in terms of tolerance or augmented range, which will form a basis for future afforestation initiatives.

1. Introduction

Restoration or afforestation endeavor on mangroves primarily requires reliable information on ecology, hydrology and sedimentology that control the successful growth of the targeted mangrove species. Among all such vital attributes, water and sediment quality are known to have supreme influence on the growth of mangroves (Thom, 1967). In light of this, the present investigation was carried out with the objective of evaluating the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species *R. mucronata* in pursuit of their utilization for species specific afforestation practices.

2. Materials and Methods

Rhizophora mucronata is a widespread common mangrove species (along marine and coastal protected areas) found in the intermediate to upstream estuarine zone in the lower to mid-intertidal region and more to the seaward side. Three heterogeneous natural habitats confining to the coastal environments of Kerala (Fig. 1) have been fixed for assessing the growth sustaining conditions of the mangrove species *R. mucronata* (Table 1). Location 1 (Ayiramthengu) was falling in Kollam district. Location 2 (Kumbalam) of Ernakulam District was 102 km far from Location 1 and Location 3 (Thekkumbad) was in Kannur district, which was 294 km from location 2.

Fig. 1. Study Area

Optimization of the growth sustaining attributes of *Bruguiera cylindrica* (L.) Blume for strategic afforestation practices

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Abstract

Reliable information on the growth supporting attributes of the targeted mangrove species is a prime requisite for any afforestation / restoration initiative. The present investigation was carried out to evaluate the hydrogeochemical, sedimentological and climatological conditions ideal for the growth and establishment of the mangrove species Bruguiera cylindrica (L.) Blume (Rhizophoraceae) in pursuit of their afforestation practices.

Appraisal of the physicochemical characteristics of water and soil / sediment along with climatological attributes from three heterogeneous habitats falling in the coastal environments of Kerala was monitored monthly for a period of one year for deriving conclusions regarding the growth requirements of B. cylindrica. Statistical analysis revealed the most vital attributes of water which influence the growth of B. cylindrica are resistivity, alkalinity, phosphorous and potassium; and also sedimentological characteristics like sediment pH, sand %, clay %, organic carbon and potassium. The study as a whole reported the capability of B. cylindrica to cope up with different hydrological and sedimentological conditions in terms of tolerance or augmented range, which will form a basis for future afforestation initiatives.

Key words

Bruguiera cylindrica, growth sustaining conditions, water quality, sediment quality, climatology

1. Introduction

Any afforestation or restoration endeavor on mangroves primarily requires reliable information on ecology, hydrology and sedimentology that control the successful growth of the targeted mangrove species. Among all such vital attributes, water and sediment quality are known to have supreme influence on the growth of mangroves (Thom, 1967). In light of this, the present investigation was carried out with the objective of evaluating the hydrogeochemical, sedimentological and

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Research Article

INVENTORY ON THE DIVERSITY AND DISTRIBUTION OF MANGROVES FROM THE COASTAL ECOSYSTEMS OF KERALA STATE, INDIA

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Mangrove ecosystems, extent and diversity, Kerala.

ABSTRACT

Consolidation of data pertaining to the extent and diversity of mangroves is a pre requisite for the selection of strategies for the conservation of existing and the introduction of newer population. In this direction, the present study has been carried out to assess the extent and diversity of mangroves confining to 10 districts of Kerala by consistent field visits, Google imageries, toposheets and GPS. The present survey estimated the total extent of mangroves in Kerala to be 19.531 km^2. It has also been highlighted that out of 10 districts studied, Kannur occupied highest mangrove cover (38.22 %), followed by Ernakulam (31.58%), Kozhikode (6.18 %), Kasaragod (3.63 %), Alleppey (5.32 %), Kottayam (5.04 %), Kollam (2.71 %), Thrissur (2.08 %), Malappuram (1.88 %) and Trivandrum (1.41%). Diversity studies revealed the existence of 15 true mangrove species falling under 9 genera and 6 families. The study concluded that, though there is technical increases in the extent of mangroves, most of the major mangrove growing areas are under drastic pressure. Since the survival of this eco system is inevitable for ensuring coastal balance, intensive and extensive conservation and ecosystem reinstatement programmes should be undertaken without delay.

INTRODUCTION

The mangroves are intertidal plant formations of tropics and subtropics, which are adapted to grow in the saline environments. They are unique in their location, structure and function. These are comparatively one of the well-studied ecosystems throughout the world and have been received attention of researchers from different fields of science.

Mangroves are mainly found between the Tropic of Cancer and the Tropic of Capricorn, covering majority of the tropical and subtropical coastlines, worldwide (Saenger, 2002). Recent reports on the distribution of mangroves reveal that they are found in 105 nations globally (Hamilton and Casey, 2016), in which Indian mangroves are one of the major forests of the South East Asia. In India, the total area of mangroves is estimated to be 6,740 km^2 (MoEF, 1987), which is about 7% of the world's mangrove area.

Mangroves of Kerala are highly fragmented and confined mostly to the estuaries of major rivers, lagoons, backwaters and creeks along the coastal belt. Mohanan (1997) estimated that, mangroves in Kerala coast are less than 50 km^2, existing in discrete and isolated patches with a total of 32 mangrove species. It has also been reported that the extent of mangroves of Kerala is 2502 ha, of which 1189 ha belongs to the State and 1313 ha under private ownership (Vidyasagaran and Madhusoodanan, 2014).

In the last two decades, mangrove populations have witnessed annual loss between 0.16 and 0.39% globally due to various anthropogenic activities (Hamilton and Casey, 2016). It has been reported that Kerala coast once supported about 700 sq.km of mangroves and presently it has been dwindled to a considerable extent. Mangrove ecosystems are receiving increasing attention in Kerala, but still lack updated information on their diversity and extent for deriving strategic plans for conservation / afforestation. The present study has been carried out to assess the extent and diversity of mangrove ecosystems in the heterogeneous environments of Kerala with a view to conserve their existing habitats from further degradation.

MATERIALS AND METHODS

Extensive literature survey has been carried out to have an idea about their habitats, together with their extent and diversity in the coastal environments of Kerala. Accordingly field visits were carried out to these mangrove habitats confining to 10 districts of Kerala. The mangrove patches distributed along various districts under study were categorized into homogeneous and heterogeneous types. The assemblage of true

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Short Communication

Assessment of seasonal changes in water quality adjoining Thekkumbad mangrove – sacred grove ecosystem of Kannur district, Kerala, India

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Abstract

Thekkumbad Island, falling in Mattool panchayat of Kannur district, is characterized by the presence of a sacred grove - Thazhekkavu, rich in mangrove populations. This sacred grove is characterized by the presence of 11 true mangroves and 6 mangrove associates. The Valapattanam estuary provides tidal waters to these mangrove habitats. The present study attempts to assess the seasonal changes in water quality influencing the growth and establishment of mangrove diversity confining to this sacred grove. Water quality parameters adjoining the mangrove habitats were monitored on a monthly basis for assessing the seasonal changes. The results indicated that there is marked difference in water quality parameters in all the three seasons studied. Variations in salinity related parameters like hardness, calcium, magnesium, sodium and chloride were higher than that of other water quality parameters, which are indicative of the differences in salinity intrusion in these habitats, with respect to seasons. Water quality parameters of Site 1 was found to be highly influenced, which is indicative of their close proximity with the estuarine system.

Keywords: Mangrove habitats, Thekkumbad, Water quality, Salinity.

Introduction

Thekkumbad is a picturesque Island in Valapattanam River, situated at Mattool panchayath of Kannur district. Kannur district occupies the highest extent of mangroves in Kerala[1] and also showed a fivefold increase in the percentage data on comparing the previous reports based on mangrove afforestation[2]. Thekkumbad is characterized by the presence of a biodiversity rich coastal sacred grove namely 'Thazhekkavu'. The Thekkumbad Thazhekkavu is bordered by Valapattanam River in the south, Pazhayangadi River in the east and backwater of the Arabian Sea in the west. Total area of Thekkumbad Thazhekkavu is 7.50 ha. and the area with vegetation is 6.50 ha.[3]. The Thekkumbad Island is supported by strong fences of mangroves that protect the Island from natural disasters. The total mangrove area is approximately 2788 m². The area composed eleven true mangrove species and six associates. This includes *Acanthus ilicifolius, Acrostichum aureum, Aegiceras corniculatum, Avicennia officinalis, Avicennia marina, Excoecaria agallocha, Kandelia candel, Rhizophora mucronata, Rhizophora apiculata, Sonneratia alba, Bruguiera cylindrica, Calamus rotang, Mimusops elengi, Pandanus tectorius, Clerodendron inerme, Cinnamomum zeylanicum etc...* The Valapattanam estuary provides tidal waters to these mangrove habitats. There are mainly two distinct pattern of arrangement noticed in this region, that is the seaward side is dominated by a long stretch of *Rhizophora mucronata* species while the opposite sides are characterized by mixed vegetation representing *Aegiceras corniculatum, Avicennia marina, Avicennia officinalis, Bruguiera cylindrica, Excoecaria agallocha, Kandelia candel, Rhizophora apiculata* and some associates[4]. This mangrove association plays an important role in the purification of water present in the nearby wells.

The water quality, comprising the environmental master factors such as temperature, salinity, oxygen, besides organic matter, nutrients and trace metals, forms the basis for the mangrove ecosystems. The interactive physical, chemical and biological processes operating in this ecosystem sustain higher levels of productivity, as reflected in a wide spectrum of flora and fauna, leading to richness in biodiversity. The mangrove ecosystems are so specialized that any minor variation in their hydrological or tidal regimes causes noticeable damages, as observed in recent studies at several locations like Guiana, Gambia, Kenya, India, Bangladesh etc...

Even though mangrove forests are highly productive, various eco physiological attributes influencing their sustenance are needed to be thoroughly assessed. Evaluation in this direction is having great importance as these ecosystems are highly sensitive and fragile.

The water quality thus forms the basis for the floral and faunal diversity of mangrove ecosystems[5].

The present study attempts to assess the seasonal changes in water quality influencing the growth and establishment of mangrove species like *Avicennia officinalis* (Site 1), *Brugueira cylindrica* (Site 2), *Excoecaria agallocha* (Site 3), *Rhizophora*

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Surveillance of the Tolerance Limit of *Sonneratia alba* Sm. to certain Hydrogeochemical Parameters from Heterogenous Natural Habitats of Kerala, South India

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Abstract

Efforts for the restoration of mangroves entail unswerving information on their growth sustaining conditions. Present study attempts to assess the tolerance of Sonneratia alba, the mangrove apple, grown in diverse natural conditions in the coastal environments of Kerala, to varied ranges of water quality parameters influencing their growth and establishment. Such information is appropriate in finding out regions which are ideal for their introduction in pursuit of coastal conservation and management. The year round study indicated a marked difference in all water quality parameters in their habitats, with respect to seasons. The range of tolerance of imperative water quality parameters like salinity (ppt) during pre-monsoon, monsoon and post monsoon seasons was noted to be 33.93 – 38.5, 0.299 – 11.68 and 7.107 – 35.15 respectively. Similarly the ranges of Hardness (6840 - 8760, 32 - 520 and 280 – 6800 mg/l), Calcium (448.56 – 528.66, 1363.4 – 1830.86, 9.62 – 134.67 mg/l), Magnesium (1.46 – 44.79, 84.17 – 488.61, 8.28 – 1397.49 mg/l), Sodium (23.9 – 29.8, 0.002 – 8.17, 5.33 – 31.1ppt) and Potassium (0 – 1.65, 0 – 0.26, 0.12 – 2.56 ppt) were analysed and reported. Correlation of these vital hydrogeochemical parameters from diverse sampling stations proved that the changing trends in related parameters are coherent and all the three sampling stations are highly unswerving and persuasive. More over wide range of tolerance of S. alba to salinity (0.299 to 38.5 ppt) is indicative of their potentialities for inclusion in various coastal restoration activities.

Keywords: *Sonneratia alba*, Water quality, Restoration/ Afforestation, Salinity.

Introduction

Mangroves are highly productive bio resources of the intertidal zone, which spread across the tropics and subtropics, offering tremendous ecosystem services[1]. Over-exploitation of these resources resulted in the degradation and thereby disruption of intertidal ecosystems[2]. These ecologically important coastal ecosystems are declining at a disquieting rate, particularly in developing countries, that they may completely disappear within the next 100 years[3]. India has a mangrove cover of 3150 km^2, of which 80% occurs along the east coast and in the Andaman Islands. It was reported that during the past 25 years, almost 30% of the mangrove forest in the country was cleared[4]. Most degraded mangrove cover reported is in the Gulf of Kutch, Gulf of Khabayat and Kerala coast[5]. A drastic decline in the mangrove cover from 700km^2 to17km^2 was evidenced in the state of Kerala that posed a 'threatened' status in the State[6]. Thus, an urgent fortification and conservation of this ecosystem is necessary.

Afforestation of mangroves seems to be a promising solution for the restoration of their lost habitats[4]. Since the establishment of mangrove population depends mostly on their growth necessities and habitat uniqueness, research regarding the above areas needs to be carried out prior to any afforestation programme. A study on "Restoration of Mangroves in Kerala and Karnataka States" during 2005-06 summarized that the major species used for plantation in Kerala are *Rhizophora apiculata*, *Kandelia candel*, *Avicennia officinalis*, *S. alba* and *Aegiceras corniculatum*. Among these *R. apiculata* and *K. candel* are the major species used for raising plantations as more than 80 % of the area planted are with these species[7].

In the present study, an attempt has been carried out to assess the range of water quality parameters favouring the growth of *S. alba* (Lythraceae), which are growing naturally in various heterogeneous conditions along the coast of Kerala. Such information on their natural growth conditions will help in the selection of sites ideal for afforestation activities in the coastal environments of any nation.

Materials and Methods

Study Area: The present investigation was carried out in three different natural habitats of *S. alba*, straddling in 3 regions of Kerala namely Vallikkunnu (Malappuram, 11°07'35.14"N, 75°49'51.77"E), marked as Station I; Kadalundi (Malappuram, 11°07'35.42"N, 75°49'50.72"E), marked as Station II and Thekkumbad (Kannur, 11°58'04.32"N, 75°17'45.38"E) marked as Station III. Station I and II are part of Vallikkunnu -

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Status of mangrove diversity in the coastal environments of Kerala

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Abstract

Mangrove habitats are an important constituent of coastal wetlands and their ecosystem services are many. In Kerala, mangroves are distributed in the coastal environments of all districts, except Idukki, Pathanamthitta, Palakkad and Wayanad. History records that the coast line of Kerala, ramified by backwaters and shallow canals were once fringed by luxuriant growth of Mangroves. Presently their extent has been dwindled drastically.

The present study envisage to find out the major changes in species composition and extent associated with the mangrove habitats confining to the coastal environments of Kerala over a period of time. The study also focuses on the causes of depletion of mangroves and the management measures to be adopted for its restoration.
Key words: *Mangrove habitats, Kerala coast*

Introduction

Mangroves are wetland ecosystems formed by the assemblage of specialized plants and animals adapted to semi saline swamps along coastal environments. They are found in more than 120 countries and territories around the world. The mangrove ecosystems cover about 0.037 % of the world's surface or 0.12 per cent of the Earth's land area (Ong, 2004).

Mangroves in India account for about 5 per cent of the World's mangrove vegetation and are spread over an area of about 4,500 km along the coastal States/UTs of the country. The total area of mangroves in India is estimated to be 6740 sq. km., which contributes to about 7% of the World's mangroves. Out of this, the Sunderbans of West Bengal has the largest area followed by the Andaman and Nicobar Islands. The remaining mangrove habitats are scattered in the states of Andra Pradesh, Tamil Nadu, Maharashtra, Orissa, Goa, Karnataka, Lakshadeep and Kerala.

Kerala with a coastal line of about 560 km and 41 rivers emptying into the Lakshadweep Sea, forms congenial and convenient environment for the growth and development of mangroves. Mangroves are distributed in all the districts of Kerala, except Idukki, Pathanamthitta, Palakkad and Wayanad. Over years, there has been drastic change in the extent and diversity of mangroves confining to the state of Kerala. The present paper is an attempt to assess the changes in the extent and diversity of mangrove habitats confining to the coastal environments of Kerala over a period of time.

Materials and Methods

Extensive literature survey has been carried out to have an idea about the earlierand recent extent

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COMPARISON OF PROXIMATE COMPOSITION OF FIVE CYPRINIFORMES FISH SPECIES OF RIVER ACHENCOVIL

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Abstract: *The proximate compositions of five cypriniformes fish species of River Achenkovil were compared. In Barilius bakeri the protein, carbohydrate, lipid, cholesterol, ash and moisture contents (%) were estimated as 14.74, 0.05, 1.44 0.41, 3.16, and 78.92 respectively whereas triglyceride, phospholipids and freefattyacids content (%) were 0.02, 0.03 and 0.4, respectively. In Barilius gatensis the protein, carbohydrate, lipid, cholesterol, ash and moisture contents (%) were estimated as 13.25, 0.08, 1.30, 0.26, 3.20 and 78.46, respectively whereas triglyceride, phospholipids and freefattyacids content were 0.03, 0.1 and 0.42 respectively. In Garra mullya the protein, carbohydrate, lipid, cholesterol, ash and moisture contents (%) were estimated as 13.45, 0.04, 1.58, 0.20, 3.23 and 79.70, respectively whereas triglyceride, phospholipids and freefattyacids content were 0.06, 0.04 and 0.42 respectively. In Labeo dussumeiri the protein, carbohydrate, lipid, cholesterol, ash and moisture contents (%) were estimated as 13.40, 0.04, 1.45, 0.22, 3.59 and 78.70, respectively whereas triglyceride, phospholipids and freefattyacids content were 0.05, 0.03 and 0.34 respectively. In Puntius sarana the protein, carbohydrate, lipid, cholesterol, ash and moisture contents (%) were estimated as 12.94, 0.02, 1.44, 0.21, 3.20 and 79.32, respectively whereas triglyceride, phospholipids and freefattyacids content were 0.04, 0.03 and 0.43 respectively. The present study comparing the proximate composition of five cyprinid freshwater fishes of Achenkovil River show significant variation in their proximate composition. They constitute a high-protein, low-fat composition and are rich in various macro and micronutrients, hence may contain low calorie per unit of protein and can be considered as an ideal source of animal protein for use in healthy point of view.*

Key words: Biochemical composition, Cypriniformes, Barilius bakeri, Barilius gatensis, Garra mullya, Labeo dussumeiri, Puntius sarana, Achencovil river

INTRODUCTION

Fish received increased attention as a potential source of animal protein and essential nutrients for human diets (Fawole et al., 2007). The chemical composition of freshwater fishes is valuable to nutritionists concerned with readily available sources of low-fat, high-protein foods (Foran et al., 2005). Moreover, the measurement of some proximate profile such as protein contents, lipids and moisture contents is often necessary to ensure that they meet the requirements of food regulations and commercial specifications (Watermann, 2000). So it is very essential to estimate the chemical or proximate or percentage composition of indigenous species in the healthy point of view, as they are valuable sources of various macro and micronutrients. The cypriniformes forms the dominating fish species of River Achenkovil, a

RESEARCH ARTICLE ISSN:2319-6955

ROLE OF DIET AND LIFESTYLE IN ALTERING THE BENEFICIARY EFFECT OF MODERATE ALCOHOL CONSUMPTION: A COHORT STUDY IN EX-SERVICEMEN OF PATHANAMTHITTA DISTRICT - KERALA, INDIA

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Abstract: *Coronary Artery Disease (CAD) or atherosclerosis is the most common type of heart disease, is known to be associated with many risk factors, which include traditional risk factors such as elevated cholesterol levels, lack of adequate exercise, smoking etc. Consumption of alcohol, though traditionally considered injurious to general health, is known to confer beneficial effect in preventing CAD by lowering blood cholesterol levels, especially when alcohol is in moderate quantities (up to 12 standard drinks a week). However, it is suspected that lifestyle factors act as modifiers in such beneficial effect and sedentary lifestyle and a diet rich in saturated fat has been suggested to negate the beneficial effect of moderate alcohol consumption. The present study was conducted from 101 ex-servicemen using a standard questionnaire. Subsequently lipid profiling was performed from 71 respondents who qualified as moderate alcohol users (≥8 standard drinks per week). 11 out of 71 moderate drinkers (15.5%) harbored CAD like symptoms (history of heart attack, stroke, angioplasty for arterial blocks and angina and/or altered ECG profile). The CAD subpopulation harbored higher, but marginally significant, levels of Triglycerides compared to 23 respondents with good health condition. Further 25 respondents with significantly elevated blood pressure also harbored significantly higher TG levels compared to the subgroup (n=23) with general good health. On further analysis, high TG and lower HDL levels were associated with lack of exercise and diet rich in saturated fat. The present study indicates the overall beneficial effect of moderate exercise along with consumption of alcohol in negating the effect of fat-rich diet in lowering the CAD risk. However, further detailed population based study to assess the role of risk factors in*

Keywords: *Coronary Artery Disease, Cardiovascular health, moderate alcohol consumption, [illegible] fat, exercise*

INTRODUCTION

CAD is the end result of build-up of atherosclerotic plaques in the arteries supplying blood to heart (Ever D Grech, 2003). The signs and symptoms of CAD may vary, and are often detected at the advanced stage of the disease. Frequently characterized as ischemia of heart (heart attack); majority of the affected individual harbor relatively few or no symptoms. The atheromatous plaques accumulating in the major arteries reduces the elasticity of the blood vessels and sometimes lead to its rupture (along

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Research Article

Evaluation of the anti-diabetic potential of aqueous extract of *Clerodendrum infortunatum* L. *in vivo* in streptozotocin-induced diabetic Wistar rats

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Abstract

Diabetes Mellitus, the metabolic syndrome where the body either fails to produce or effectively utilize insulin, is associated with chronic morbidity. While a definitive cure for the disease is lacking, with the modern medicine offering mainly the means to control the extent of the disease, Complementary and Alternative Medicine (CAMs) offers additional/alternate means to tackle the disease. On the other hand, the lack of evidenced medical practices is a lacuna in most of the traditional medical applications. *Clerodendrum infortunatum*.L (Lamiaceae family), a perennial shrub found in the tropics, has been known for many pharmacological properties and is found as a constituent in many Ayurvedic and Siddha drugs, especially for skin and respiratory ailments. The plant has a noted potential as anti-hyperglycemic and has been found to be used in traditional medicine for the treatment of diabetes. However, evidence based evaluations have not been conducted on the anti-hyperglycemic effect of the plant, especially with respect to the general mode of intake, i.e, the aqueous form. In the current study, the aqueous extract of *C. infortunatum* (Cl), was scientifically assessed for its effect on streptozotocin induced diabetes in Wistar albino rats. The diabetic rats were divided into 5 groups of 6 animals each. For testing the efficacy of extracts, two groups were intra-orally provided with dosages of 200 mg/Kg and 400 mg/Kg of body weight of animals, respectively, of aqueous extracts of Cl. Control groups were maintained for evaluation, which included vehicle control as well as with Glibenclamide, a standard anti-diabetic drug. The extracts at a dose of 400 mg/Kg body weight was found to be associated with significant amelioration of many of the diabetes induced conditions, suggesting that the plant extract could be a strong potential CAM candidate for therapeutic management of diabetes.

Keywords

Complementary and alternative medicine; *Clerodendrum infortunatum*; diabetes; streptozotocin

Citation

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Method validation and dissipation kinetics of flubendiamide and spiromecifenin brinjal (*Solanummelongena.*L)

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Abstract

In order to understand the respective dissipation kinetics, two of the new-generation insecticides, *viz.*flubendiamide and spiromecifen, was field evaluated on brinjal (*Solanummelongena.L)*in the farmer's field at Vellayani, Kerala. QuEChERS, the simple and prompt analytical method was adopted for the quantification of residues in brinjal fruit and method validation was performed and the samples (after method validation) were injected in LC-MS/MS, where the samples were compared with serially diluted pure standards of flubendiamide and spiromesifen for the authentication of the procedure. The dose applied was 90 and 180 , 150 and 300 g a.i. ha^{-1} respectively. The initial deposit of flubendiamide in brinjal after the application of single dose was 0.141± 0.003µg $g^{-1}$and 0.305± 0.008µg g^{-1} for the double dose. Similarly, the initial deposit of spiromesifen was measured at 0.614± 0.003µg g^{-1} in fruit after the application of single dose and 1.105± 0.008 µg g^{-1} for double dose. The residue of flubendiamide detected in brinjal fruit had dissipated below the limit of quantification (LOQ) of 0.02µg g^{-1} at the third and fifth day of spraying, respectively, for single and double doses. The half-life of flubendiamide was identified to be 0.91 days at single dose and 1.108 days at double dose, respectively. In the case of spiromecifen, single and double doses dissipated below LOQ (0.02 µg g^{-1}) at seventh and tenth day, respectively. The half-life of the same was 1.78 days for single dose and 1.42 days for double dose. The study asserts that the waiting period of flubendiamide (less than three day for both doses) and spiromesifen (less than seven day for both doses) is low compared to other class of pesticides. These kind of new generation insecticides play an important role in management of many pests with good efficacy, high selectivity and low mammalian toxicity, thereby

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Conventional risk factors and DNA Repair Efficiency in Coronary Artery Disease

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ABSTRACT
Coronary artery disease (CAD) is a multifactorial disease caused by the interplay of environmental risk factors with multiple predisposing genes. Many studies were conducted to evaluate the role of conventional risk factors in CAD patients of Kerala. No systematic studies were conducted to assess the alteration in DNA repair efficiency in patients with conventional risk factors associated with CAD. The present study was undertaken to assess and to correlate the role of DNA repair efficiency with the conventional risk factors of CAD. One hundred and twelve clinically proved patients with fifty age and sex matched control subjects were included in this study. Detailed clinical characteristics were recorded using proforma. Peripheral blood lymphocyte micro culture was performed as described by Moorhead (1960) for determining the in vitro mutagen sensitivity. The mean number of bleomycin-induced breaks per cell was calculated WHICH is an indicator of mutagen sensitivity and DNA repair efficiency. 't' test, chi-Square test and logistic regression analysis were performed for data analysis. The result was presented as odds ratio (OR) with 95% confidence intervals. Smoking, alcoholism, diabetes, hypertension and family history of CAD were found to be significantly associated with CAD. Various risk factors like smoking, diabetes mellitus, dyslipidemia and hypertension was found to be significantly associated with increase in mean b/c value. This study clearly indicates that the mean b/c value was higher in subjects with abnormal risk factors like smoking, alcoholism, diabetes and hypertension.

Keywords: Coronary artery disease; DNA damage; DNA repair efficiency; in vitro mutagen sensitivity analysis; mean break per cell (b/c) values

INTRODUCTION

Coronary artery disease (CAD) is the pivotal disease entity in terms of both morbidity and mortality in the entire world population. CAD is epidemic in India and it is one of the major causes of disease-burden and deaths. Mortality data from the Registrar General of India shows that cardiovascular diseases are the major cause of death in India [1]. The huge burden of CAD in the Indian subcontinent is the consequence of the large population and the high prevalence of CAD risk factors [2]. Conventional risk factors like hypertension, hyperlipidemia, diabetes mellitus, family history, smoking etc contribute only 50% of the total risk of CAD [3]. This suggests that the major CAD risk factors still to be identified. The study of these risk factors is important since the ability to accurately predict the CAD risk of a specific individual based on his or her conventional risk factor profile is limited [4]. DNA damage has been found as an emerging risk factor to play an important role in atherosclerosis and coronary artery disease [5]. DNA damage is caused by multiple endogenous and exogenous factors such as oxidative stress, age, smoking, hypertension, hyperlipidemia and diabetes mellitus [6]. Usually the cells have repair mechanisms that identifies and correct such defects. Therefore DNA repair is essential to an individual's ability to respond to the damage caused by environmental mutagens and reactive cellular metabolites [7]. Inter individual variability in DNA repair capability is an important factor influencing the risk of CAD. Hsu et al [8] developed an assay in which the frequency of chromatid breaks induced by bleomycin in cultured lymphocytes in vitro was quantified as a combined measure of mutagen sensitivity and DNA repair capacity; the number of bleomycin-induced breaks per cell was used to identify sensitive subjects. In an earlier study by Simon et al [9] the mean break per cell (b/c) values which is an indicator of decreased DNA repair efficiency was found to be significantly increased in CAD patients ($P < 0.05$). A systematic approach to evaluate the impact of various lifestyle risk factors on the molecular mechanisms in CAD is not fully understood.

No serious attempts were made earlier to correlate DNA repair efficiency with conventional risk factors of CAD. Hence present study was undertaken to assess alterations in DNA repair efficiency in patients with conventional risk factors associated with CAD. An attempt was also made to correlate the DNA repair efficiency with risk factors such as obesity, diabetes, hypertension and also the habit of smoking and alcoholism.

MATERIALS AND METHODS

One hundred and twelve clinically proved CAD patients from Pushpagiri Heart Institute and fifty healthy age and sex matched controls were included in this study. Detailed clinical characteristics were recorded using proforma. Ethical approval from the Institutional ethics committee, Pushpagiri Institute of Medical Sciences and Research Centre and informed consent were obtained. Three ml of venous blood was collected and used for peripheral lymphocyte culture and in vitro mutagen sensitivity assay for determining DNA repair efficiency. Peripheral blood lymphocyte micro culture was performed as described by Moorhead [10] for determining the in vitro mutagen sensitivity. Bleomycin (mutagen) was added to induce

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A Study to Evaluate the Severity of Coronary Artery Disease (CAD) in Relation to Oxidative Stress and Antioxidant Status

Short Running Title: Association of lipid peroxidation with CAD severity

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Pushpagiri Institute of Medical Sciences and Research Centre, Thiruvalla, Kerala, India.

Abstract: **Coronary artery disease (CAD) is a multifactorial disease with no known definite cure, but preventable and treatable. Many studies have linked excess generation of reactive oxygen species (ROS) with cellular damage and CAD. No systematic studies were conducted to evaluate the role of oxidative stress and antioxidant status on CAD severity. Hence we have undertaken this study. One hundred and twenty four angiographically proved CAD patients were included in this study. CAD severity was assessed by angiography. The patients with 0 vessel disease were taken as control to study the correlation of lipid peroxidation with CAD severity. Lipid peroxidation product, Malondialdehyde (MDA), antioxidants such as Super Oxide Dismutase (SOD), Glutathione (GSH) and Ascorbic acid of all patients were estimated in the serum. Our results revealed that there was higher lipid peroxidation with CAD severity as indicated from lower values of MDA and higher values of SOD in 0 vessel disease compared to single vessel, double vessel and triple vessel disease patients ($p<0.05$). The severity of CAD is closely related to increased lipid peroxidation and decreased antioxidants status as indicated by the MDA and SOD levels.**

Keywords: **Coronary artery disease (CAD); Reactive oxygen species (ROS); CAD Severity.**

1. INTRODUCTION

Coronary artery disease (CAD) is a complex multifactorial and polygenic disorder where multiple environmental and genetic factors are involved simultaneously (1). Second half of the 20th century witnessed a global spread of the coronary artery disease epidemic especially in developing countries, including India (2). A constant supply of oxygen is indispensable for cardiac viability and function. As oxygen is a major determinant of cardiac gene expression and a critical participant in the formation of free radicals commonly known as reactive oxygen species (ROS) which plays a major role in the pathogenesis of cardiac dysfunction (3).

In the vascular system, the formation of ROS from endothelial cells, smooth muscle cells and macrophages may be of major relevance in atherogenesis. This oxidative stress is recogonised as a key mechanism for atherogenesis and in the development of atherosclerosis (4,5). Under normal conditions, numerous cellular antioxidant systems exist to defend against oxidant stress and maintain the redox balance of the cell. ROS are cleared from the cell by enzymatic systems including superoxide dismutase, catalase, and glutathione peroxidase or the non– enzymatic system including vitamin E, ascorbic acid and glutathione (6).

Lipid peroxidation is a free radical mediated process, which is potentially harmful to membranes, lipoproteins and polyunsaturated fatty acids leading to the formation of malondialdehyde (MDA). The physical habits like cigarette smoking and alcohol consumption of patients also contributed to lipid peroxidation (7,8).

A good antioxidant status may be important for human health and especially for the prevention of chronic diseases such as cancer and CAD. Low plasma levels of antioxidant as well as low intake of dietary antioxidants have been associated with an increased risk of atherosclerotic heart disease patients (9). The potential damage that can be caused by free radicals is minimized by a combination of biological antioxidant systems both enzymatic and non-enzymatic (10).

J Basic Clin Physiol Pharmacol. 2016 Jun 1;27(4):403-9. doi: 10.1515/jbcpp-2015-0081.

Protective effect of Scutellaria species on AAPH-induced oxidative damage in human erythrocyte.

Salini S, Divya MK, Chubicka T, Meera N, Fulzele DP, Ragavamenon AC, Babu TD.

Abstract

BACKGROUND: Scutellaria baicalensis is a well-known plant in traditional Chinese medicine. Recently, several Scutellaria species with therapeutic potential have been recognized worldwide. Scutellaria colebrookiana and Scutellaria violacea, native to the Western Ghats of India, are reported to possess free radical scavenging efficacy. At present, the protective effect of these Scutellaria spp. against 2,2' azobis (2-amidinopropane) hydrochloride (AAPH)-induced oxidative damage in human erythrocytes has been analyzed.

METHODS: Oxidative stress in erythrocyte was induced by AAPH. The inhibition of hemolysis, membrane lipid peroxidation, and protein damage by chloroform extracts of Scutellaria spp. was assessed biochemically. Phytochemicals of the extracts were analyzed by Fourier transform infrared spectrophotometer (FTIR).

RESULTS: Approximately 95% of erythrocytes were lysed by AAPH over 3 h of incubation. Significant reduction in hemolysis was observed by the extracts, and the IC50 values were 18.3 and 23.5 µg/mL for S. colebrookiana and S. violacea, respectively. Both the extracts were found to inhibit AAPH-induced lipid peroxidation in ghost membrane with IC50 92±2.8 and 70±5.6 µg/mL. In the analysis of the membrane proteins using sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE), the AAPH-induced degradation of actin was found reduced by both the extracts. The FTIR spectrum revealed the presence of polyphenols, carboxylic acids, alkanes, and aromatic compounds in extracts. In quantitative analysis, the total polyphenolic content estimated was 380±0.23 and 203.7±1.4 mg of gallic acid equivalent per gram extract of S. colebrookiana and S. violacea.

CONCLUSIONS: Results indicate that S. colebrookiana and S. violacea are capable of protecting erythrocytes from oxidative damage. This cytoprotective effect of the extract is possibly by its antioxidant property.

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[Indexed for MEDLINE]

Format: Abstract

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A parasporin from Bacillus thuringiensis native to Peninsular India induces apoptosis in cancer cells through intrinsic pathway.

Chubicka T[1], Girija D, Deepa K, Salini S, Meera N, Raghavamenon AC, Divya MK, Babu TD.

Author information

Abstract

Parasporins, a class of non-insecticidal crystal proteins of Bacillus thuringiensis (Bt) are being explored as promising anticancer agents due to their specific toxicity to cancer cells. The present study has identified 25 Bt isolates harbouring parasporin genes from Western Ghats region, the hotspot of biodiversity in India. Among these, the isolate, KAU 41 (Kerala Agricultural University isolate 41) contained non-hemolytic homogenous crystals showing specific cytotoxicity towards cancer cells. SDS-PAGE analysis of this crystal, isolated by aqueous biphasic separation, revealed a 31 kDa sized peptide. The N-terminal sequence deciphered in BLAST analysis showed homology to a hypothetical Bt protein. Upon proteolysis, a 29 kDa active peptide was generated which exhibited heterogenic cytotoxic spectrum on various cancer cells. HeLa cells were highly susceptible to this peptide with IC 50 1 lg/mL and showed characteristics of apoptosis. RT-qPCR analysis revealed the overexpression of APAF1, caspase 3 and 9 by 14.9, 8 and 7.4 fold, respectively which indicates the activation of intrinsic pathway of apoptosis. However, at higher concentrations of peptide (greater than 3 lg/mL), necrotic death was prominent. The results suggest that the 31 kDa protein from Bt isolate, KAU 41 is a parasporin that may have high therapeutic potential.

PMID: 29872027

Free full text

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Kingiodendron pinnatum, a pharmacologically effective alternative for *Saraca asoca* in an Ayurvedic preparation, *Asokarishta*.

Shahid AP[1], Sasidharan N[1], Salini S[2], Padikkala J[2], Meera N[2], Raghavamenon AC[2], Babu TD[2].

Author information

Abstract

Saraca asoca (Fabaceae) is a prime ingredient in *Asokarishta*, a well-known Ayurvedic preparation for gynecological ailments. Due to scarcity, adulteration or substitution of related raw drugs is a common practice in its preparation. The bark of *Kingiodendron pinnatum* (Roxb. ex DC.) Harms, morphologically similar to *S. asoca* (Asoka) is a widely used substitute. The present study aimed to evaluate the pharmacological effectiveness of *K. pinnatum* as an alternative for *S. asoca* in *Asokarishta* by determining the inhibitory effect of estrogen induced uterus endometrial thickening in immature female rats. *Arishta* was prepared using *S. asoca* and with the substitute, *K. pinnatum* as per Ayurvedic Pharmacopeia. Uterus endometrial thickening was induced by the administration of estradiol (20 μg/kg b. wt, i.p) to 8-day-old rats for 5 alternate days. On day 16, following estradiol administration, the serum estrogen level was found elevated to 156.5 ± 8 pg/ml from the normal value 32.4 ± 5 pg/ml and consequently increased the thickness of uterus endometrium from 16.7 ± 1.4 to 75.2 ± 15.3 μm. Upon oral administration of 400 μl/kg b. wt *Asokarishta* (ASA) and *Arishta* made with *K. pinnatum* (AKP), the thickening was reduced to 42.5 ± 12.7 and 47.1 ± 10.5 μm and the estrogen level diminished to 102.6 ± 10 and 97.3 ± 8 pg/ml, respectively. *Arishta* also reduced the chronic/acute inflammations in mice and improved the antioxidant status of rats. No toxic symptom was observed in the animals by the treatment of *Arishta*. The study supports the use of *K. pinnatum* as an alternative to *S. asoca* in *Asokarishta* and gives a scientific validation for *Asokarishta* in gynecological ailments.

KEYWORDS: Anti-estrogenic; Anti-Inflammatory; Asokarishta; Cornification; Metaplasia; Substitutes; Uterus endometrium

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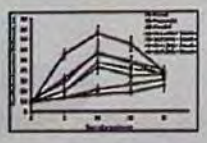

J Basic Clin Physiol Pharmacol. 2015 Sep;26(5):509-15. doi: 10.1515/jbcpp-2014-0124.

Effect of Saraca asoca (Asoka) on estradiol-induced keratinizing metaplasia in rat uterus.

Shahid AP, Salini S, Sasidharan N, Padikkala J, Raghavamenon AC, Babu TD.

Abstract

BACKGROUND: Estrogen-mediated uterus endometrium instability is considered as one of the etiological factors in dysfunctional uterine bleeding (DUB) and uterine cancer. Saraca asoca (Family: Fabaceae) and its fermented preparation, Asokarishta, are extensively used as uterine tonic to treat gynecological disorders in Ayurveda. The present study evaluated the effect of S. asoca (Asoka) on estrogen-induced endometrial thickening of rat uterus.

METHODS: Endometrial thickening was induced by intraperitoneal injection of estradiol (20 µg/kg b.wt) to 8-day-old immature rats for alternate 5 days. Methanolic extract (200 mg/kg b. wt) from S. asoca bark was given orally along with estradiol. Uterus endometrial thickening was analyzed histopathologically and serum estrogen level by radioimmunoassay (RIA). Cyclooxygenase (COX-2) expression in rat uterus was also estimated by Western blot. Anti-inflammatory activity of the extract was analyzed by formalin- and carrageenan-elicited paw edema models in mouse.

RESULTS: Uterus endometrium proliferation and keratinized metaplasia with seven to eight stratified epithelial layers on day 16 was observed in rats administered with estradiol. Treatment with S. asoca reduced the thickening to two to four layers and the serum estrogen level diminished significantly to 82.9±12.87 pg/mL compared to rats administered with estrogen alone (111.2±10.68 pg/mL). A reduction of formalin- and carrageenan-induced paw edema in mouse by S. asoca extract was observed. Lower level of lipopolysaccharides (LPS)-induced COX-2 enzyme in rat uterus by the extract further confirms its anti-inflammatory activity.

CONCLUSIONS: Present study reveals the antiproliferative and antikeratinizing effects of S. asoca in uterus endometrium possibly through its anti-estrogenic and anti-inflammatory properties.

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[Indexed for MEDLINE]

Pharm Biol. 2016 Sep;54(9):1564-74. doi: 10.3109/13880209.2015.1107747. Epub 2016 Feb 15.

Attenuation of DMBA/croton oil induced mouse skin papilloma by Apodytes dimidiata mediated by its antioxidant and antimutagenic potential.

Divya MK[1], Salini S[1], Meera N[1], Lincy L[1], Seema M[1], Raghavamenon AC[1], Babu TD[1].

Author Information

Abstract

Context Considering the role of cellular oxidative stress in mutations and subsequent transformation, phytochemicals with antioxidant potential has become a primary choice as chemopreventives. Apodytes dimidiata E. Mey. Ex. Arn (Icacinaceae), a widely used plant in Zulu traditional medicine, is reported to possess antioxidant activity. Objective To investigate the chemopreventive efficacy of methanol extract of A. dimidiata leaf (AMF). Materials and methods Antimutagenic potential of AMF (25, 50 and 75 µg/plate) was evaluated by the Ames test. The ability of AMF (100 and 250 mg/kg orally) on restoration of depleted antioxidant status by sodium fluoride (NaF) was analysed on BALB/c mice. 7,12-Dimethylbenz[a]anthracene/croton oil induced mouse skin papilloma model was studied up to 20 weeks to analyse the anticarcinogenic effect of AMF (1%, 3% and 5% topically, twice weekly for 6 weeks). Phytochemicals of AMF were characterized by GC-MS. Results AMF (75 µg/plate) reverted 4-nitro-o-phenylenediamine (NPDA) induced mutations in Salmonella typhimurium strains, TA 98, 100 and 102 by 74.8%, 72.5% and 69.3%, respectively. Against sodium azide, the percentage reversion was 80.4, 71.3 and 71.3. In mice, AMF (250 mg/kg for 4 days) increased the serum superoxide dismutase (SOD) and catalase activities by 48.71% and 30.3% against the NaF-induced drop. GSH level was improved by 48.59% with a concomitant decrease in TBARS (57.67%). The skin papilloma reduction was 79.32% for 5% AMF. Squalene, dodecanoic, tetradecanoic and hexadecanoic acids are the known antioxidant and chemopreventive molecules identified by GC-MS. Discussion and conclusion Antioxidant and antimutagenic activities of AMF might have contributed to its anticarcinogenic potential.

KEYWORDS: Chemoprevention; mutation; oxidative stress; phytoconstituents; skin tumourigenesis

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PubMed

Format: Abstract

Full text links

Planta Med. 2015 Dec;81(18):1705-11. doi: 10.1055/s-0035-1557751. Epub 2015 Jul 28.

Evaluation of Cytotoxic and Antitumour Properties of Apodytes dimidiata and Characterisation of the Bioactive Component.

Divya MK[1], Salini S[1], Chubicka T[1], Raghavamenon AC[1], Babu TD[1].

Author information

Abstract

Apodytes dimidiata, belonging to the family Icacinaceae, is used for treating inflammation and various gastrointestinal ailments in Zulu traditional medicine. In the present study, significant cytotoxicity was exhibited by the methanolic extract of the A. dimidiata leaf against various cancer cell lines. The extract was purified partially through silica gel column by successive elution using various solvents of increasing polarity. Among these, the active methanolic fraction was found to be the most cytotoxic with IC50 values ranging from 0.92 to 3.95 µg/mL for Ehrlich's ascites carcinoma (a carcinoma cell line), Jurkat (human T lymphocyte cell line), and SK-BR-3 (mammary tumour cell line). The treated cells showed morphological alterations characteristic of apoptosis. Upon oral administration of active methanolic fraction at a dose of 250 mg/kg body weight, the solid tumour volume in mice was significantly reduced to 55.14% and the life span of the ascites tumour-bearing mice increased to 44.65% compared to untreated control. The active fraction with Rf value 0.56 was purified from the methanolic fraction by preparative thin-layer chromatography and was subjected to high-performance thin-layer chromatography, high-performance liquid chromatography, liquid chromatography-mass spectrometry, and nuclear magnetic resonance analysis. The iridoid glycoside genipin was identified as the active component.

PMID: 26218335 DOI: 10.1055/s-0035-1557751

[Indexed for MEDLINE]

Publication type, MeSH terms, Substances

LinkOut - more resources

फरवरी २०१४

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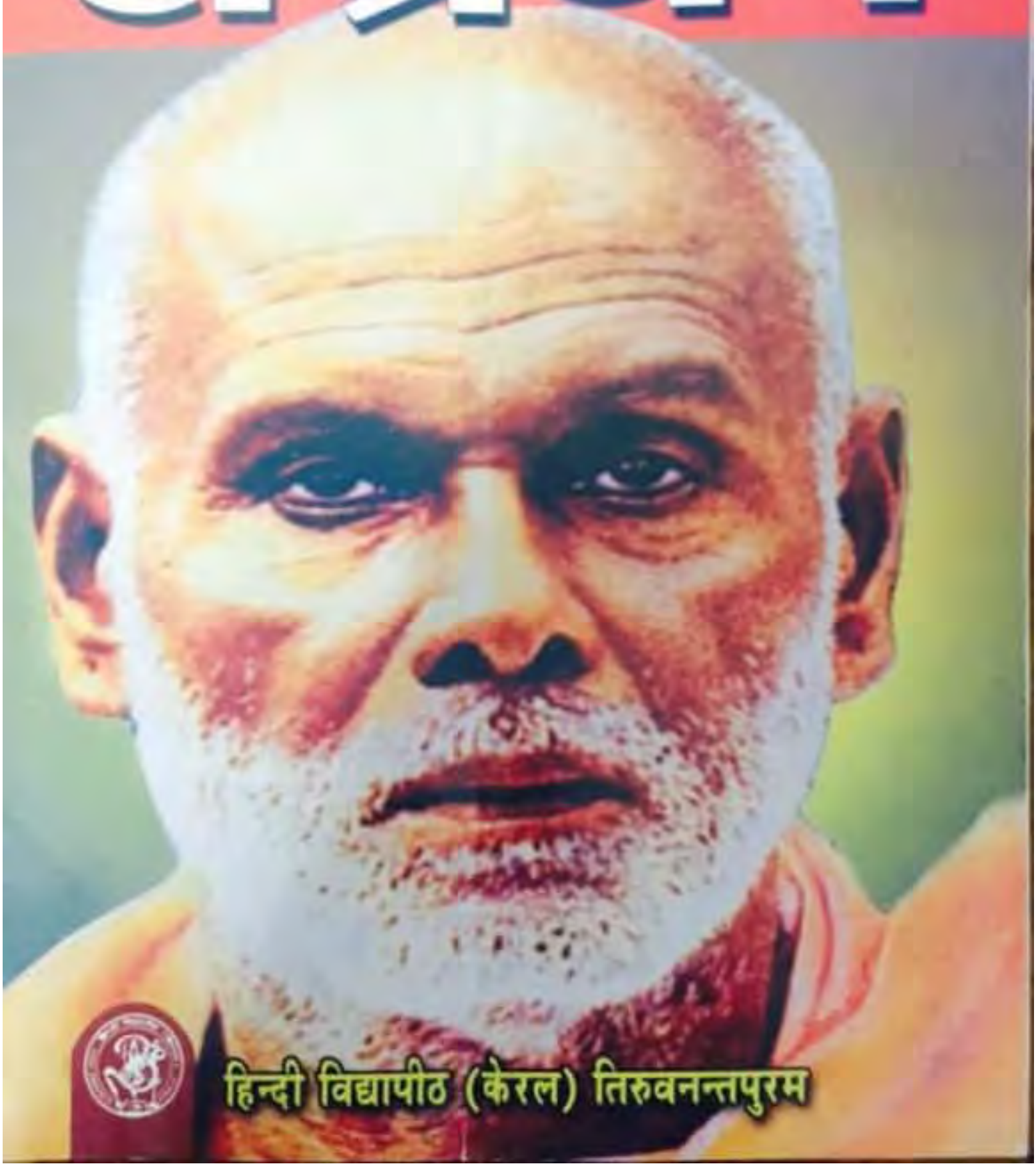
संग्रथन



हिन्दी विद्यापीठ (केरल) तिरुवनन्तपुरम

'आवाँ' में चित्रित नारी-जीवन की बहुआयामी स्थितियाँ

डॉ. लता कुमारी .के

समकालीन हिन्दी उपन्यास की सुविख्यात लेखिका श्रीमती चित्रा मुद्गल का, नारी-जीवन की बहुआयामी स्थितियों को उभारनेवाला उपन्यास है 'आवाँ' । इसमें नारी-जीवन के विशद विश्लेषण प्रस्तुत हुआ है । सामाज के विभिन्न वर्गों की नारियों के जीवन की विभिन्न पहलुओं पर चित्रा जी ने सामयिक दृष्टि से विचार-विमर्श किया है । इस सिलसिले में श्रमिक महिलाओं के जीवन की कई विवशताओं, नारी की आभूषण प्रियता तथा मॉडलिंग की दुनिया से उत्पन्न विभिन्न समस्याओं तथा नारी को परिवार में नंग करनेवाली अनेक स्थितियों पर चर्चा की गई है । कई आलोचकों ने इस उपन्यास की खूब प्रशंसा भी की है । श्री शिवकुमार मिश्र के शब्दों में -" 'आवाँ' औरत के वजूद से जुड़े सवालों का दहकता-सुलगता दस्तावेज़ और एक बड़े आकार का विचारोत्तेजक उपन्यास है ।"[1] श्रीमती कुसुम वार्ष्णेय के अनुसार -" 'आवाँ' नारी को हर तरह के अवमूल्यन से बचने को उत्प्रेरित करता है । रूढ़ियों और अवमूल्यन दोनों से जब नारी मुक्त होगी, तो वही मुक्ति चेतना का सही अर्थ होगा ।"[2] नारी-जीवन के विभिन्न पहलुओं पर चर्चा करने के साथ-साथ चित्रा जी ने सामाजिक जीवन की समस्याओं तथा मज़दूर यूनियन के नेताओं के दोगले चरित्र पर भी प्रकाश डाला गया है । इस अर्थ में यह उपन्यास दलित विमर्श का भी उपन्यास है । सुप्रसिद्ध समीक्षक श्री बलराम जी कहते हैं - " 'आवाँ' आज के स्त्री-विमर्श के साथ-साथ दलित विमर्श का महाकाव्य भी है ।"[3]

यद्यपि इस उपन्यास में चित्रा जी ने समकालीन जीवन के सामाजिक, आर्थिक, पारिवारिक और वैयक्तिक समस्याओं का चित्रण किया है तो भी नमिता पांडे और अन्य नारी पात्रों के ज़रिए आधुनिक समाज में नारी की स्थिति, उसका संघर्ष, उसका शोषण, अस्मिता की तलाश आदि को विशेष महत्व के साथ प्रस्तुत किया है । नारी-जीवन की समस्याओं की ओर अधिक ध्यान न देनेवाले समाज के सामने उसकी सच्चाइयों सहित प्रस्तुत करके उस समाज को जगाने का प्रयत्न चित्रा जी ने किया

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1. पहल ६७, जनवरी २००१, - पृ. २८४
2. तद्भव ३, अप्रैल २००१, पृ.२४०
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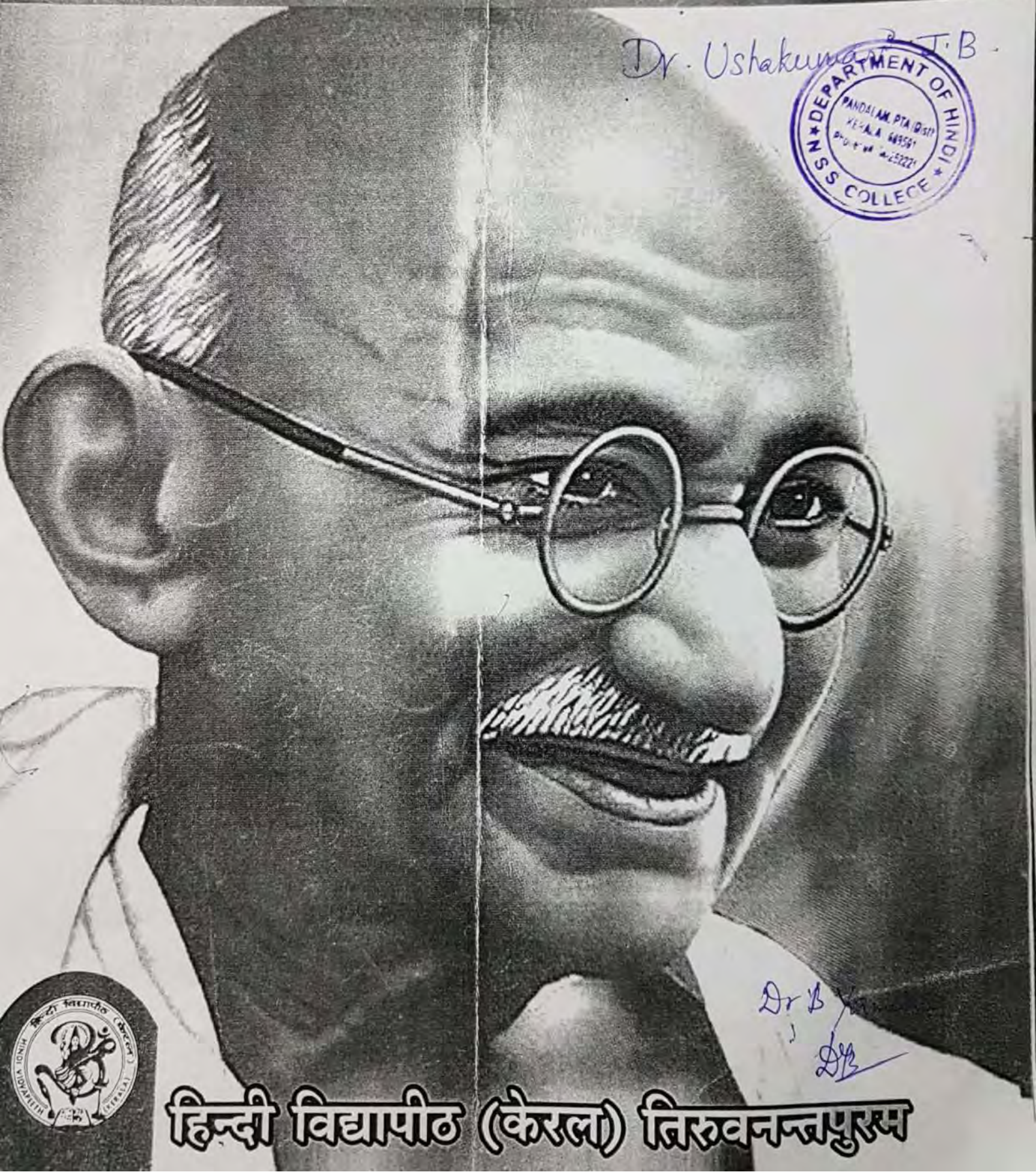
संगठन



हिन्दी विद्यापीठ (केरल) तिरुवनन्तपुरम

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संग्रयन

शब्दश्रयणि निष्णातः परम् ब्रह्मणिगच्छति

(यू.जी.सी. से अनुमोदित मासिक पत्रिका)

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वार्षिक चन्दा : दो सौ रुपये मात्र

Dr. B. Yamuna Devi
H.O.D

सम्पादक मण्डल

इस अंक में....

मुखचित्र : राष्ट्रपिता महात्मागाँधी

Dr B Yamuna Devi 29/2
(H.O.D)

'जस तस भई सवेर' में अभिव्यक्त दलित-नारी-चेतना

डॉ.उषाकुमारी.जे.बी.

महात्माओं के नकार और विद्रोह भरी चेतना ही दलित-साहित्य को सशक्त रूप और मार्ग प्रशस्त करके लक्ष्य तक पहुँचाने का महनीय कार्य करती है। मानव जीवन का यथार्थ वर्णन करनेवाले सशक्त माध्यम के रूप में उपन्यास की सार्थकता और रोचकता सिद्ध हो चुकी है। दलित जीवन के विविध पहलुओं और बदलाव को लेकर लिखे जानेवाले उपन्यासों में 'कला कला के लिए' की अपेक्षा 'कला जीवन के लिए' तत्व की सार्थकता और प्रयोजनात्मकता पर अधिक बल दिया जाता है।

कामातुर सवर्णों से अपनी इज्जत की भीख माँगनेवाली दलित-नारी पुराने ज़माने में अपने परिवार की चिन्ता में उससे समझौता करने को विवश होती थी। लेकिन आज समाज के बदलते दृष्टिकोणों के साथ बदली वह किसी की परवाह किये बिना अपनी इज्ज़त की रक्षा के लिए लड़ने तक जागरूक हुई है। आज की नारी अपनी इज्ज़त को जान से भी बढ़कर मानती है और उसकी रक्षा में वह कठिन से कठिन संघर्ष करने को तुली रहती है।

हिन्दी के दलित उपन्यासकार सत्यप्रकाश के 'जस तस भई सवेर' में एक ओर सवर्णों से अपने मान की रक्षा के लिए कराहनेवाली दलित नारियों का दीन-रोदन सुनायी पड़ता है तो दूसरी ओर अपनी इज़्ज़त पर मज़ा करनेवाले सवर्णों की अमानवीय वृत्ति पर संगठित संघर्ष करने वाली दलित-नारियों की मनोवृत्ति द्रष्टव्य है। दलितों को एक मुट्ठी भर अनाज के लिए मौसम की परवाह किये बिना काम करना ही पड़ता है। बरसात की मौसम में, रामरती, घुसिया और सन्नो चौधरी देवीपाल के खेत में घास काटती रहीं तो वर्षा बलवत हुई। भीगे वस्त्रों में तीनों युवतियों पर आसक्त देवीपाल की दृष्टि में घुसिया अधिक सुन्दर लगी। उसके साथ छेडछाड करने और उसका यौवन भोगने में आतुर चौधरी के सामने अछूतपन एक अडचन नहीं बनती। अर्थात दलित स्त्रियों का भोग और तदनन्तर उनकी निन्दा करना सवर्ण सज्जनों की झूठी सभ्यता का द्योतक रहा। उपर्युक्त उपन्यास में घुसिया का अनुरोध इसका सशक्त उदाहरण है - "मैं भूखी रह लूँगी पर इज़्ज़त नहीं बेचूँगी।"[1] आज भूखी प्यासी और दबाव में रहनेवाली दलित-नारी को अपनी इज़्ज़त ही सबसे अधिक मूल्यवान है। इस दृष्टि से देखने पर यहाँ यह भी स्पष्ट होता है कि उच्चकुल जात चौधरी की सवर्ण-सभ्यता के आगे अवर्ण-नारी का स्वत्वबोध और आत्मसम्मान की भावना विजय प्राप्त कर लेती है।

सन्नो घुसिया को चौधरी की

१. जस तस भई सवेर, सत्यप्रकाश, पृ.सं.१२

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केरलज्योति

केरल हिन्दी प्रचार सभा, तिरुवनन्तपुरम

'मृदुला गर्ग की रचनाओं में स्त्री पक्षीय चिंतन'

डॉ.षीला.टी.नायर

हर युग के साहित्य में स्त्रीपक्ष को उद्घाटित करने का प्रयास हुआ है। समय के अनुसार मनुष्य के जीवन स्तर में परिवर्तन हुआ है, यहीं परिवर्तन स्त्री के जीवन में लगातार होता रहा है। स्त्री पक्षीय चिंतन के तहत महिला लेखिकाएँ अपने अनुभूत सत्यों को भी प्रकाश में लाने के लिए सक्षम है। मृदुला गर्ग आधुनिक लेखिकाओं में एक महत्वपूर्ण नाम है जिन्होंने नारी की स्वतन्त्रता और उसकी अस्मिता को बखूबी लेखन का विषय बनाया है। आधुनिक कालीन नारी के रूप मृदुला गर्ग की रचनाओं में चित्रित हैं।

मृदुला गर्ग का उपन्यास 'उसके हिस्से की धूप' में एक स्त्री जो अपने पति और प्रेमी के बीच बंटी हुई है। उपन्यास की नायिका मनीषा महत्वाकाँक्षी स्त्री है। वह अपनी अस्मिता को प्रतिष्ठित करना चाहती है। घर वालों की इच्छा के अनुसार मनीषा, जितेन से विवाह करती है। उसका घर आधुनिक सुख-सुविधाओं से पूर्ण है। लेकिन जितेन इतना व्यस्त रहता है कि मनीषा के लिए थोडा भी समय नहीं निकाल पाता है, इसलिए मनीषा अपने आप को एकदम अकेली महसूस करती है। अतः वह जितेन से पूछती है - "क्या हम कभी इकट्ठे कहीं बैठकर इधर-उधर की मामूली बातें नहीं कर सकतें? क्यों हम एक दूसरे से यूँ कटे-कटे इस आलीशान कोठी की चारदीवारी में पडे सड रहे हैं?"(1) मनीषा अपनी ऊब को मिटाने के लिए कॉलेज में नौकरी करने लगती है। वहाँ उसका परिचय कॉलेज के एक अध्यापक मधुकर नागपाल से होता है। मनीषा, जितेन से तलाक ले लेती है और मधुकर से विवाह कर लेती है।

मधुकर हर पल मनीषा के साथ रहता है, वह हर कार्य में मनीषा का साथ चाहता है। मधुकर के इस तरह के व्यवहार से मनीषा सोचती है कि हर पल मधुकर के साथ रहने के कारण वह अपना कार्य स्वतन्त्रता पूर्वक नहीं कर पा रही है। इस बीच नैनिताल में मनीषा की भेंट पूर्व पति जितेन से होती है। अगले दिन मनीषा, जितेन से मिलने होटल जाती है और वहाँ यौन तृप्ति करती है। लेकिन इसमें किसी प्रकार का अपराध बोध नहीं है। जैसे-जैसे समय व्यतीत होता है मनीषा, मधुकर के साथ भी खुश नहीं है। वह रचनात्मक कार्यों की ओर मुड़ जाती है। इस उपन्यास में एक ऐसी आधुनिक नारी का चित्रण मृदुला गर्ग ने किया है जो अपने जीवन में क्या चाहती है उसकी वह पूर्ति करती है। मनीषा अपनी इच्छा, अपनी खुशियों को महत्व देती है। भारतीय वैवाहिक जीवन की अवधारणाओं से भिन्न, स्त्री का एक रूप इस उपन्यास में चित्रित है।

मृदुला गर्ग का उपन्यास 'चितकोबरा' में नायिका मनु है। लेखिका ने मनु के जरिए आधुनिक नारी-मन वह भी स्त्री का सेक्स के प्रति क्या दृष्टिकोण हो सकता है उसे प्रस्तुत किया है। एक भारतीय स्त्री सेक्स की इच्छा का आग्रह खुलकर कहती है तो यह उपन्यास चर्चा का विषय बन जाता है। चितकोबरा उपन्यास की नायिका मनु को खुले रूप से सेक्स की माँग करते हुए दिखाया गया है। अपने प्रेमी रिचर्ड के साथ रहने पर उसे पूर्ण तृप्ति मिलती है वह कहती है - "प्यार करना खेल है, कला है, जरूरत है, शरीर की माँग है।"(2) अपने पति महेश के साथ रहने पर

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AN ANALITICAL VEIW OF KERALA SANSKRIT CHAMPU LITERATURE

KRISHNAVENI, Research Scholar, Dept of Vyakarna,
Sree Sankaracharya University of Sanskrit, Kalady

Sanskrit Champu Kavyas of Kerala is a vast branch of literature with varied themes. More than hundred Sanskrit Champu Kavyas are written in Kerala. Champus dealing with different topic like Puranic themes, Eulogy of gods, Kings, Regional festivals etc. were produced here. The period from 13th to 19th centuries A D can be considered the most exuberant age in the history of the Champus in Kerala. Most of the important Champus in Malayalam as well as in Sanskrit composed during this age in Kerala.

The rich and varied Sanskrit Champu literature of Kerala can be divided in to three categorizes as shown below.

1. Major Champus which comes under the preview of the poetic type defined by poeticians.
2. Champus related to Kerala Sanskrit theatre.
3. Other minor works.

Among the Kerala Sanskrit Champus, those that can be included in the first category are very few. Amogharaghavam of Divakara, Uttararamayana of Mahishamangalam Narayanan , Vidhuvamsa of Kesavan Namboodiri, Purvabharata Champu of Manavikrama etc are comes under this category.

The largest number of works from Kerala Sanskrit Champus can be included in the second category. Though the poeticians have included the Champu variety in Sravya Kavya type, its connections with stage is a peculiar feature that is worthy to be examined. This is an important aspect of Akhyana or story telling tradition in Sanskrit.

Tradition says that it was Melputtur Narayana Bhattathiri who was the pioneer to compose Prabandhas for the use of 'kuttu' of Chakyars. Following the path of Melputtur Narayana Bhattathiri many other poets have written similar works. Chakyar who were great scholars used to compose such works for immediate use offer the stage and they might have been preserved as their family tradition.

Smaller works sometimes not related to the theatre, were also composed in plenty in the flourishing period of Champu literature. Often they dealt with episodes connected with Kings, Temples, Festivals and the like. Tulabharaprabandha, Tirunalprabandha, Astamimahotsava etc. are some examples.

The structural peculiarities of Kerala Sanskrit Champus

Sanskrit rhetoricians have defined Champu as an admixture of prose and verse.

In the opinion of C. R Deshpande, all these definitions lay down five essential and one optional feature of Champu. In Kerala Sanskrit Prabandhas most of these rules are violated. The first rule is

1. A Champu must be a poetic composition.

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his noble deeds because evil acts of disciples affect the teacher and not the parents or relatives.

The sociological conditions of the period regarding pastoral life, details of relationship and regards between the Brahmins and the Kṣatriyas and the imminensity and ruthlessness of war are also discernable from the play as portrayed in this drama.

Firm proof of identity of Arjuna is just then brought in by a soldier. He brings an arrow, with the name of the owner inscribed, and hands it over to Śakuni. Śakuni throws it away after reading the name Arjuna. The arrow falls at the feet of Droṇa, who takes it as the homage paid by his disciple. Droṇa then demands of Duryodhana to fulfill his part of the promise. Duryodhana agrees to part with half the kingdom for the sake of the Pāṇḍavas. But Śakuni disagrees with him. At this time, Uttara from the capital of the kingdom of Virāṭa reaches there. The errand of Uttara as a messenger from Yudhiṣṭira to inform the marriage of Uttarā and Abhimanyu clears all doubts about the whereabouts of the Pāṇḍavas. Droṇa, then, reminds Duryodhana of his promise. Five days were not yet over. Hence, the Pāṇḍavas may be awarded their share. Hearing the words of Droṇa, Duryodhana declared that half the kingdom is being given to the Pāṇḍavas. Duryodhana kept up his promise.

Conclusion

Violence, especially war, is an important element in literature. Many works in Sanskrit literature portray war and violence. The intention of the authors is creation of awareness in the society on the dark side of the impacts of violence and war. They are trying to condemn war and violence.

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Punnaśśeri's Contributions Towards Sanskrit Wisdom

Krishnaveni

The power of knowledge that leads us to light of supreme reality from darkness of ignorance and the power of knowledge that given to us by the great 'Guru'. Guru, the one who is like the God because of only the Guru conveys that what is God. So,

ajñānatimirāndhasya jñānāñjanaśalākayā
cakSurunmīlitam yena tasmai śrī gurave namah.

Śrī Punnaśśeri Nampi Neelekaṇṭa Śarmā was such a Guru for Keralites and he still alive in the memories of Keralites through his contributions for Sanskrit. He was born in 1858 June 17 at the Perumudiyoor village, situated near by the Pattampi in Palakkadu district. Nārāyana śarma and Pāppimanayamma were his parents. They included in the caste 'Mūssat' but they did not use the term 'Mūsath' with their names. The male persons in that family generally use the term 'Nampi' with their names after the Samavarthana. The position 'Nampi' was given by Zamorin.

The primary education was began at his five years old. His first teacher was Aranńoṭ wāryar. After that he learned Sanskrit,Mathematics,Vyakarana, Jyothisha, Ayurveda etc. under the teachers like Tṛttāla edavittil Govindan mārār, Kulukkallūr Unnikkaṇṭa wāryar, Celūr Keralavarma unittiri, Cittilappalli Appu śāstri, Tṛppaṅṅoṭṭ kizhakke pullat kuññunni mūssat etc.

Caste System As Envisaged in Purāṇas

Asadevi G.

Purāṇas occupy a very important place in the ancient literature of India. The study of Veda was reserved for the highly educated upper classes called dvijas and was, therefore, not accessible to the lower strata of the society. Purāṇa was meant both for the upper classes and the masses in general and so it became a valuable and important medium for educating the people at large. The name Purāṇa signifies 'old traditional story' composed chiefly in śloka meter with occasional passages in prose. Purāṇas deal with a vast range of subjects. Vyāsa is said to be the author or compiler of the Purāṇas. Purāṇas are records of history. They also deal with some other matters of secular and religious interests. They teach the doctrine of human responsibility.

Purāṇas are the reliable sources of Indian mythology. They preach the duties and rights to be observed by men in their respective Varṇa or caste. Indian life is being guided mostly by the ideas preached by Purāṇas. They are one of the important sources of ancient Indian religion, society and

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വിജ്ഞാനകൈരളിയിലെ ലേഖനങ്ങളിൽ പ്രകടിപ്പിക്കുന്ന അഭിപ്രായങ്ങളുടെയും ആശയങ്ങളുടെയും ഉത്തരവാദിത്തം ലേഖകർക്കായിരിക്കും. അവ കേരള ഭാഷാ ഇൻസ്റ്റിറ്റ്യൂട്ടിന്റെയോ ഗവണ്മെന്റിന്റെയോ ഔദ്യോഗികാഭിപ്രായമായിരിക്കണമെന്നില്ല. ലേഖകർ പൂർണവിലാസവും ഇ മെയിലും ഫോൺ നമ്പരും ഒപ്പം ചേർക്കുവാൻ താൽപ്പര്യപ്പെടുന്നു.

- എഡിറ്റർ

ഓണത്തിന്റെ പുരാണങ്ങളും

ആശാദേവി ജി.

ഓണം ഇന്ന് ഔദ്യോഗികമായി കേരളത്തിന്റെ ദേശീയോത്സവമാണ്. കേരളത്തിന്റെയെന്നു പറയുന്നതിനെക്കാൾ മലയാളിയുടെയെന്നുപറയുന്നതാവും കൂടുതൽ ശരി. 1961-ൽ പട്ടം താണുപിള്ള മുഖ്യമന്ത്രിയായിരുന്ന കാലത്താണ് ഓണത്തെ കേരളത്തിന്റെ ദേശീയോത്സവമായി പ്രഖ്യാപിച്ചത്. കേരളത്തിലെ സവർണഹിന്ദുക്കളുടെ മാത്രം ആഘോഷമാണ് ഓണമെന്നും അതുകൊണ്ട് ഓണത്തെ ദേശീയോത്സവമായി പ്രഖ്യാപിച്ചത് അഹിന്ദുക്കളെ ഹൈന്ദവവൽക്കരിക്കാൻ നടത്തിയ ശ്രമമാണെന്നും അടുത്തകാലത്ത് ചിലർ ആരോപിക്കുകയുണ്ടായി. മഹാകവി ഒ.എൻ. വി. കുറുപ്പ് മാൽപ്പറഞ്ഞ അഭിപ്രായത്തോടു വിയോജിക്കുകയും മലയാളിക്ക് എന്നും ഓമനിക്കാവുന്ന ഓർമകളുണർത്തുന്ന ഓണത്തെ മതത്തിന്റെ പേരിൽ തള്ളിപ്പറയുന്നത് കഷ്ടമാണെന്ന് പ്രതികരിക്കുകയുണ്ടായി.

കഴിഞ്ഞ ഓണക്കാലത്ത് മറ്റൊരു വിവാദവും ഓണത്തിന്റെ പേരിൽ ഉയർന്നുവന്നു. ഓണത്തിന്റെ അവസരത്തിൽ കേരളീയർക്ക് ഒരു കേന്ദ്രമന്ത്രി ആശംസകളർപ്പിച്ചതാണ് വിവാദമുയർത്തിയത്. വാസ്തവത്തിൽ ആശംസയർപ്പിച്ചതിന്റെ പേരിലായിരുന്നില്ല വിവാദം. ഓണത്തെപ്പറ്റി അദ്ദേഹം നടത്തിയ പരാമർശമാണ് വിവാദമായത്. വാമനമൂർത്തിയെ ആരാധിക്കുന്ന മഹോത്സവം എന്നാണ് അദ്ദേഹം കേരളീയരുടെ ഓണത്തെ വിശേഷിപ്പിച്ചത്. അതായിരുന്നു വിവാദകാരണം. ഓണം മഹാബലിയെ വരവേൽക്കുന്ന മഹോത്സവമാണോ? അതോ വാമനമൂർത്തിയെ പൂജിക്കാനുള്ള വിശേഷാവസരമാണോ? എന്നതാണ് പ്രശ്നം.

ഈ സന്ദർഭത്തിൽ ഓണത്തെ സംബന്ധിച്ച് പുരാണങ്ങളിൽ എന്തുപറയുന്നുവെന്ന് പരിശോധിക്കുന്നത് സംഗതമായിരിക്കുമല്ലോ. പുരാണങ്ങൾ എന്ന വാക്കു കേൾക്കുമ്പോൾ അവ വളരെ പഴയ ഗ്രന്ഥങ്ങളാണ് എന്നൊരു പ്രതീതി ഉണ്ടാകാറുണ്ട്. എന്നാൽ അത് പൂർണമായി ശരിയല്ല. ചില പുരാണങ്ങൾ പിൽക്കാലീനങ്ങളാണ്. ചരിത്രം, സംസ്കാരം, സാമൂഹികജീവിതം എന്നിവയെ സംബന്ധിച്ച രേഖകളാണ് പുരാണങ്ങൾ. സൃഷ്ടിയുടെ ആരംഭം മുതലുള്ള ചരിത്രങ്ങളും, സദാചാരകഥകളും, തത്ത്വശാസ്ത്രങ്ങളും, ധർമശാസ്ത്രങ്ങളും, വേദാന്തതത്ത്വങ്ങളും, ചരിത്രവസ്തുതകളും, ജ്യോതിശാസ്ത്രവും കലകളുമെല്ലാം പുരാണങ്ങളിൽ പറയപ്പെട്ടിട്ടുണ്ട്. പുരാണങ്ങൾ പൊതുവേ ശ്ലോകങ്ങളായിട്ടാണ് രചിക്കപ്പെട്ടിട്ടുള്ളത്.

പതിനെട്ടു മഹാപുരാണങ്ങളും അതുതന്നെ ഉപപുരാണങ്ങളും ഉണ്ട്. പതിനെട്ടു മഹാപുരാണങ്ങളിലായി നാലുലക്ഷത്തോളം പദ്യങ്ങൾ ഉണ്ട്. മഹാപുരാണങ്ങളിൽ അഗ്നിപുരാണം,

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TEXT & CONTEXT

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Indian Theories of Verbal Comprehensions And Modern Linguistics

Editors
Dr. Rekha R
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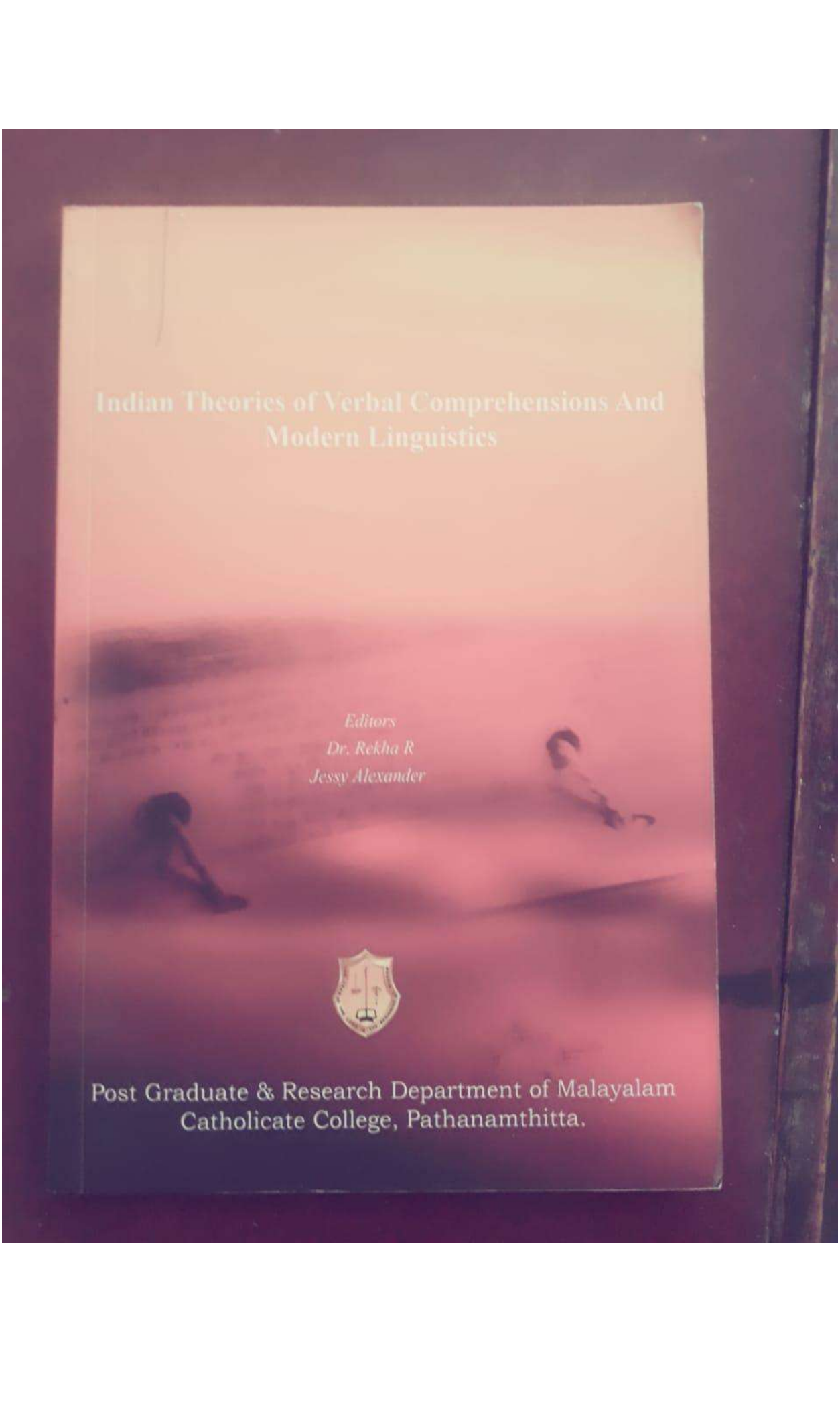

Post Graduate & Research Department of Malayalam
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The purpose of the Vakyapadiya or of the science of grammar in general is the acquisitation of merit (dharma) is to say that one canacuiresvarga and also attain moksa. Bharthari brings this idea out, not only in thisVakyapadiya but also in his commentary on the Mahabhasya. While explaining the purpose of the fourteen Mahesvarasutras which form the very basis ofpanini'sAstadyayi, patanjali uses the words puspitah and phalitah, suggesting that they yield flowers as well as fruit.Commenting on there two words, Bhartrhari equates flower with paradise (adhyadaya) and the fruit with liberation (nihsreyas) and kaiyata does the same in his pradipa, repeating the very words of Bharatrhari.

Nihsreyasa or Moksa, as a purpose of Grammar is mentioned several times in the Vakyapadiya. In one place, Bhartrhari says that Vyakarna is the door leading to liberation and in another that it is the straight royal road to take for those who desire salvation. Again he says that by mastering the science of Grammar, one attains the Supreme Brahman. All this is found in the opeingkarikas of the Vakyapadiya. But Bhartrhari comes back to this idea towards the end of the first kanda. There he tells us that the purification of the word is the means to the attainment of the supreme self. One who knows the essence of its activity attains the immortal Brahman.

Vakyapdiya begins with a statement on the nature of Brahman for two reasons. (1) Brahman is the source of everything including vakya and pada, the two main subject of the work.(2) because Brahman would come under preyojana or phala (purpose,goal). This is the subject matter of vakyapadiya.Brahman is the source of everything Bhartrhari has to say about Brahman as the goal to be attained.

The attainment of Brahman has been declared to the ultimate goal of vyakarana. Bhartrhari start his work , vakyapadiya with a statement on the transcendence as well as the immense of the ultimate reality on his philosophy. As for its transcendence, he states a number of characteristics anadhinidhana,brahman, sabdatattva and aksara.All these characteristics are looked upon as the best and the highest conceptual designations of 'the one' which,strictly speaking, is an indescribable identity. As for its immanence,Bhartrhari tells us that the same is the genesis of the cosmic world. The ultimate reality Brahman,which is without beginning or end,is of the nature of the word (sabdatattva) and from it are manifested all the object and the whole cosmos.

in such a comprehensive manner that, ultimately, the work touches upon a large number of topic. It should be worth one's while to understand how these topics are arranged in the three kandas and the logical sequence between them.

'Vakyapadiya' contains three chapters (kanda). It is called 'Tarikandi'. The first chapter as already pointed out, is called Brahmakanda (Agamakanda).

It begins with the statement of Brahman.In the Vakyapadiya itself, there is a statement of the subjects dealt with in it.

The work deals with eight subject : two kinds of meaning (artha) : that which is obtained by analysis and that which is of a fixed character (Sthitalaksana), two kinds of word (Sabda) : that which is to be grammatically explained and that which is a means of explaining it (pratipadaka), two kinds of relations : Causality and fitness to express to express the meaning and two kinds of result or purpose : spiritual merit (dharma) and tbe understanding of meaning. The commentator gives us to understand that these are the eight subjects, notonly of the vakiyapadiya, but of the science of Grammar in general.

Brahman would come under prayojana or phala (purpose, goal), one of the eight topics traditionally accepted as forming the subject matter of the Vakyapadiya or the Vijakaranasastra in general. The attainment of Brahman has been declared by Bhartrhari to be the ultimate goal of the study of vyakarna. This Brahman is the ultimate source of everything. It is, therefore the source of Vakya and pada, the two main subject of the Vakyapadiya.

Bhartrhari is not only speaking about the goal to be attained but also about the ultimate origin of everything. Brahman is the eternal and undifferential word principle (Sabdatattva). All cosmos, all differentiation proceeds from it.

The Veda is the means of attaining this Brahman of which it is a manifestation. It is agama, Supreme knowledge. It is the source of all traditional sciences, including that of Grammar. Agama is more trustworthy that reasoning in some maters such as dharama. Reasoning which does not go against the sruti and smrti is helpful. Reasoning not based on agama is not reliable because the reasoning of one can be set aside by that of another. It is only strictly following agama that some individuals acquire divine vision.

CONTENTS

THE CONCEPT OF SABDABRAHMA IN VAKYAPADIYA

Dr. Sandhya B Nair

INTRODUCTION

The Sanskrit term for 'Grammar' in general is Vyakarna. Vyakarana or the science of grammar is the most important supplement of Vedas or Vedanga. This science is equally important for the study of spoken and literary Sanskrit and it has developed as a separate, branch of study in the post-vedic period. The grammar of Sanskrit language is so elaborate, accurate, complete and comprehensive that it has become one of the most important and independent branch of learning. While in other language, grammar is treated only as a part of their literature.

THE CONCEPT OF 'BRAHMA' IN VAKYAPADIYA

The Supreme word principle or the sabdabrahman is the source, the sustenance and the end of all manifestation. The vedas reflect this brahman. They are also the means of knowing it. We learn from the vedas a multiplicity of spiritual disciplines, but all there disciplinessub serve action.

Bhartrhari is a well-known Sanskrit-Grammarian. His most important work vakyapadiya consist of three kandas and contains little under 700 karikas. According to its title, vakyapadiya is supposed to deal with the vakya (sentence) and the pada (word). These two subjects are deal with

CONCLUSION

Grammer or Vyakarana is the most important branch of science which have arisen from Vedas. Among the six vedangas, sciences of language or grammar take first. (Mukham vyakaranam smritam). Bhartrhari begins his work vakyapadiya with the statement of Brahman. The attainment of Brahman has been declared by Bartrhari to be the ultimate goal of the study of vyakarana. This Brahman is the ultimate source of everthing.

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KUNTI - A TRAGIC MOTHER IN THE MAHABHARATA

Dr.Sandhya B Nair, Assistant Professor, Department of Sanskrit, N.S.S College,Pandal...

INTRODUCTION

The Mahabharata is universally accepted as an encyclopedia of ancient Indian culture ... civilization. This great epic, composed in different ages, presents conflicting views on wo... The Women characters in the Mahabharata express the power of dharma in the form of ... patience, steadfastness and their sincerity. The epic depicts the life and destiny of many ... women like Kunti, Gandhari ,Draupadi and so on.

In the Mahabharata, Kunti is presented as a tragic mother. She happens to be an innocent vi... in the hand of cruel destiny. Many lessons have to be learnt from her sad plight. Kunti is st... living character in the present day Indian context. Kunti in the Mahabharata is elegantly superi... to all the other female characters such as Draupadi, Gandhari, Madri, Satyavati etc. One ... legitimately designate Kunti as the human form of righteousness. The epic character Kun... capeable to keeping the path of righteousness at every trying juncture of her life,and also ha... uncanny ability to prompt and persuade her husband and children to think of dharma. In ... Mahabharata Kunti appears a aunique personality who never deviates from the right path ... Dharma one all occasions, right from the time of her attending saga Durvasa dutifully ... diligently, as depicted in the Adiparvan of the epic, to the Asramavasi kaparvan where ... accompanies Dhritarastra and Gandhari to the forest.

Kunti – a tragic Mother

Manu, the ancient Indian law - giver effectively recorded the position of women ... Manusmrti He states:

The Concept of Dhvani in Indian Poetics

Dr. Sandhya B. Nair

Introduction

The history of kāvya- śāstra or poetics in Sanskrit is very rich. The concept of kāvya and kavi, the utility, cause, effect, guṇās, doṣās, alaṅkārās and so on of kāvya constitute the scope of Sanskrit poetics. For centuries, ideas were put forth and controversies were raised in an attempt to find out the criterion of good poetry and the nature of aesthetic delight. Right from Bharata's Nāṭyaśāstra, the first great contribution on theories of dramaturgy, till the composition of Paṇḍitarāja Jagannāthā's Rasagaṅgādhara, the history of Sanskrit poetics passed through a revolutionary period and culminated in many concepts mainly Rasa, Alaṅkāra, Guṇa, Rīti, Dhvani, Vakrokti, Anumiti and Aucitya. As alaṅkāra is the most important element in Kāvya, the name of that particular śāstra should be alaṅkāraśāstra or Kāvyaśāstra.

Alaṅkāraśāstra or Kāvyaśāstra occupies a lofty position in Sanskrit literature. The contribution of Sanskrit to Indian poetics is very rich. Therefore the study of Kāvyaśāstra deserves careful attention.[1]

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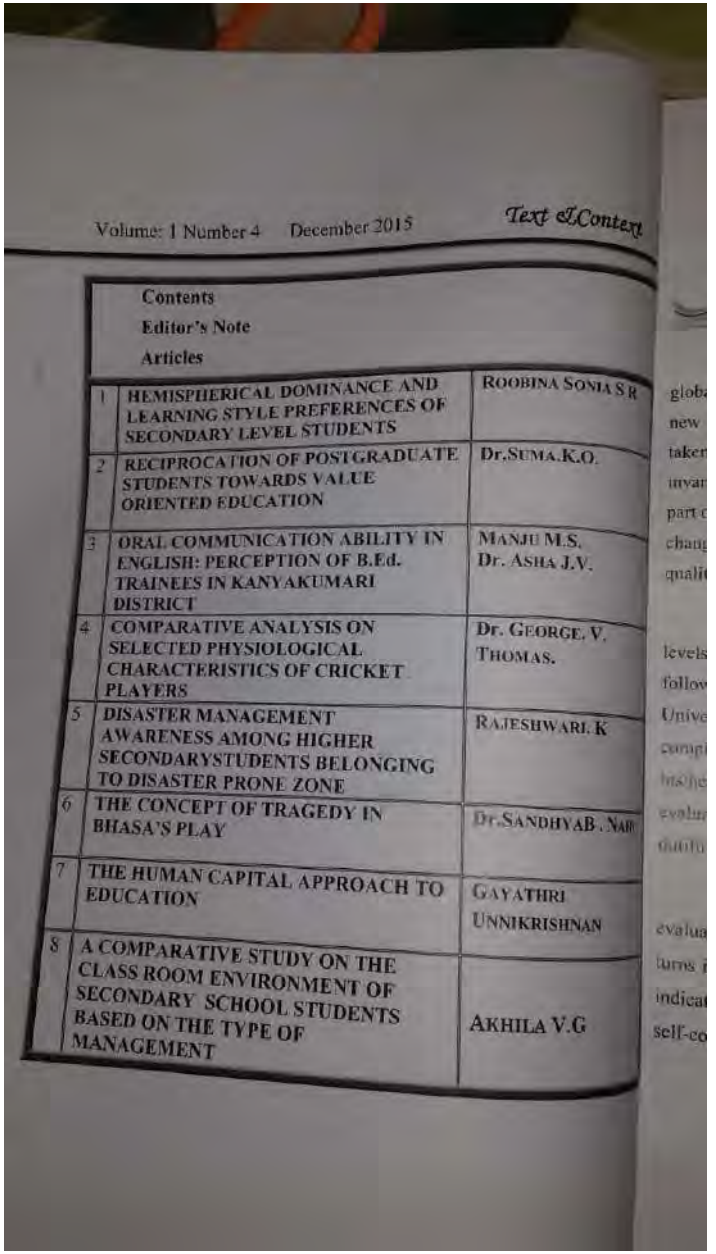

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Editor's Note

Articles

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THE CONCEPT OF TRAGEDY IN BHASA'S PLAYS

Dr. SANDHYA. B . NAIR, ASSISTANT PROFESSOR, DEPARTMENT OF SANSKRIT, NSS COLLEGE, PANDALAM

ABSTRACT

The present study is mainly based on Bhasa's two well known dramas. Urubhanga and Karnabhara., Tragedy is a fascinating problem for literary and aesthetic study. In the context of literary art, a main spectacle of sorrow that has power to bring us to the brink of tears becomes tragic. The concept of tragedy in bhasa's plays is highlighted by giving special reference to Duryodhana of Urubhanga, and Karna of Karnabhara. Bhasa showers heroic nobility and virtue on Duryodhana and makes him a tragic hero. Karnabhara envisages the generosity of the great Karna

The different varieties of poetical compositions the most entertaining and serious one is the drama. "*Kavyesunatakamramyam*"-is a famous saying in Sanskrit. There are a number of dramas in Sanskrit literature that had drawn their plot from the epics and other tales. These plays were composed taking into account the depth of thought contained in the epics and their impact on the imagination of the dramatist. 'The concept of tragedy in bhasa's plays ', the present study is mainly based on Bhasa's two well known dramas. Urubhanga and Karnabhara, The tragic characters of these plays viz, Duryodhana and Karna are highlighted here. According to Aristotle a tragedy possesses the entire essence of an epic. In a tragedy, imitation possesses in short life span to reach its end it gives up the time lag by telling the story timely by avoiding the unwanted explanations. The level of acceptance of the viewers is quite different when they see Sophocles' Oedipus and its elaborated vision in the format of Iliad.

TRAGEDY IN GENERAL

The word tragedy itself comes from the Greek term 'tragOidia' which means a goat song[1]. Dante writes, tragedy in the beginning is good to look upon and quiet, in its end or exit is fates and horrible, for this reason it gets its name from 'tragos' – which is goat, and oidia (meaning, song) as though to say goatish song, that is fetid on the manner of a goat, this is made plain by the example of Seneca in his tragedies.

To understand the requirements of tragedy, we must begin with

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RESEARCH ARTICLE

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CARYL PHILLIPS'S *FOREIGNERS* AS A HISTORICAL NARRATIVE

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ABSTRACT
Born in 1958 in the West Indies, Caryl Phillips' life has revolved around issues of belonging and displacement. *Foreigners* (2007) engages eloquently with the idea of home. Phillips is certainly an authority on feeling like a foreigner, growing up as one among the few black faces in a working class English town who had travelled extensively with his writing. And it is important to note that such a point of view came from his concrete experiences as an immigrant in Europe in contrast with the American black exiles in Europe. My intention is to analyse the narrative techniques employed in Phillips' *Foreigners*. With his alluring pen, he illuminates the complexities of race relations through the lens of personal history and narrative. Phillips with a biographer's aim for facts, elucidates his readers with detailed portraits of the three men and their circumstances who were caught up in the African diaspora. He ponders the question of how one retains a sense of individuality under the annihilating onslaught of racism. In the contemporary political and social context of conflicts, Phillips's approach to seek common ground and humanity stands out as an act of courage and sanity.

Caryl Phillips is perhaps the perfect candidate to address what has become one of his favourite themes - identity. And at a time in which the meaning of nationality and the composite nature of our identities are being explored once again, Phillips's works lands in the appropriate ground. Phillips' writing has been categorized by critics in various ways. Location and rootlessness or the ambiguity of identity and sense of belonging were its core themes. Phillips is a writer who has been devoted to the exploration of immigrant stories and the destruction of historical myths. His essay collection *A New World Order* (2001) illustrates Phillips' relation to four places - Africa, New York, St. Kitts, Leeds - firmly: "I feel at home here, but I do not belong. I am of, and not of, this place" (Phillips 2002: 1-4).

Caryl Phillips' novels reflect deeper changes in the British society especially in terms of discrimination, survival quest and British identity. He skillfully combines fiction and history to convey the complex nature of national, personal and racial identities in modern day British life. This paper tries to find out the ways in which Caryl Phillips's *Foreigners* (2007) narrate black history in Britain and thereby becomes a factual representation of modern day misery in the contemporary political and social context of racial conflicts.

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Nuances of Multiculturalism: A Strategic Response to Postcolonial Hegemony.

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Introduction

Postcolonial literature directs the readers to new arrays of interpretations – whether it is ideological, political, societal or familial – the individual voice is now having more strength rather than mere echoes. The role of the individual in the 'glocalised' scenario is clearly throwing light on the contradictory patterns in appreciating literature as such. The angst and perils of the contemporary human being is illuminated through the gloomy rays of the artist's weapon for justice.

The writers in the latter half of the twentieth century expound serious issues in their works for a more just and democratic existence with the portrayal of usually underprivileged others. These characters' search usually intersects with social and civil movements. Therefore we can say that the real intention behind the postmodern thought is to re-establish the 'individual self and its relations' in a more pragmatic way than mere depiction of commonalities.

Celebration of estrangement, dilapidation, ethical binaries, realistic narratives, diversified mythical patterns of story telling, all have their own predominance in the genre of fiction. One man's voice in the mouths of many and vice versa could be experienced more fruitfully in the literature of the period. The ways in which the present day writers approach

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literary texts, vehemently puts forth the significance of the literature in mankind's struggle for existence.

The individual is one who is also the representative voice of his period whether it can be generalised or not. Whatever happens to the individual is also a matter of due relevance because he is one among the many, who still plays his role in society, affecting others and is responsible for his actions. It is meaningful to people who made it, live and understand it, precisely because they are at home in it. The transformative power of postmodern ethics elevates the path where one's knowledge translates into ethics. To live in a multicultural society, one needs an efficacy which should be formulated from the vivified

A Comparative Study of Antimicrobial Activity with Selected Hand Washes on the Human Skin Flora

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ABSTRACT

Antibacterial hand wash is one of the best options to cleanse the hand and to make it germ free. For the purpose of hygiene and health care it is important to include an antibacterial hand wash in routine and thus can prevent harmful invading pathogenic bacteria to an extent. There is an abundant offering of hand care options in the medical marketplace. An attempt has been done in this study to analyze the performance of some selected antibacterial hand wash products as inhibitory agent skin micro flora. Five hand wash products viz. Lifebuoy, Lux, Dettol, Fiya and Santoor were selected to finding out their antibacterial effects on human hand micro flora. Results from this study have shown that hand washes formulation with synthetic antimicrobial agents were more effective in controlling the skin micro flora and Dettol that shows higher anti microbial activity. Among the hand washes, Dettol showed maximum antibacterial activity 71% followed by Lifebuoy, Santoor, Lux and Fiya. Hand washes play a vital role in the daily health and hygiene practices, most of the invading pathogenic microbes can be destroyed to a certain limit by using antibacterial hand wash.

Key words *Dettol, Lifebuoy, Santoor, Lux and Fiya, Antibacterial hand wash*

Proper skin hygiene is the best way to keep our skin healthy. Removing dead cells, dirt and microbes on the skin surface is the key way to good hygiene. Human skin serves as a barrier between body and environment. Our skin is the major place for pathogenic and non-pathogenic organisms. It is difficult to remove all the pathogenic bacteria from our skin but in the globalised world, variety of methods have been adopted to remove most of the microbes such as cleansing antibacterial hand washes, soaps, lotions etc. for the purpose of the hygiene and health care.

Now a days, it is not difficult to find a wide array of anti bacterial hand wash products. It is common in daily life that antibacterial hand washes products being used as the perfect solution to get rid of the most pathogenic bacteria. It is common condition especially among teenagers, through many adults develop chronic acne. Because of social pressure to have flawless skin, finding ways to get rid of acne has become almost essential. That's where an antibacterial hand wash come to rescue. With proper washing of the skin and deeply penetrating ingredients like salicylic acid, acne-causing bacteria can be flushed away. Cleaning hands with antibacterial hand washes stops the spread of microbes or loose transient flora thus preventing infections (Vineeta, 2004). Human skin provides a good environment for the growth of different type of bacteria.resident gram-positive bacteria include *Staphylococcus, Micrococcus,and cornybacterium sp.Staphylococcus aureus* and *Streptococcus pyogenes* are notoriously pathogenic in the skin (Capone *et al.*, 2011). Institutions need to consider several factors when selecting hand hygiene products (Larson, 1988 and 2006). The present study aimed to analyze the effect of various hand wash solutions on skin bacteria. The hand wash tested in the present study were selected based on the popularity in market. Hand washing a better option for disease prevention than any single vaccine (Lucet *et al.*, 2002).

MATERIALS AND METHODS

Contents of materials used

Nutrient Agar, hand washes (Lifebuoy, Lux, Dettol, Fiya and Santoor)

Culture media preparation and Preparation of culture plates

The culture media used was Nutrient agar 2.8gm of agar was dissolved in 100ml distilled water, boiled on a hot plate to mix evenly, cotton plugged and sterilized in an autoclave at 121°C and 15 lb/in² pressure for 15 minutes. Dry sterilization of petriplates, cotton swabs, test tubes and conical flasks were done in hot air oven. The semi fluid nutrient agar medium was transferred to a pre sterilized petriplate and then the plate was kept undisturbed inside an inoculation chamber for preventing possible cross contamination. As the medium solidifies, inoculums were introduced.

Sampling

Test was performed as an *in vivo* study. Five volunteers were selected and asked to engage in daily activities in laboratory and class room. After 3 hours, sampling of the hand bacterial population was done by using a pre sterilized cotton swab dipped in sterilized distilled water from the flat surfaces of palm and bacteria were transferred to 10ml sterilized distilled water in a test tube. One sample was considered as the control for estimating the normal microbial population on the hand and the effect of washing with distilled water was also

ROLE OF DIET AND LIFESTYLE IN ALTERING THE BENEFICIARY EFFECT OF MODERATE ALCOHOL CONSUMPTION: A COHORT STUDY IN EX-SERVICEMEN OF PATHANAMTHITTA DISTRICT - KERALA, INDIA

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Abstract: *Coronary Artery Disease (CAD) or atherosclerosis is the most common type of heart disease, is known to be associated with many risk factors, which include traditional risk factors such as elevated cholesterol levels, lack of adequate exercise, smoking etc. Consumption of alcohol, though traditionally considered injurious to general health, is known to confer beneficial effect in preventing CAD by lowering blood cholesterol levels, especially when consumed in moderate quantities (up to 12 standard drinks a week). However, it is suspected that lifestyle factors act as modifiers in such beneficial effect and sedentary lifestyle and a diet rich in saturated fat has been suggested to negate the beneficial effect of moderate alcohol consumption. The present study was conducted from 101 ex-servicemen using a standard questionnaire. Subsequently lipid profiling was performed from 71 respondents who qualified as moderate alcohol users (≥8 standard drinks per week). 11 out of 71 moderate drinkers (15.5%) harbored CAD like symptoms (history of heart attack, stroke, angioplasty for arterial blocks and angina and associated altered ECG profile). The CAD subpopulation harbored higher, but marginally significant, levels of Triglycerides compared to 23 respondents with good health condition. Similarly 26 respondents with significantly elevated blood pressure also harbored significantly higher TG levels compared to the subgroup (n=23) with general good health. On further investigation high TG and lower HDL levels were associated with lack of exercise and diet rich in fat. Thus the current study indicates the overall beneficial effect of moderate exercise along with moderate consumption of alcohol in negating the effect of fat-rich diet in lowering the CAD risk and the need for a further detailed population based study to assess the role of risk factors in CAD.*

Keywords: *Coronary Artery Disease, Cardiovascular health, moderate alcohol consumption, lipid profile, diet, exercise.*

INTRODUCTION

CAD is the end result of build-up of atheromatous plaques in the arteries supplying blood to heart (Ever D Grech, 2003). The signs and symptoms of CAD vary, and are often detected at the advanced state of the disease. Frequently characterized as ischemia of heart (heart attack); majority of the affected individual harbor relatively few or no symptoms. The atheromatous plaques accumulating in the major arteries reduces the elasticity of the blood vessels and sometimes lead to its rupture (along with activation of blood clotting) resulting in limiting of blood supply to heart muscles (Elizabeth *et al.*, 2012). CAD is a major cause of mortality

RESEARCH ARTICLE

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HAEMATOLOGICAL EFFECT OF METHYL PARATHION AND NEEM LEAF EXTRACT ON *RANA HEXADACTYLA* LESSON

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Abstract: Pesticides are serious pollutants of the environment because of their environmental persistence and ability to accumulate in the body of organisms. The green frog Rana hexadactyla was exposed to the chemical pesticide- Methyl parathion and biological pesticide Neem leaf extract for 24 days, and the Sub lethal concentrations were tested to find out the effects of longevity. The sub lethal concentration of methyl parathion was found to be 4.4085 ppm and 7.1101 ppm for neem leaf extract. After 24 days exposure, the red blood cell count (595450/mm^3 (methylparathion) and 675417/ mm^3 (neem leaf extract) and Haemoglobin content (3.42 gm% (methylparathion) and 3.54 gm% (neem leaf extract) were decreased when compared to the control (RBC- 1044858/mm^3 and Hb 4.88 gm%). The number of white blood cells (WBC) increased towards normal after exposure up to 24th day. The results are statistically significant at P< 0.05 level.

Key words: Haematological study, Neam extract, Green frog, Methyl parathion

INTRODUCTION

The green frog *Rana hexadactyla*, is one of the most economically important frogs of India because of the superior quality of its meat. The severe exploitation of these species has drastically affected its population density. The indiscriminate use of different pesticides has led to the contamination of water bodies and gross loss in population. A decline in the amphibian population can have an adverse effect on the whole of an ecosystem because they not only control pests but also act as prey for other large animals (Mohanty- Hegmadi and Dutta, 1981). Pesticide induced haematological changes have great significance in assessing the impact of exposure under natural conditions and may also serve as a tool for biological monitoring (Murty, 1986). The present work is to study the effect of two pesticides on the haematological parameters of green frog *Rana hexadactyla*. The two pesticides

COMPARATIVE STUDY ON THE EFFICACY OF DIFFERENT CHEMICAL AND NATURAL TOOTH BLEACHERS ON ORAL MICROFLORA THROUGH *in-vitro* ANTIBACTERIAL ASSAY

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Abstract: The present study focused on the antibacterial activity of two classes of mouth and teeth cleaners used by people: four categories of toothpastes and plant phytochemicals. Representatives of each group were selected and treated in an invitro film of oral bacteria collected directly from oral habitat using disc diffusion method (Kirby- Bauer method) on Muller Hinton agar medium. Among chemical toothpastes tested, Close Up showed highest antibacterial effect on the test bacteria (19.75mm). The IZD of Pepsodent (18.75mm) and that of Colgate (18.25mm) were differ by 0.50mm and were comparable. Ganozhi showed medium effect on tested lawn of oral microflaura, producing an average IZD of 17.5mm, which is lower than toothpastes under category I, II and IV, but higher than mango leaf extract. Among the three pastes under category IV, KP Namboothiri's showed highest average inhibition zone with diameter 21.00mm which is greater than Himalaya (19.75mm) and Dabur (19.25mm) by more than 0.50mm. Mango leaf extract should be modified for preparing a remedy against peridontal diseases as its IZD is lower (13.25mm) than any other tooth bleachers used in the study. Purification and isolation of efficient antimicrobials from mango leaf extract can improve its anti bacterial efficacy. The study indicated that toothpastes with natural ingredients often produced equivalent or more effect on the oral pathogen than chemical toothpastes.

***Keywords:** Oral bacteria, Kirby Baeur method, toothpaste, Mango leaf extract, inhibition zone*

INTRODUCTION

Mouth is the gateway of body to the external world and it represents one of the most biologically complex and significant sites in the body (Marsh and Martin, 2009). Oral cavity includes the teeth and gums surrounded by the lips, cheeks, tongue, palate and throat (Takahashi, 2005) and harbor a diverse, abundant and complex microbial community vary between 500-700 different species. The normal members of the microbial community are *Neisseria*, *Leptotrichia*, *Bacteriodes*, *Veillonella*, *Streptococci*, *Diphtheroids* and *Corynebacteria*. Bacteria cause many harmful effects on the oral cavity of the host, like Periodontal diseases, Venereal

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Comparative Study on the Seasonal Variations in the Soil Edaphic and Chemical Factors of Agricultural and Grass Land Habitats of Central Travancore Kerala

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Abstract: *Comparison between agriculture land and grass land habitats in Alapuzha district on the basis of soil edaphic factors like temperature, p^H, Organic carbon content (OC), moisture content, Exchangeable Acid (EA), Exchangeable Base (EB), sand , silt , clay and soil chemical factors like nitrogen , phosphorous, potassium , calcium and magnesium contents. 20 agricultural land site and 20 grass land sites were selected. Soil samples of 5×5 cm^2 area from a depth of 5 cm were randomly collected from agriculture and grass land habitats. Monthly samples were collected and pooled into four seasons like pre monsoon, monsoon post monsoon and summer. Mean with standard deviation were taken. Seasonal and site wise variation were analyzed by using two way Anova. The study shows that the agriculture land soil has high nitrogen content (2844.83 ppm), Phosphorous content (10.24 ppm), and potassium content (144.2 ppm). The grass land soil has high organic carbon content (4.56 %); calcium content (1564.43ppm) and magnesium content (292.84 ppm).*

Keywords: soil edaphic factors, organic carbon content, soil chemical factors, soil fertility, habitat

1. Introduction

Soil is the vital part of the natural environment that covers much of the earth's land surface. Soil is important because it provides a place for plants to grow and contains a lot of living and non living materials like rocks, minerals, bacteria, animals and nutrients. The significance of nutrient cycling depends on the quantity of plant detritus available for decomposition and the rate at which decomposers. Soil composition changes due to environmental factors, along with the influence of man and land use.

The soil ecosystem is an interdependent life-support system composed of air, water, minerals, organic matter, and macro- and micro-organisms. Mineral portion of the soil which consists of three distinct particle sizes sand, silt, clay. Sand cannot hold nutrients, so sandy soils are not productive in nature. Moisture and temperature also influences the fertility of the soil. In most soil the majority of carbon is held as soil organic carbon. The amount of organic carbon in the soil depends on various factors like soil texture, climate, vegetation and land use. Soil organic matter is the major source of energy for soil microorganisms. The soil containing primary nutrients like Nitrogen, Phosphorus, Potassium and the secondary nutrients like Calcium and Magnesium also influences the fertility of the soil.

The present study was under taken for the comparative study between agricultural land habitat and grass land habitat on the basis of soil edaphic factors like soil temperature, pH, exchangeable acid, exchangeable base, organic carbon content, moisture content, sand silt, and clay content and soil chemical factors like nitrogen, phosphorus, potassium, calcium and magnesium content.

2. Methodology

2.1 Study area

The study areas were selected in Central Travancore area of Alappuzha district, lies between 9°5' and 9°54' North latitude and between 76°17' and 76°40' East longitudes.

2.2 Collection and transportation of sample

20 agricultural land sites and 20 grass land sites were selected. From these sites soil samples of 5×5 cm^2 area from a depth of 5 cm were randomly collected using soil auger. Collected soil was taken to laboratory in polythene covers. Monthly samples were collected from the study sites during pre monsoon (March, April, and May), monsoon (June, July, and August), post monsoon (September, October, and November) and summer (December, January, February) seasons 2014.

2.3 Soil edaphic factors analysis

From the soil samples the soil edaphic factors like soil temperature, pH, exchangeable acid, exchangeable base, organic carbon content, moisture content, sand silt, and clay content were detected. The soil chemical factors like nitrogen, phosphorus, potassium, calcium and magnesium content were analyzed. The soil temperature was measured from the site itself using soil thermometer. Soil pH was measured using soil pH meter. Exchangeable acid and exchangeable base were measured using the procedure of Trivedy and Goel (1987). Soil organic carbon content was measured by using the procedure of Walkley and Black (1934). Soil moisture content was measured by gravimetry method.

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Hydrological Assessment of Trace Metal Components from Some Lentic Fresh Water Aquifers, South West Coast of India

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Abstract: ***The current study was carried out for examining the heavy metal pollution profile of seven urban ponds in Chavara industrial area, south west coast of India. The study was conducted seasonally for a period of one year from January 2014 to December 2014. Results obtained from AAS analysis showed that toxic heavy metals such as copper (Cu), Munganese(Mn), zinc(Zn), Iron(Fe), lead(Pb), Cadmium(Cd), Nickel(Ni), Cobalt (Co), and Chromium(Cr) in the water samples were found to be higher than drinking water standards prescribed by WHO, BIS and FAO. This study is an attempt to compare the hydrological assessment of heavy metals in water of different ponds due to pollution from near industry-KMML, situates in Chavara, Kollam, India.***

Keywords: industrial area, toxic heavy metals, heavy metal pollution, hydrological assessment.

1. Introduction

Water, the universal solvent is the most vital component for all forms of life on earth. Over 71% of earth crust is covered with water. Of these only 0.3% is available as fresh water in rivers, streams, lakes and ponds. Safe and pure drinking water is the right of humans and all life forms on earth. Nevertheless industrialization and urbanization always leads to deterioration of water quality profile of most of the aquatic ecosystems. Fresh water bodies such as rivers, lakes, ponds etc are always under threat due to unscientific waste disposal strategies. Of these ponds have great ecological importance as they control flood, soil erosion and act as a good buffering system [1]. Ponds are lentic shallow water bodies, have an immense water retention capacity to maintain a balanced water column of an ecosystem. At local level ponds contribute more to biodiversity by supporting more unique and scare species [2].Hence monitoring and conservation of aquatic ecosystem are gaining importance due to its uniqueness. Urban watersheds are getting polluted mainly due to dumping of both solid and liquid untreated industrial and domestic wastes. This long term discharge results in percolating these pollutants in to ground water leads to destroying the natural habitats of both aquatic and terrestrial ecosystems. Kerala Minerals and Metals Ltd (KMML) is one of the leading profits making public sector, sited at coastal belt, Chavara, Kollam District in Kerala. KMML produces hazardous sludge as waste product during the production of titanium dioxide. This sludge contain large amount of heavy metals [3]. The improper management of waste products results in percolating them in to the surrounding water column which leads to degradation of complete ecosystem. These heavy metal contaminants will destroy the neighboring aquatic and terrestrial ecosystem completely and permanently.

2. Materials and Methods

Water samples were collected from seven different fresh water ponds from the study area, during pre monsoon, monsoon, post monsoon and summer from January 2014 to December 2014. Residents were not using the pond water in this area for any house hold purposes but utilize the water for fishing, cattle raring, and duck rising. Seven sampling stations (S1 to S7) were preferred for this study based on the requirement of this investigation. For analysing the trace metals contents of water from the elected stations, water samples were collected in clean polyethylene, white two litre cans. After proper labelling, the samples were brought to the laboratory for further analysis using AAS.

2.1 Sample examination.

Water Samples were subjected to atomic absorption spectrometer for being analyzed for metals like Cu, Mn, Zn, Fe, Pb, Cr, Cd, Ni, Co. Instrument was operated according to manufacturer's stipulation.

3. Results and Discussion

The data of trace metal components from seven selected fresh ponds were recorded during pre monsoon, monsoon, post monsoon and summer from January 2014 to December 2014 are presented below. Standard limits for drinking water prescribed by BIS, WHO and FAO was also given in Table 1.

Copper (Cu): The common sources of copper pollution in aquatic ecosystems were mainly from industrial sources, domestic wastes, metal plating or mineral leaching [4]. Copper concentration ranged between 1.45mg/l to 9.46mg/l

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Pollution Study of Pallickal River water Based on Pesticidal Compounds

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Abstract: *Pallickal River is one of the smallest river of Kerala, it originate from the cliffs of 'Nellimukal' in Pathanamthitta. People are making use of this river water for their domestic use and agriculture. This river system is less studied by the scientific community. Influx of water into this river is mainly from nearby agricultural paddy fields, where intensive chemical fertilizers and pesticides are in use. The purity of water for portable and other domestic use is to be scientifically assessed. For this assessment pesticide analysis can be used to determine the purity status of the river water. The pesticide residue analysis of Pallickal River water revealed that, these chemicals pose a huge threat to this River. Among organophosphorous pesticides Malathione (4.08 mg / l) and Methidathione (2.64mg/l) showed highest concentration. Pyrithroid Cypermethrin (4.05 mg/l) Cyfluthrin- B (2.33 mg/l) Deltamethrin (2.33 mg/l) showed a slight increase in concentration. Carbamate pesticides, Oxamyl (0.918 mg/l) and Thiodicarb (1.97 mg / l) showed a high concentration among fungicides, Indofil (1.419 mg/l) and Hexaconazole (1.296 mg/l) showed highest concentration. Herbicide such as 2,4-D(2.39 mg/l) Oxyfluorfen (2.638mg/l) and Pendimethalin (2.186mg/l) showed highest concentration. The study revealed that the water from the river Pallickal is of moderate quality*

Keywords: Pallickal River, Pesticides, Herbicides, Purity assessment, Fungicides

1. Introduction

Pallickal River is one of the smallest river of Kerala it is originating from the cliffs of Nellimukal in Pathanamthitta district a small stream from the wetlands of 'Tengamam' joints the main river at 'Anayadi 'and flows through 'Panmana' and'Karunagappally'Panchayath and part of 'Anwarssery' People are making use of this river water for their domestic use and agriculture. This river system is less studied by the scientific community. Influx of water into this river is mainly from nearby agricultural paddy fields, where intensive chemical fertilizers and pesticides are in use. The purity of water for portable and other domestic use is to be scientifically assessed. For this assessment the pesticide analysis can be used as an indicator to determine the purity status of the river water.

The Pallickal River is a wet land origin river and the upstream segment of the river is passing through the settlement area. There is all the possibilities of anthropogenic pollution, which leads the habitat loss. As far as considering Kerala's agriculture sector, farmers are using a large amount of pesticide combinations to improve the yield and quality of the crop products.

Malathione is the common compound of Organophosphorus that widely used in Kerala farms, and the Carbofuran is the most common carbamate pesticides. Malathione, Parathione along with Endosulfan combination are common in vegetable gardens of Kerala. In Kerala, the river bank cultivation is a practice with heavy use of chemical fertilizers and pesticides during the summer season, and it lasts till the onset of Monsoon. The Monsoon rain brings all these compounds to river water and finally to river bed as sediments. Dilution may occur in sediments (Eger, 1974). This will cause a drastic effect on the food web of riverine ecosystem. The agro farming near the riparian ecosystem and the small scale industrial units near the Pallickal River are the major source of such pesticidal contaminations. Hence an attempt has been made to assess the pesticidal contamination of Pallickal River.

2. Methodology

2.1 Sampling

The samples were collected from the three segments of the Pallickal River. Monthly samples were collected from each segment sampling method outlined by Radtke (2005). The water samples were collected from 2013 June to 2014 May. Samples were collected in a 500 ml sterile glass bottle and chilled immediately using ice bags and brought to the laboratory and kept below 0°C.

2.2 Analysis

Five samples were taken for analyzing pesticides and heavy metals. The organophosphorus pesticides were determined by Liquid- Liquid extraction and Gas Chromatography with flame photometric detector (Kesteska *et al.*, 2008). The carbamate pesticides were determined by High performance Liquid Chromatographic method (APHA, 2012). Herbicides were estimated by micro Liquid-Liquid extraction gas chromatographic method (APHA, 2012). The fungicides were estimated by SPME and Gas Chromatography with Electron Capture and Mass Spectrometric Detection method (Lambropoulou *et al.*, 2000).

2.3 Statistical Analysis

The statistical analysis and test of significance of differences were determined by Analysis of Variance (ANOVA)(SPSS 22). Descriptive statistics were done using Microsoft Excel.

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Optimization of media and temperature for antimicrobial activity of *Enterobacter* sp. associated with entomopathogenic nematode *Rhabditid* sp.

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ABSTRACT: An entomopathogenic bacterium isolated from the nematode, *Rhabditis (Oscheius)* sp. was found to produce secondary metabolites with antimicrobial activity. The bacterium isolated from the entomopathogenic nematode was identified as *Enterobacter* sp. by using biochemical and 16S rDNA sequence analysis. Media for the production of the bioactive metabolites were standardized with six carbon sources viz. glycerol, maltose, fructose, glucose, sucrose and lactose, and four nitrogen sources viz. tryptone, yeast extract, beef extract and peptone. Antimicrobial activity was found highest for culture filtrate solvent extract (CFSE) obtained from tryptone plus glycerol (T+G) combination. Addition of peptone to the media, irrespective of carbon sources, had the least antimicrobial activity. Fermentation with tryptone plus glycerol medium when carried out at temperature ranging from 25 to 40 °C, the highest antimicrobial activity was observed at 37 °C.

KEYWORDS: *Rhabditis (Oscheius)* sp., antimicrobial, entomopathogenic bacteria, *Enterobacter* sp.,

INTRODUCTION

The bacteria *Xenorhabdus* and *Photorhabdus* are symbiotically associated with nematodes belonging to the families Steinernematidae and Heterorhabditidae, respectively Poinar (1990). Virulence of entomopathogenic nematodes (EPN) to insects is attributed due to its symbiotic bacteria associated with EPN Babic *et al.*, (2000). The importance of entomopathogenic bacteria (EPB) as a source of antibacterial and antifungal molecules has been studied in detail (Webster *et al.*, 2002; Bode *et al.*, 2009).

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RESEARCH ARTICLE

Concentration Study of Antimicrobial Activity with Selected Oral Cleansers on Oral Microflora

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ABSTRACT:
The present study was aimed to screen antimicrobial effect of four selected tooth paste, on heterogenous human mouth, with an objective to evaluate performance of daily usable toothpastes, avoiding bacterial contamination of the mouth. In this investigation, all toothpaste has shown results. Among them, Colgate shown appreciable microbial resistance, 34.33 at a concentration of 9 gm/3 ml, followed by Closeup. Dabur and K.P. Namboothiris both ayurvedic products show similar results. In the study of all the toothpastes have proved their antimicrobial action in terms of inhibition in the bacterial culture. These toothpastes are currently running commercial commodities in the market. The study could prove that the bacteria inhabiting mouth can effectively controlled by optimal usage of this commodities. Present investigation may be considered as excellent products for preventing accumulation of heterogenous bacteria on human oral microflora. Study was based on in-vitro experiments. Results from this study have shown that toothpaste formulation containing synthetic antimicrobial agents like triclosan were more effective in controlling the oral micro-flora compared to toothpastes containing microbial agents. It cannot be assumed that the results of antimicrobial efficacy could be proportional for transferable to the oral activity and translated into clinical effectiveness. This was an *in vitro* study therefore it is not necessary that the result that we obtained shows the same effects on in-vivo experiments, hence it is needed to proceed this study under in-vivo conditions. The study can further be taken as an approach to evaluate the antimicrobial efficacy of various toothpastes and compare them with conventional dentifrices known antibacterial effect. HPLC technique can further be performed for extracting pure molecular form of antibacterial components to increase the efficacy dentifrices. It has been concluded from our results that certain dentifrices has shown less zone of inhibition due to less solubility of antibacterial components, so it is required to study further and perform certain experiments which could increase their solubility.

KEYWORDS: Antimicrobial effect, tooth paste, Colgate, Closeup, Dabur, K.P.Namboothiris.

INTRODUCTION:

Dental problems are the most common health problem in the human Communities (Loesche, 1996). A significant proportion of dental problems are due to microbial infections. Dental problems are of three types- Formations of dental plaque, Dental caries, Peridontal disease. Oral microbiology is the study of micro organisms residing in oral cavity and the interactions between the oral microorganisms with each other and with the host. The normal members of the microbial community seen in the oral cavity are *Neisseria*,

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RESEARCH ARTICLE

Antimicrobial Activity of Selected Medicinal Plants Against Oral Microflora

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ABSTRACT:

Antibiotic resistance and side effects of antibiotics are major problem in the medicinal field, in the present study four selected medicinal plants were used to find out the antibacterial activity against oral pathogen. Plant extracts of *Azadirachta indica*, *Syzygium aromaticum*, *Piper nigrum* and *Mangifera indica* were used for the study. By disc diffusion method these medicinal plant extracts produced clear and circular inhibition zones on the swab culture of oral microflora after 34 hrs of incubation. The inhibition zone for each medicinal plant varied in diameter. The inhibition zone indicates the destruction of microbial population in the culture by the antimicrobial activity of the medicinal plants. Three different treatments were conducted for each medicinal plant and each treatment shows a slight variation in diameter. Among four medicinal plants Azadirachta indica showed maximum zone of inhibition and *Mangifera indica* showed least inhibition zone diameter. One way ANOVA showed that there was no significant difference among the four medicinal plants in their antimicrobial effect on oral bacteria, there was a slight variation among them. As per the result from the present study, all of the selected medicinal plants showed their excellent efficiency against oral microflora. Since the tested extracts of selected plants were effective against pathogenic micro-organisms present in the oral cavity. The anti-microbial efficacy can be enhanced if the phyto constituents of these plant extracts are purified using different solvents like ethanol, methanol, acetone etc., antibacterial activity of these medicinal herbs, if translated into clinical practice would lead to the development of indigenous, chemical free, cost effective and holistic oral hygiene aids, which can be incorporated into various oral hygiene formulations like dentrifices, mouth rinses, gum paints etc.

KEYWORDS: *Azadirachta indica*, *Syzygium aromaticum*, *Piper nigrum*, *Mangifera indica*, disc diffusion method, oral microflora, inhibition zone.

INTRODUCTION:

Micro-organisms are found almost everywhere in our environment as well as on different part of eukaryotic body system. Symbiotic microbes associated with human body are of two types; resident floras are found inside the body, they are reestablished. Transient floras are found on skin and mucous membrane which are temporary.

Oral micro-biome is a complex ecological system where up to 700 species of microorganisms that have been identified. Oral microfloras are most commonly found in gingival crevices, tongue dorsum, buccal mucosa and saliva. Oral diseases continue to be a major health problem worldwide. Oral disease in an individual can be caused due to a combination of lack of oral hygiene and factors influencing the oral microbial community structure, such as diet. The most common oral bacteria include *streptococci*, *lactobacilli*, *staphylococci*, *corynebacteria* and various anaerobes. The most common type of pathological diseases in the mouth are

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RESEARCH ARTICLE

Study on the Length-weight Relationship of Four Common Edible Marine Fish Species from Shanghumugham and Valiyathura Beaches – Kerala, India

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ABSTRACT:

The present study was aimed to determine the length-weight relationship of fishes. The samples of fishes were collected from the catches of *Shanghumugham* and *Valiyathura beaches* during a period of one year from January to December 1991. The total length and weight of all the specimens were recorded to the nearest mm and mg respectively. The data were pooled and subjected to regression analysis, to determine the growth pattern of fishes. The length-weight relationship of *Rastrelliger kanagurata* revealed a linear relationship which can be represented as TW=3.2392 log TL-2.3777, the 'b' value of 3.2392. The linear relationships of *Sardinella gibbosa* revealed a regression equation of TW=1.47454 log TL-0.27006. *Encrasicholina devisi* also showed allometric growth rate, it has the 'b' value of 2.54733. The length-weight relationship of *Nemipterus japonicas* also reveals an allometric growth form. The 'b' value was found to be 1.56103. The linear relationship can be expressed as TW= 1.56103log TL-0.2365.

KEYWORDS: Length-weight relationship, *Rastrelliger kanagurata, Sardinella gibbosa, Encrasicholina devisi, Nemipterus japonicas*

INTRODUCTION:

The mathematical relationship between the length and weight of fishes is of great importance in relation to morphology, biology, growth rate and population dynamics and it also enables to estimate fish population. A perusal of previous literature on the length-weight relationship of fishes reveals its species dependence and its difference among populations (Bwathondi and Pratap, 1981; Seshappa, 1981; Safran, 1992). Natarajan *et al.*, (1977) reported the difference in the length-weight relationship of intraspecific populations of fishes inhabiting in same water body. Generally it is expected that the weight of fishes would vary as the cube of length (Brody, 1945; Lagler, 1952; Rounsefell and Everhart, 1953; Brown, 1957).

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But the actual relationship may depart significantly from this, as fishes normally do not retain the same shape or body outline throughout their life span and the specific gravity of the tissues may not remain constant (Le-Cren, 1951).

The length weight relationship of mackerels has been investigated by several workers (Pradhan, 1956; Rao, 1962; Sekharan, 1962; Luther, 1973; Yoharman, 1977; Udupa and Bhat, 1983; Azad and Udupa, 1989 and Gopakumar, 1991). The important contributions on the length-weight relationship of *Sardinella gibbosa* is that of Ganapati and Rao (1957), Sekharan (1968), Rao (1981) and Bwathondi and Pratap (1981). The noteworthy work on the length-weight relationship of *Encrasicholina devisi* is that of Syda Rao (1988a). The length –weight relationship of nemipterids has been recorded from east and west coasts of India (Krishnamoorthy, 1971; Vinci and Nair, 1974; Acharya and Dwivedi, 1981; Murty, 1983; Mohan and Velayudhan, 1984 and Hamsa et al., 1994).

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A COMPARATIVE STUDY ON THE ANTIMICROBIAL POTENTIAL OF SELECTED MEDICINAL PLANTS AGAINST THREE PATHOGENIC BACTERIA

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ABSTRACT

Ethanolic extract of ten Indian medicinal plants, *Ayapana triplinervis, Biophytum sensitivum, Boerhaavia diffusa, Catharanthus roseus, Centella asiatica, Chromolaena odorata, Glycosmis pentaphylla, Murraya koenigii, Psidium guajava* and *Punica granatum* and four commonly available antibiotics, ampicillin, amoxy clav, norfloxacin and amikacin were screened for potential antibacterial activity against *Escherichia coli, Klebsiella pneumoniae* and *Pseudomonas aeruginosa*. The antibacterial susceptibility test was done by adopting disc diffusion method. All the ten plants showed inhibitory effect on selected microbes. *Biophytum sensitivum* exhibited strong antibacterial effect on *K .pneumoniae* with mean inhibition zone of 26.7mm and on E.coli with 29.1mm. *Ayapana triplinervis, Catharanthus roseus* and *Chromolaena odorata* also showed good inhibitory effect on *Klebsiella pneumoniae* and *Centella asiatica* and *Punica granatum* showed fair effect on *Escherichia coli*. They can be further considered for usage among alternative therapeutic medicines for antibiotics.

Key words: Medicinal plants, Antibacterial activity, *Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa.*

INTRODUCTION

Microorganisms are found everywhere in our environment as well as on different parts of eukaryotic body system. They are essential for our survival as we share symbiotic relation with them, but at the same time pathogenic microbes are to be focused in research to avoid severe attacks. Both gram negative and gram positive bacteria occur among pathogenic category, but gram negative bacteria are more resistant to antibiotics because of their complex lipopolysaccharide cell wall. The gram positive bacterial genera that cause disease in humans are *Streptococcus, Staphylococcus, Corynebacterium, Listeria, Bacillus* and *Clostridium*. *Pseudomonas aeruginosa, Klebsiella pneumoniae, Neisseria gonorrhoeae, Chlamydia trachomatis* and *Yersinia pestis* are gram negative bacteria that cause disease in humans like nosocomial blood stream infections, respiratory or urinary tract infections, meningitis, etc.

Plants are prospective source of antimicrobial agents in different countries (Alviano and Alviano, 2009). By tradition different types medicinal plants are used for various treatments in humans. So researchers are focusing on natural products to develop better medications against multidrug resistant microbial strains. The antioxidant and antimicrobial properties of most medicinal plants is believed to be due to tannin, saponins, phenolic compounds, essential oils and flavonoids. The effectiveness of plant extract against a particular pathogen is affected by various intrinsic and extrinsic factors. Traditional plants are new sources of antimicrobials with stable, biologically active components that can establish a scientific base for the use of modern medicine (Zwetlana *et al.*, 2014). The present study showed the antimicrobial activity of ten medicinal plant extracts against *Escherichia coli, Klebsiella pneumoniae* and *Pseudomonas aeruginosa*.

METHODOLOGY

Collection and extraction of plant materials:

Ten medicinal plants were selected for the antibacterial susceptibility test (Table 1). Plant materials were collected from different locations of Alappuzha, Pathanamthitta, and Kollam districts of Kerala, India. The cleaned leaves were shade dried and powdered using electric blender. The powder was kept in air tight bottles till extraction. Extraction was done in soxhlet apparatus using air-dried powder of plant leaves with ethanol in the ratio 1:10. Three different concentrations of 10mg/ml, 15mg/ml and 20mg/ml of extract in DMSO were prepared for each selected plant.

BIOMONITORING POTENTIALS OF AQUATIC INSECTS FOR WATER QUALITY MONITORING AT TWO SEGMENTS OF KALLADA RIVER, KERALA

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Abstract: Biomonitoring using aquatic insects is one of the modern techniques for monitoring pollution in riverine system. It is a cost effective technique since it exploits the sensitivity of the aquatic organisms towards pollution. These biological indicators give adequate information to detect long term changes. Kallada River is one of the major rivers flowing through Kollam district in Kerala. An attempt has been made here to monitor water quality of Kallada River with the aid of Rapid Bio assessment Protocol. Sampling was done during post monsoon, summer and monsoon season. Benthic metrics for all the collected samples were calculated and tabulated, between-site tests of both the reference and test sites were also computed. The results from between-site test computed for comparative analysis of pollution for test sites of selected segments and the limited number of EPT (Ephemeroptera, Plecoptera and Trichoptera) taxa shows the test site of both segments were polluted. Hilsenhoff's family biotic index values were in the range 6.86-8.53 at test sites. So Kallada River requires an immediate attention to prevent the source of pollution otherwise it may lead to the depletion of the aquatic biota and thereby affect the human population inhabiting around the riverine system.

***Keywords:** Biomonitoring, aquatic insects, Rapid Bioassessment Protocol*

INTRODUCTION

Biomonitoring is one of the standard techniques of monitoring pollution in riverine ecosystems. It is a cost-effective technique because it involves the use of pollution sensitive resident biological organisms (macro invertebrates, fish & plants). For the assessment of water system, aquatic insects have been given priority since they are sensitive to wide range of pollutants and they are resident form of biota with longer life cycle than sampling schedule (Bass, 1995). The Rapid Bioassessment Protocol (RBP) have developed for aquatic assemblages that is periphyton, benthic micro invertebrates and fish. The benthic macro invertebrate protocols were originally developed by consolidating procedure by various water quality agencies in United States during 1985.The use of biological indicators gives more adequate information to detect long term changes. The tolerance of those biological indicators will be different in different

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Seasonal soil micro-arthropod association in different habitats with special reference to a terrestrial isopod, *Phyloscia javanensis* (Rich)

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Abstract- Population density, diversity, and species association of soil groups in general and species association of a soil isopod *Phyloscia javanensis* in particular was studied. The monsoon season has maximum soil animal group density followed by post monsoon and summer. The vertical migration and thermal sensitivity of most of the soil animals contributes to the decrease of population density of most of the groups in summer in both ecosystems. The species under special study showed maximum association in monsoon in both ecosystems and least during summer. This species has low association ability when compared with others micro-arthropod groups. This is because the soft bodied animal often happens to be the prey of many of the soil macro arthropods and Gastropods. So they always go to the seat of safety in the crevices of pebbles and stones. So their density will be always low in the collecting samples.

Index Terms- Animal association, seasonal variation, soil macro invertebrates, isopod, *Phyloscia*

I. INTRODUCTION

The soil is at the inter phase between the atmosphere and lithosphere. It also has an interphase with water bodies of fresh and salt (Anderson *et.al.*, 1978). The soil sustains the growth of many plants and animals and forms part of the biosphere. Soil macrofauna includes vertebrate animals mainly of burrowing types such as mole and rabbits which live partially or wholly underground. Microfauna represent small invertebrate animals included in the phylum annelida, arthropoda, nematoda and mollusca. The microbiota includes the soil algae, bacteria, fungi and protophyta

Soil microfauna play an important role in all the decomposition process in the soil. The most important groups involved in he turnover of organic matter are Arthropods and Annelids. Soil microarthropods include the Isopods, Arachnids Insects and Myriapods. The more numerous are the mites and many of the insects present as adults and larvae. Mites and spring tails feed on plant emains and fungi in the litter especially where thick mats build up agricultural land and undisturbed grassland. Their droppings ppear as characteristic pellets in the litter. They may also be found in the large pores. Some species of mites prey on spring tails Ulrich and Fiera, 2009. White, 1979.).

Many beetles and insect larvae live in the soil. Some of them feed saprophytically whereas others feed on living tissues and re serious pests of agricultural crops. The termites have been called the tropical analogue of earth worms and indeed they are mportant of all forms of litter-tree trunks, branches and leaves in the forests and especially the seasonal rainfall regions (Savanna) of he tropics. Most species are surface feeders and build nests called termitaria by packaging and amenting together soil particles with rganic secretions and excrement (Anderson *et. al.*, 1978, Wood, 1988). Millipedes feed on vegetation much of which in the form of iving roots, bulbs and tubers. Earthworms are more important in the consumption of litter than all other invertebrates. Earthworms eed purely on dead organic matter (Bhatnagar, 1975).

Relevance of soil studies based on the relationship of soil organisms and their association had been a subject of curiosity mong pedologists for long time. Various types of soil organisms interact with each other. This interaction may be either interspecific r intraspecific in nature (Choudhuri and Roy, 1970). Extensive data in this regard is quite helpful to arrive at conclusions. Presen tudy assesses the correlative basis for the association among the soil organisms, their density and diversity with special reference t oil isopod, *Phyloscia javanensis* (Rich).

II. MATERIALS AND METHODS

Experimental groups

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Ecosystem Threat Assessment Using Relative Scoring Method Analysis – A New Methodology Approach to River Achencovil, Kerala

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Abstract: ***Threat factor assessment of river Achencovil, a major river originating from Southern Western Ghats, was carried out. The study attempted to fill the knowledge gap in the potential of using Relative Scoring Method Analysis on tropical riverine ecosystem for rapid threat assessment. Eighteen threat factors obtained through reconnaissance survey were subjected to RSMA for assessment purpose. The analysis revealed that the midstream of the river face severe threat with high impact values of 11 threat factors (Grant Index value – 382). Downstream segment also face commentable threat from 7 factors having maximum impact values (GI- 346) whereas upstream was the least affected (GI-81). From this study, it is revealed that midstream and downstream segment of this river is highly prone to pollution load and it is high time to formulate a management plan to rejuvenate this river and to eradicate the worst sources of contamination. The study recommends the restriction of high impact threat factors such as unscientific river bank cultivation, improper usage of agrochemicals, untreated discharge of industrial contaminants, waste disposal and sand mining to protect the river from degradation.***

Keywords: *Achencovil River, Relative Scoring Method Analysis, Western Ghats, Threat factor, Pollution.*

1. Introduction

Conservation of river has become a major priority for region to withstand the impact of water scarcity to its local public. Human societies extract great quantities of water from rivers, lakes, wetlands and underground aquifers to meet agricultural, municipal and industrial demands. But their impact on rivers and other surface waters is staggering (Postel & Richter, 2003; Meifeiren *et al.*, 2004). Recent trends in polluting rivers have crossed the limits in terms of long-term effects on to the aquatic biota and local people sustaining on the stream ecosystem. Time consuming ecological assessment methods and transient pattern of remedial measures for conservation of aquatic ecosystems have to be functionally replaced with rapid assessment protocols in order to protect the dying rivers. The present study is a threat factor assessment approach to monitor the impact on Achencovil River, a major tropical river originating from Southern Western Ghats of Indian subcontinent.

The area, through which this river flows, is economically very rich and ecologically highly distributed with lot of interconnecting backwaters, lagoons interspersed with high degree of agricultural activity comprising mainly of paddy and coconut cultivation along with pineapples and rubber plantations. The formation of labour intensive commercial plantations, urbanisation, increased industrialisation and sandmining altered the river through chemical contamination and biotic habitat destruction (Prasad *et. al.*, 2006; Padmalal *et.al.*, 2008). All these caused deterioration of micro-climate and edaphic changes in the river and its biodiversity. Many of the anthropogenic activities resulted in such a state of affairs that caused the disappearance of many of the species from the riverine localities. Many animals have become rare and many are threatened with extinction (Molur *et. al.*, 2011). So far, no detailed studies have been conducted for rivers of Kerala using threat factor assessment through rapid protocols. Hence an attempt is taken in this direction to assess the threat of Achencovil River from all possible threat factors and to quantify the threat caused by various threat factors and their intensity.

2. Materials and Methods

1) Study Area

Three segments were demarcated along the river for the analysis of threat factors, which were the upstream segment including the river origin [$9^0$0'N- $9^0$10'N, $77^0$0'E-$77^0$16'E]; midstream segment [$9^0$13.59'N - $9^0$15.40'N and $76^0$40.49'E - $76^0$34.37'E]; and downstream segment [$9^0$21.01'N - $9^0$19.39'N and $76^0$27.37'E - $76^0$27.57'E].

2) Data Collection and Analysis

A reconnaissance survey was conducted throughout the bank of Achencovil River to identify the threat factors of this riparian ecosystem. Relative Scoring Method Analysis (RSMA) was used to analyse the data obtained (Sanalkumar & Sankar, 2009). Relative importance value of the obtained threat factors and their impact on the riparian ecosystem were expressed on a 10 point scale categorisation. The relative weighting of each determinant was done in three predetermined classes (high, moderate and low). Each class was given a weightage '3' for high, '2' for moderate and '1' for low. This was subjected to site-specific evaluation. The threat factors and the standards for deciding their degree of impacts are given in Table 1. Impact values and grand index values were computed for finding out the degradation status of each segment of the riparian system.

Toxicological Studies on a Soil Micro-Arthropod: An Indication on the Potential Threat in Soil Humus Formation

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Abstract: *The soil dwelling organisms do a responsible function in the ecosystem by organic matter breakdown, nutrient cycling and soil structure stability. Agrochemicals have long been used in agriculture to control pests and diseases in crops and thereby increasing agricultural production. However most of them are toxic to non target species and may cause negative impacts on beneficial soil macro invertebrates. The four agrochemicals which are toxic in nature are tested for their toxicity to Phylosciajavanensis at different concentrations. The results of the experiments revealed that all the agrochemicals tested viz., indofil, 2, 4-D, furvdan and sevin, are highly toxic to the test animal even at low concentrations. The values LC-50 and LC-100 values obtained in the present study underlined the toxicity of these chemicals to soil organisms like Phyloscia. Also the residual remains of these agrochemicals in the soil pose a threat to the habitat of soil isopods.*

Keywords: *Phyloscia*, soil isopod, agrochemical, toxicity, LC-50

1. Introduction

Isopods group of organisms play a dominant role to increase soil fertility. Indiscriminate use of pesticides,herbicide and fungicide in virtue of agricultural purposes has deleterious effects on the biology of soil arthropods.The chemical treatments that eliminate the group of microorganism undoubtedly create a partial biological vacuum in soil. Many pesticides, fungicide and herbicides can kill more than just their intended targets, namely necessary microorganism in the soil. Once in the soil, they can kill the microorganism living in the soil that breaks down organic material and aid in plant growth. It can take years before microorganism can once again live in soil that has had toxic chemicals applied to it.

Pesticides are the worst enemy of many of the soil organisms on this planet. Pesticides widely affect the life of aquatic fauna which are manifested as change in physiology, biochemistry and activity levels of many enzymes... In isopods, digestive gland epithelial thickness is related to contaminated food (Odendaal and Reinecke, 2004). Drobne*et.al.* (2008) confirmed the occurrence of epithelial thinning as a result of stress and that reduced feeding rate coincides with reduced epithelial thickness. The action of pesticide may bring external or internal damage to many parts of the organism.

Only recently a few studies on toxicity to soil invertebrates were published, including earthworms, springtails and enchytraeids (Wislocki*et.al*,. 1989; Sun *et.al*,. 2005; Jensen *et.al*,. 2007; Kolar*et.al*,. 2008). However, its effects on terrestrial isopods are not well known (Kolar*et.al*, 2008). Terrestrial isopods are abundant in different ecosystems and habitats, and have an important ecological role as macro decomposers. These animals have been recognized as useful for the characterisation of chemical toxicity (Hornung*et.al*,. 1998; Walker *et.al*,. 2001), because they are easy to sample, handle and culture, and large enough to perform a variety of sub-organism studies. A multi-level approach in toxicity testing with terrestrial isopods has previously been successfully used to identify the hazard of different pesticides and nanomaterials (Stanek*et.al*,. 2006; Drobne*et.al*,. 2009).Due to their important ecological role as decomposers of organic material, terrestrial isopods are widely accepted as test organisms in terrestrial ecotoxicology and ecophysiology (Lapanje*et al*., 2007).

Pesticide can serve farmers money by preventing crop losses to insect and other pests. Pesticide can be classified by target organism, chemical structure, and physical state. Pesticide can also be classified as inorganic, synthetic, and biological.Like modern insecticides, herbicides were first applied on a large scale basis shortly after world war –II. Generally herbicide falls into two groups depending upon their mode of action which include Mounron and Simazin, interfere with photosynthesis and thus cause the plant to die from lack of energy. The second group is typed by the commonly used 2, 4-D (2, 4-Dicholoro phenoxy acetic acid).

A preliminary survey in the study area revealed that agrochemicals of common use in the study area are 2,4-D, indofil, carbofuran and sevin.The study assess the toxicity of commonly used agrochemicals, 2, 4 D, carbofuran, indofil and sevin on soil isopod, *Phylosciajavanensis* (Rich).

2. Materials and Methods

1. Collection and rearing of mother culture

Phylosciajavanensis (Rich) were collected from the study area. They were transferred to large culture chambers of which plaster of paris and activated animal charcoal in the ratio 5:2 as base. They were acclimatized in the laboratory condition for about 20 days prior to experiment. Decayed leaf bits soaked in water were given as food.

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A Study on Hydrochemical Characteristics of Fresh Water Lentic Ecosystems in Chavara Industrial Area-South West Coast of India

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Abstract- The pollution status of freshwater ponds in Chavara, an industrial area in Kollam district, south west coast of India was studied seasonally for a period of one year from January 2014 to December 2014. The parameters determined for the study were pH, conductivity, total dissolved solids, alkalinity, total hardness, Chloride, Dissolved oxygen (DO), Biological oxygen demand (BOD), Chemical oxygen demand (COD), sulphate and nitrate concentrations. The study revealed that maximum conductivity, TDS, Chloride, Total Hardness, BOD, sulphate and COD were recorded during summer and minimum during the monsoon season. pH and total alkalinity was found to be high in post monsoon period and low on summer. Maximum DO was recorded during monsoon and minimum on summer. Highest value of Nitrate was observed during pre monsoon and lowest value on summer. The study indicated that the waste water from the industrial area is deteriorating the water quality of nearby water bodies.

Index Terms- Physico-chemical Parameters, Chavara industrial area, Pollution status, COD, DO.

I. Introduction

Fresh water availability is the most important criteria for the survival of life on earth. Without water, life will not exist in this planet. Ponds, lakes, rivers and reservoirs form the important fresh water bodies on earth. Ponds and lakes are lentic water bodies and have tremendous capacity to retain water in an ecosystem .They play a chief role in maintaining the water balance in the ecosystem. Even though water is that much vital for life, fresh water bodies are not getting hold of great botheration. Rapid industrialization always leads to waste disposal issues. Most of the industries are to be found on the banks of aquatic water bodies and consider them as easiest and cheapest place for disposing their waste products. Such indiscriminate disposal of toxic industrial effluents always leads to severe environmental problems. So it is important to monitor the water quality profile of aquatic ecosystem using Physico-chemical Parameters and pollution status of aquatic ecosystems can be monitored time to time for proper utilization of water bodies.

In Kerala as per Kerala State Pollution Control Board (KSPCB), 423 hazardous waste generating units were present. Kerala Minerals and Metals Ltd (KMML) is one such public sector, sited at Chavara, Kollam District, Kerala produces 40,000 MT waste product (sludge) per annum during the production of titanium dioxide pigment. (Jayasree *et al.*, 2009). Accidental leakage of this industrial effluent has led to the degradation of adjacent area of industry along with surrounding aquatic ecosystems. Compared to other water bodies less research work have been carried out related to the conservative status of pond ecosystem. (Linton *et al.*, 2000). In the recent years several studies have been made on KMML related issues (Humsa *et al.*, 2015; Krishnan *et al.*, 2013; Shaji *et al.*, 2009 and Divakaran *et al.*, 2013) but not much information is available on Physico-Chemical parameters of the pond water bodies in this area.

MATERIALS AND METHODS

The sites selected for the study include seven naturally occurring fresh water ponds from Chavara taluk, an industrial area in Panmana panchayat where KMML, one of the few profit-making public sector units in Kerala, situated in the south west coast of India. Seven sampling stations (S1 to S7) were preferred for this study based on the requirement of this investigation. For analysing the physic-chemical properties, water samples were collected from selected stations for a period of one year from January 2014 to December 2014. For analysis, the samples were collected in clean polyethylene, white two litre cans. After proper labelling, the samples were brought to the laboratory for further analysis of various physico-chemical parameters. The physico-chemical characteristics of water was analysed using standard methods of (APHA, 2008).

RESULT AND DISCUSSION

The values of each parameter during different seasons (pre monsoon, monsoon, post monsoon and summer) and different stations (seven pond ecosystem in Chavara industrial area) during Jan-2014 to Dec 2014 are given in different Tables (1 to 11. The result obtained was compared and discussed with other water quality standards and also with other works related to this study.

pH

In the present investigation the pH in different pond ecosystem (Table 1) varied between 3.1 (S7) summer and 8.4 (S4) Post monsoon. Seasonal average showed a high pH in the post monsoon and low in the summer in the study period. The station average showed a very low pH in station S7 where pH dropped to highly acidic nature. The (WHO, 1993) and (BIS, 1991) recommendation of pH is 6.5- 8.5. Minimum value of 3.1 recorded at S7 representing good evidence on the effect of the

Seasonal Fluctuations in the Pollution Indicators, Microorganisms and Aquatic Insects in the Vettiyar Segment of River Achankovil

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Abstract: *Achencovil River with a length of 128 kms is a major river of Kerala. Physico-chemical parameters, microbiological and pollution indicators of the River Achencovil, Kerala, India was determined during summer season. The physico-chemical parameters like Turbidity, Temperature, pH, Total Dissolved solids (TDS), Conductivity, Dissolved Oxygen, Biological Oxygen Demand, Nitrate, Phosphate; microbiological analysis like Total Coliform Count were studied and analyzed during summer season, 2012 using standard procedures. The water samples were collected from three different sites of mid stream Vettiyar segment during summer season. All most all parameters showed significant ($p< 0.05$) variation between sites,and was determined by analysis of variance (Anova). Water Quality Index and microbiological characterisic like Total Coliform Count(TC) were also analyzed. The aquatic insects ordrer like Odonata, Hemiptera were obtained during the study period. Overall water quality index of Vettiyar segment in river Achenkovil during summer season was 59.*

Keywords: Achencovil river water, Physico-chemical parameters, Water quality index, Microbiological analysis

1. Introduction

The Achenkovil River is one of the important rivers in Kerala, formed from the streams of Rishimala River, Pasukidamettu River and Ramakkalteri River. This river enriches the Pathanamthitta district of Kerala State. It joins the Pamba River at veeyapuram in the Alappuzha district of Kerala in South India

Water Pollution is a phenomenon that is characterized by the deterioration of the quality of land water (rivers, lakes, marsh and ground water) or sea water as a result of various human activities (Triveni and Guru Deep, 1996). Pollution represents wastage of world resources, an economic burden on a nation and a financial loss to an enterprise. The pollution can be reduced and minimised by reducing the inefficiencies.

Rivers contains waste materials these include sewage, garbage and liquid waste from factories and homes. Wastages from chemical factories contain many toxic or poisonous chemicals, these are discharged into rivers. The river water becomes poisonous for fish other aquatic animals and plants (Agarwal, 1995). Anthropogenic activities such as the river valley projects have drastically transformed the riverine ecosystems all over the world. In addition to the river valley project the landscape transformations are probably responsible for the most widespread damage to the rivers and streams (Allan, 1995; Dudgeon, 2000 and Allan, 2004). It is apparent that an assessment of water quality cannot focus on chemical indicators alone, but must instead focus on indicators alone, but instead focus on indicators that integrate the effects of physical, chemical and biological contaminations (Genet and Chirhart, 2004).

There are few studies conducted in river Achenkovil. Ever increasing issues of water pollution and its consequences on rivers like Achenkovil needs urgent attention in order to cease or lower the threatening problem faced by the laymen for their survival. Physico-chemical and microbiological analysis is the most effective way to monitor the water quality of rivers. When you submit your paper print it in two-column format, including figures and tables [1]. In addition, designate one author as the "corresponding author". This is the author to whom proofs of the paper will be sent. Proofs are sent to the corresponding author only [2].

2. Methodology

2.1 Study area

The study area was Vettiyar mid sueam segment of River Achankovil. Four study sites were selected in this segment and samples are collected from each site. They were Site I. Muttumpattu Kadavu it located at latitude 09° 14' 46.2'N and longitude 076° 35'42.9'E, Site II. Kanjirathummoodu is located at latitude 09° 14' 44.0'N and longitude 076° 35' 38.9'E with elevation, Site III. Sanchayakadavu is located at latitude 09° 14' 55.5'N 076° 35' 24.6' E with elevation and longitude Site IV. Pattenkadavu is located at latitude 09° 14' 57.0'N and longitude 076° 35' 22.4' E with elevation

2.2 Collection and Transportation of sample

Monthly samples were collected from Vettiyar segment during summer (February, March, April, 2012) seasons. Three samples were taken from each site with an average distance of 500 metres. Samples were collected in pre-sterilized containers and transported to the laboratory within shortest possible time to avoid erroneous data variation due to physical and bacteriological change.

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POLLUTION MONITORING IN THAZHKKARA SEGMENT OF RIVER ACHENKOVIL BASED ON ENTAMOLOGICAL AND PHYSICO-CHEMICAL PARAMETERS

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Abstract- Present work was designed to study the water quality of Thazhakkara segment of Achenkovil River based on physico-chemical, entomological and microbiological aspect following Water Quality Index and Family Biotic Index of aquatic insects. Sampling was done during summer season 2012. Three study sites were selected from the study segment as Vazhuvadi, Pottamelkadavu and Kunnam. Physico-chemical parameters like TDS (Total Dissolved Solids), Conductivity, Salinity, P^H, Temperature, Turbidity, Dissolved Oxygen, BOD, Nitrate, Phosphate were analyzed. Mean with standard deviation and ANOVA were taken. Water Quality Index was also analyzed. It has been observed that overall water quality index of Thazhkkara segment of river Achenkovil during summer season was 53, that is some of the parameters substantially exceeded the limit. Microbiological analysis showed that the level of fecal coli form was moderate during summer season. An average of 2.9 Family biotic index of aquatic insects were obtained during the study period. The results showed that the Achenkovil river water at Thazhkkara segment was polluted with numerous organic pollutants.

Index Terms- Achenkovil River, Physico-chemical parameters, Water Quality Index, Family Biotic Index

I. Introduction

Achenkovil River is one of the major rivers in Kerala. The river originates from Pasikidamedu of Thoovalmala of Achenkovil mount as two streams namely "Kallar" and "Kanayar". Both streams unite near Kulathuppuzha and form the river Achenkovil and join river Pampa at Veeyapuram in Alappuzha district which later joins Arabic sea through Vembanadu Lake. River Achenkovil flows through three districts of Kerala Kollam, Alappuzha and Pathanamthitta. Most of this river flows through Pathanamthitta and Alappuzha districts. The recent trend of planting rubber trees on the sides of river and paddy fields have caused severe problems to the portability of water.

Biological assessment of the fresh water habitats aims at characterizing and monitoring the conditions of the aquatic resources (Sivaramakrishnan *et al.*,1996). The temperature is one of the important physical factors, which affects the chemical and biological reactions in water. It regulates the rate of photosynthesis in aquatic ecosystem. The temperature variation is one of the factors in the swamp and estuarine system, which may influence the physico-chemical characteristics and also influence the distribution and abundance of flora and fauna (Soundarapandian, *et al.*, 2009). The fluctuation in river water temperature usually depends on the season, geographic location, sampling time and temperature of effluents entering the stream (Ahipathi, 2006). Dissolved oxygen values were found maximum during winter and minimum during summer, which might be due to natural turbulences and higher algal productivity produces oxygen by photosynthesis in rainy period and active utilization in bacterial decomposition of organic matter (Rajkumar, 2004).

Phosphate and Nitrate determinations are important in assessing the potential, biological productivity of surface water. Increasing concentration of phosphorus and nitrogen compounds in lakes and reservoirs leads to eutrophication. Phosphates and nitrates were maximum in monsoon and minimum in summer, this could be due to agricultural runoff during rainy season and utilization as nutrients by algae and other aquatic plants (Ahipathi, 2006). The maintenance of healthy aquatic ecosystem is depended on the physico-chemical properties and biological diversity. A regular monitoring of water bodies with required number of parameters with reference to the quality of water not only prevents the outbreak of diseases and occurrence of hazards but checks the water from further deterioration. Bacteriological assessment, particularly for coli forms – the indicators of contamination by faecal matters is therefore routinely carried out to ascertain the quality and potability of water to ensure prevention of further dissemination of

POLLUTION MONITORING IN PUNALUR SEGMENT OF RIVER KALLADA BASED ON MICROBIOLOGICAL AND ENTOMOLOGICAL PARAMETERS

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Abstract: The study was conducted in Kallada River. The entomological indicator organisms with respect to the microbiological studies were done during summer season 2012. Four study sites were selected, monthly samples were collected from these study sites during three months February, March, April. For microbiological analysis, culture technique was adopted. The bacterial population in different samples was calculated on MacConkey agar for Total Coliform Count (TC). Microbiological analysis showed that the level of fecal coli form was moderate during summer season. The Aquatic insects order like Odonata, Hemiptera, Coleoptera, Ephemeroptera, Trichoptera were obtained during the study period. Tolerance value and Family Biotic Index value of insects were also calculated. An average of 6.5 Family biotic index of aquatic insects were obtained during the study period. The results showed that the Kallada river water at Punalur segment was polluted with organic pollutants.

Key words: Kallada River water, Microbiological analysis, Aquatic insects

INTRODUCTION

Kerala is a land gifted with 44 rivers and a continuous chain of backwater extending throughout the state. Among the rivers 41 flow from east to west wards criss-crossing 38,590 km area of the Kerala state where as 3 flow eastwards. The important rivers in Kerala are Bharathapuzha, Periyar, Pamba, Achenkovil, Kallada, Chalyar, Manimala etc.

The present study was designed and conducted in the water of River Kallada. Kallada River originates from the Kulathupuzha hills near Ponmudi, which has a length of 121 km and flows through places like Punalur, Pathanapuram, Kotarakara, Kallada, Kunnathur and Kollam and finally empties in Astamudi kayal. The river bed is usually rocky. The river is formed by the confluence of 3 rivers, the Kulathupuzha, the chenthurni, and Kalthuruthy.

Kallada River is one of the distressed or dying rivers in Kerala due to uncontrolled sand mining, pilgrimage, encroachment, reclamation, poaching etc., but a few scientific studies were published regarding the pollution monitoring of river water. Therefore it is highly valid to study the entomological indicator organism with respect to microbiological analysis of Kallada River.

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ORIGINAL ARTICLE

Molecular characterization and amplified ribosomal DNA restriction analysis of entomopathogenic bacteria associated with *Rhabditis* (*Oscheius*) spp.

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Abstract Bacterial strains associated with entomopathogenic nematodes (EPNs) *Rhabditis* (*Oscheius*) spp. were isolated from infected cadavers of *Galleria mellonella*. The obtained 18 isolates were subdivided into nine phylogenetically different genera based on comparative sequence analysis of their 16S rRNA genes. The isolates were affiliated to three different class namely γ-*proteobacteria* (*Enterobacter*, *Proteus*, *Providencia*, *Pseudomonas*, *Stenotrophomonas*), β-*proteobacteria* (*Alcaligenes*) and *Bacilli* (*Bacillus*, *Enterococcus*, *Lysinibacillus*). It was observed that Gram-positive strains (*Bacilli*) were more frequently associated with the EPN, whereas Gram-negative isolates were affiliated to six different genera with more genotypic diversity. Subsequently, all bacterial isolates used in this study were analyzed by amplified ribosomal DNA restriction analysis (ARDRA). Eight restriction endonucleases (*Cfo*I, *Hin*fI, *Rsa*I, *Dde*I, *Sau*3AI, *Alu*I, *Hae*III, and *Msp*I) were examined and a total of 15 different genotypes were obtained, forming two heterogenous main clusters after analysis by un-weighted pair-group method using arithmetic averages.

Keywords *Bacillus* · *Enterobacter* · Entomopathogenic nematode · 16S rDNA

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Introduction

Entomopathogenic nematodes (EPNs) lead a symbiotic association with specific enterobacteria. *Xenorhabdus* and *Photorhabdus* are two genera of bacteria that are symbiotically associated with specific nematodes belonging to the families Steinernematidae and Heterorhabditidae, respectively (Poinar 1990). The nematodes invade the larvae of susceptible insects and penetrate to the hemocoel, where they release their symbiotic bacteria. The bacteria proliferates, kills the insect larvae, and promotes nematode reproduction by providing nutrients from the actions of degradative enzymes on the insect cadaver and by producing antibiotics that inhibit the growth of other microorganisms (Akhurst and Boemare 1990). A striking feature of *Xenorhabdus* and *Photorhabdus* is phase variation, which affects a large number of membrane-bound, intra and extracellular proteins and secondary metabolites (Akhurst 1996; Forst et al. 1997). Phase I variants are involved in the symbiotic relationship with EPN and are isolated from the non-feeding infective stage nematodes and from the body cavities of insects killed by these nematodes. No role in symbiosis has yet been determined for phase II, which is associated only with EPN under laboratory conditions. They represent one important part of the spectrum of biocontrol agents that are used to control insect pests of economically important crops. The importance of entomopathogenic bacteria (EPB) as source for the discovery of antibacterial and antifungal molecules has been studied in depth, as highlighted in various reviews (Paul et al. 1981; Webster et al. 2002; Bode 2009).

Rhabditis (*Oscheius*) spp. isolated from different agroclimatic zones of Kerala resembles EPN and was found to be effective for the control of areca nut spindle bug in the field (Mohandas et al. 2004). These were found to kill a

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STUDIES ON SEASONAL VARIATIONS IN THE DIVERSITY PATTERN OF SOIL ARTHROPODS IN RUBBER PLANTATIONS - CENTRAL TRAVANCORE AREA

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Abstract- *The diversity of soil arthropod fauna inhabiting in rubber plantations at Central Travancore area of South Kerala regions were studied. The soil arthropods were collected during the year 2014. Soil samples were periodically and regularly collected from 10 different sites of rubber plantation. At each station, soil samples were collected between the hours of 8 am to 10 am. 17 orders of soil arthropod were collected and extracted using Berlesse tullgren funnel. Arthropods were collected, using 70% alcohol. The obtained soil arthropods belonging to order Isopoda, Diplopoda, Pauropoda, Chilopoda, Symphyla, Araneida, Acari, Chelonethi, Collembola, Protura, Diplura, Hymenoptera, Isopteran, Psocoptera, Diptera, Coeleoptera, Dermaptera and Psocoptera. Seasonal variations of soil arthropod fauna in rubber plantations were studied. Data collected from the rubber plantation sites were subjected to appropriate statistical analysis. Shannon Weiner Diversity, Simpson's dominant index, Berger parker dominance, Hill's abundance, Mergaleff richness and McIntosh territorial indices were calculated. The order Collembola, Acari, Hymenoptera, Diplopoda, Isopoda were the dominant and abundant groups in all rubber plantation study sites. Diversity of soil arthropod population in each season was similar among all of the study sites. In all the sites, maximum diversity, richness, dominance, abundance and evenness were noted in monsoon and post monsoon seasons, while the minimum was during the summer season. Seasonality exerted a strong effect on the abundance and diversity of rubber plantation arthropods.*

Index Terms- Soil arthropods, Diversity, Berlesse tullgren funnel, Rubber plantation, Isopoda, Collembola

I INTRODUCTION

Biodiversity is the key factor of the structure and function of ecosystems (Lee, 1991 and Wall *et al.*, 2005). Soil is an extremely dynamic, complex and highly heterogeneous system that allows the development of large number of ecological habitats, home of an array of live organisms and performs important functions for the ecosystem (Gardi and Jeffery, 2009). Soil creates a favorable habitat for micro organisms and it is inhabited by a wide range of them namely; algae, fungi, bacteria, arthropods and protozoa (Koehler 1992). Soil organisms range from microscopic forms to the macroscopic forms (Franke, 2003). Arthropods are the most diverse group of animals on earth and functional component of the major soil food web, such as soil accumulation of organic matter, soil structure and nutrient cycling also encouraging plant root development (Basset *et al.*, 2003; Gardi and Jeffery 2009).

Soil arthropods are a vital link in the food chain as decomposer (Samways,1994; Mattson, 1997; Trombetti and Williams, 1999; Coleman *et al.*, 2004, Devi and Singh, 2006;). Acarina and collembolans usually account for 90% of the soil arthropod fauna. Arthropods are the dominant animal group throughout the world. Population density and composition of the fauna in soils are indicators of soil condition (Lussonhop, 1992; Stork and Eggleton, 1992). The abundance of microarthropods in soil determined by resource availability, pH, disturbance and climatic factors (Curry, 1994). Without arthropods most terrestrial ecosystem would rapidly collapse (Iloba and Ekrakene, 2008). (Wallwork 1970).Hence an attempt has been taken to estimate the biodiversity of soil arthropods in rubber plantations, Central Travancore area of South Kerala.

II METHODOLOGY

a) Study area:

The study was conducted in ten rubber plantation sites at Central Travancore area of South Kerala state during the year of 2014.

b) Sampling sites:

Ten study sites were selected in random from the study area for soil and soil arthropod sampling.

c) Collection, extraction, sorting and preservation:

Soil samples were collected from 10 rubber plantation sites. Soil samples of 5×5 cm^2 area, from a depth of 5 cm randomly collected with soil auger. Soil samples were collected in all seasons this was carried out between the hours of 8.00 am to 10.00 am in the morning. Soil samples were placed in a labelled polythene covers and taken to the laboratory.

Collected soil samples placed into a 15×25 cm tray and hand sorted to collect large soil microarthropods. Remaining soil samples were transferred to the Berlese Tullgren funnel for soil arthropods extraction. Berlese Tullgren Funnel extractor is the best extraction method for extracting soil arthropods (Hopkins, 1970; Frith and Frith, 1990; Iloba and Ekrakene, 2008). The soil micro arthropods were extracted overnight into a picric acid

RESEARCH ARTICLE

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A SYSTEMATIC ASSESSMENT OF THREE SPECIES OF GOBIOID FISHES (TELEOSTEI: PERCIFORMES: GOBIOIDEI) FROM KERALA

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Abstract: *Analysis of selected body characters of the three gobioid species Glossogobius giuris, Butis butis and Eleotris fusca from Kerala studied revealed a clear propensity of some of the characters towards each species sufficient enough to discriminate each other. Euclidean one way single linkage cluster analysis based on the selected body characters revealed two distinct clads. E.fusca forming a single clad, whereas B. butis and G. giuris forming the second clad with high Bootstrap support (BP=100). The second clad is composed of two linkages representing B. butis and G. giuris having high bootstrap support (BP=100). The two species remains as a sister group sharing many characters. The same pattern of relationship was noted among the three species using head as well as meristic characters.*

Keywords: *Clad, Cluster analysis, Gobioid fishes, Meristic, Morphometrics*

INTRODUCTION

Morphometrics study the co-variation between the patterns of morphological variations (Bookstein, 1991). The most common approaches referred to as traditional morphometrics, are only a few decades old (Marcus, 1990; Rohlf and Marcus 1993; Adams *et al.*, 2003). The family Gobiidae is the largest marine fish family with separate spinous and rayed dorsal fins and pelvic fins often joined into a disc. Recent molecular phylogenetic analysis (Thacker, 2009) have demonstrated that Butidae is sister to a clad containing Gobiidae and Gobioinellidae with Eleotridae sister to that clad of three families. Considering the systematics and taxonomy of gobiids, the most notable contributions are those of Hoese and Allen (1983), Hoese and Gill (1993), Winterbottom (1993), Larson (2001), Thacker (2001, 2011 a,b), Cheng *et al.*, (2005), Tornabene and Pezold (2011), etc.

In the molecular phylogeny of several groups of gobioid fishes the contributions of Thacker and her group (Thacker, 2003, 2009; Thacker and Cole, 2002; Thacker and Hardman, 2005; Thacker

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Research Article

OMICS International

Isolation and Identification of Bioactive Molecules Produced by Entomopathogenic bacteria, *Acinetobacter calcoaceticus*

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Abstract

Objective: To isolate and identify the bioactive metabolites produced by *Acinetobacter calcoaceticus* associated with entomopathogenic nematode, *Steinernema* sp.

Methods: In order to get maximum growth of bacteria and thereby maximum yield of organic extract optimization of basal media, temperature, pH and agitation speed was done. Effect of additional carbon source was also studied by doing fermentation using selected basal media at optimized conditions. Cell free culture obtained after fermentation is separated using ethyl acetate and the organic part is concentrated. Organic compounds were purified by column chromatography and identified using spectral techniques like HPLC, NMR and FTIR. Antimicrobial activity of the cell free extracts and organic compounds were tested by well diffusion technique.

Results: Cyclo (Pro-Tyr) and cyclo (Pro-Leu) were the compounds identified from organic extracts produced by *Acinetobacter calcoaceticus*, associated bacteria of entomopathogenic nematode, *Steinernema* sp. Cyclo (Pro-Tyr) showed antifungal activity against Candida albicans with 10 mm ZOI.

Conclusion: From the results it is possible to conclude that the entomopathogenic nematode and the associated bacteria could be promising source of bioactive compounds, and warrant further study.

Significance and interest of study: The information obtained can be useful for commercial utilization.

Keywords: Entomopathogenic nematodes; EPN; *Acinetobacter calcoaceticus*; Antifungal; *Steinernema*

Introduction

Entomopathogenic nematodes are insect pathogenic nematodes and are the organisms considered for use in biological control. They have certain advantages over chemicals as control agents. Nematodes are non-polluting and thus environmentally safe and acceptable. Research into the use of entomopathogenic nematode as biocontrol agents has focussed mainly on the investigation of the families' steinernematidae and heterorhabditidae. Entomopathogenic nematodes are highly virulent due to its symbiotically associated bacteria. The bacterial symbiont is *Photorhabdus* in nematodes of the genus *Heterorhabditis* and *Xenorhabdus* in nematodes of the genus *Steinernema*. In addition to *Xenorhabdus* and *Photorhabdus* sp. a novel entomopathogenic bacteria is isolated from a new entomopathogenic nematode, *Rhabditis* (*Oschieus*) sp., of the family Rhabditidae [1,2]. Entomopathogenic bacteria are potential source of antibacterial, antifungal, antiulcer, anti cancerous, insecticidal and nematicidal compounds, which might become promising pharmaceutical antibiotics or bio pesticides. EPB produce bioactive molecules which inhibit the growth of a wide range of bacteria, fungi and other microbes [3].

Entomopathogenic nematodes on entering the host insect, pathogenic bacteria are released by the nematode, and resulting in bacterial infection which causes the insect's death [4,5]. The bacterial symbionts must perform three separate tasks to allow successful proliferation of the nematodes within the insect host, These are 1) to overcome insect immune defences and cause septicaemia and death, 2) to break down the tissues of the dead insects to release nutrients for the nematodes to proliferate and 3) to successfully re colonise the infective juvenile nematodes which will then be released [6].

Entomopathogenic bacteria encode a wide range of toxins that are exported by various secretion systems [7]. These toxins are involved in defense mutualism. A large number of novel genes are involved in the pathogenic and symbiosis of these organisms [8]. It was found that about 6% of genome is involved in secondary metabolite production [9] which is more than that of *Streptomyces*. Entomopathogenic nematodes are known for their antibacterial activity [10,11], antifungal activity [12-14], nematicidal activity [15,16], insecticidal activity [17] and cytotoxicity against various cell lines [18].

This study mainly aims at isolation and identification of bioactive molecules produced by entomopathogenic bacteria associated with a nematode strain NL among the collection of 65 entomopathogenic nematode isolates maintained at the CTCRI laboratory and its activity against fungi and bacteria.

Materials and Methods

Microorganisms and culture maintenance

EPN culture: The nematode isolate, NL (Accession No: CTCRI/EPN/38) collected from the soil of Namakkal district, Tamil Nadu was selected for this study. It was taken from the nematode culture collection maintained in CTCRI laboratory.

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Research Article

OMICS International

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Conclusion: From the results it is possible to conclude that the entomopathogenic nematode and the associated bacteria could be promising source of bioactive compounds, and warrant further study.

Significance and interest of study: The information obtained can be useful for commercial utilization.

Keywords: Entomopathogenic nematodes; EPN; *Acinetobacter calcoaceticus*; Antifungal; *Steinernema*

Introduction

Entomopathogenic nematodes are insect pathogenic nematodes and are the organisms considered for use in biological control. They have certain advantages over chemicals as control agents. Nematodes are non-polluting and thus environmentally safe and acceptable. Research into the use of entomopathogenic nematode as biocontrol agents has focussed mainly on the investigation of the families' steinernematidae and heterorhabditidae. Entomopathogenic nematodes are highly virulent due to its symbiotically associated bacteria. The bacterial symbiont is *Photorhabdus* in nematodes of the genus *Heterorhabditis* and *Xenorhabdus* in nematodes of the genus *Steinernema*. In addition to *Xenorhabdus* and *Photorhabdus* sp. a novel entomopathogenic bacteria is isolated from a new entomopathogenic nematode, *Rhabditis* (*Oschieus*) sp., of the family Rhabditidae [1,2]. Entomopathogenic bacteria are potential source of antibacterial, antifungal, antiulcer, anti cancerous, insecticidal and nematicidal compounds, which might become promising pharmaceutical antibiotics or bio pesticides. EPB produce bioactive molecules which inhibit the growth of a wide range of bacteria, fungi and other microbes [3].

Entomopathogenic nematodes on entering the host insect, pathogenic bacteria are released by the nematode, and resulting in bacterial infection which causes the insect's death [4,5]. The bacterial symbionts must perform three separate tasks to allow successful proliferation of the nematodes within the insect host, These are 1) to overcome insect immune defences and cause septicaemia and death, 2) to break down the tissues of the dead insects to release nutrients for the nematodes to proliferate and 3) to successfully re colonise the infective juvenile nematodes which will then be released [6].

Entomopathogenic bacteria encode a wide range of toxins that are exported by various secretion systems [7]. These toxins are involved in defense mutualism. A large number of novel genes are involved in the pathogenic and symbiosis of these organisms [8]. It was found that about 6% of genome is involved in secondary metabolite production [9] which is more than that of *Streptomyces*. Entomopathogenic nematodes are known for their antibacterial activity [10,11], antifungal activity [12-14], nematicidal activity [15,16], insecticidal activity [17] and cytotoxicity against various cell lines [18].

This study mainly aims at isolation and identification of bioactive molecules produced by entomopathogenic bacteria associated with a nematode strain NL among the collection of 65 entomopathogenic nematode isolates maintained at the CTCRI laboratory and its activity against fungi and bacteria.

Materials and Methods

Microorganisms and culture maintenance

EPN culture: The nematode isolate, NL (Accession No: CTCRI/EPN/38) collected from the soil of Namakkal district, Tamil Nadu was selected for this study. It was taken from the nematode culture collection maintained in CTCRI laboratory.

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Landuse Pattern of Neyyar River Basin (2015-2016), Kerala, India

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bstract- In order to understand the landuse pattern of Neyyar iver basin, very extensive field investigation was conducted, and ie findings were cartographically illustrated with the help of eographic Information System (GIS), to provide an applicable utlook for a better landuse framing, as landuse has an inevitable ole in the mere existence of the river. Geospatial pattern of the resent landuse of the study area indicated that the sustainability f this river ecosystem is in danger due to unscientific landuse ractices such as deforestation, reclamation of paddy fields, xtensive rubber cultivation, sand mining, pollution and gglomerated settlements. The major landuse category observed s this region is settlement with mixed tree crops.

ndex Terms- Landuse, GIS, Reclamation, Neyyar.

I. Introduction

Neyyar is the southern-most river of Kerala State has a total basin area of 483sq.km lies between 8°15' to 8°40'-N atitudes and 77°00' to 77°20'-E longitude. The basin covers 24 rama panchayats in Thiruvananthapuram District. The river's ain tributaries are Chittar, Kallar, Karavaliar, Mullar, Aruvikod odu, Maruthur thodu, Edamalai thodu and Talakke thodu. This outhern most small river originates from Agasthya malai in the Western Ghat mountain ranges and flows through extremely ottled geologic and physiographic provinces of the area for a ength of about 56km.

As far as the landuse pattern and change of Neyyar river asin is concerned, the cultural, socio-economic and population ensity in the basin has a decisive influence in framing the nduse. The existence of aquatic ecosystem and prosperity in iodiversity is clearly under the impacts that have shaped by nduse (Turner *et al.*, 2001). It is therefore inevitable to describe ie landuse regularly, which helps in better conservation and anagement of natural resources. The foremost hinder for nplementing such strategies is the lack of regular monitoring in ie study area. In this context, the present study aims to vestigate the landuse pattern of Neyyar river basin in neticulous.

II. Methodology

The landuse pattern of Neyyar basin is prepared using urvey of India Topographic Sheets (Nos.58 H/2 and 58 H/3) of :50,000 scale surveyed during 1966-68 (Brigadier Paintal, 969), Google satellite images and with the help of extensive ield visits during the period May 2015 to April 2016 to nderstand the landuse pattern of the basin in general and that of ie six sites such as Neyyar Dam, Kallikadu, Mandapathinkadavu, Aruvipuram, Neyyattinkara and Poovar in particular. The sites are fixed representatively covering three physiographic components such as high land, mid land and low land. The current landuse pattern is input in the GIS software version Arc GIS 10.1 and a map is prepared. There are fourteen categories of landuse are designed in the map (Fig-1). The stream order map of Neyyar River basin was also prepared by using GIS (Fig-2). The latitude and longitude obtained by using Global Positioning System receiver was input in GIS for locating sites in the prepared map.

III. Results And Discussion

The landuse categories in Neyyar river basin mainly constitute forest area, mixed crop, settlement with mixed tree crops, built-up area and reclaimed area. The forest area includes dense forest, fairly dense forest, open forest, grassland, land with or without scrub and forest plantations such as eucalyptus, teak etc. The major landuse change observed in the forest area is deforestation and the cultivation of plantations. In Neyyar river basin the forest area is disperses in the highland physiographic region. The region well known for its biodiversity is under the verge of degradation. Forest fire and deforestation are the main threat for the biodiversity. Landslides and widening of river valleys due to physical weathering during the heavy rainy season are also common in the forest area.

Mixed crop category includes all type of agricultural crops and other tree crops. In the mixed tree crops category, the settlement or built up area will be minimal. Mixed crops are mainly concentrated at the midland physiographic area of the Neyyar basin which is dispersed mainly at the moderate relief area. In settlement with mixed tree crops category, settlements are found intercalated with the mixed crops including tree crops. In Neyyar basin majority of the area comes under this category.

Built-up are non-agricultural usage areas with buildings, transport network, communication utilities and other engineering structures. The mere ignorance of the people to consider the construction of huge buildings, transport network, communication utilities and other engineering structures, without considering sustainable ecosystem, as the symbol of development is the main ill-effect in the landuse change of our small and sensitive state. As the paddy fields and wetlands were low cost and easily available, people used to purchase and reclaim it for constructions thereby converting them into built-up areas. In Neyyar river basin majority of built-up areas are dispersed mainly at the lowland area.

The other landuse change is the extensive reclamation of paddy fields and wetlands for agricultural crops, plantation crops and other tree crops. These areas are called reclaimed area.

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ASSESSMENT OF WATER QUALITY OF NEYYAR RIVER, KERALA, INDIA

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Abstract: Neyyar is popularly known as the southernmost river of Kerala, which is under the verge of destruction due to indiscriminate pollution activities. In order to understand the river water quality, the physico-chemical characteristics are analyzed on monthly basis from May 2015 to April 2016. Six sampling sites namely Neyyar Dam, Kallikkadu, Mandapathinkadavu, Aruvippuram, Neyyattinkara and Poovar are fixed considering physiography as well as pollution. The parameters such as Water temperature, Total alkalinity, TDS, Salinity, Dissolved oxygen, Sodium, Nitrate and Phosphate are analyzed for this study. The river water seemed to be of poor quality in downstream stretches probably due to the high anthropogenic activities associated with the region together with the cumulative effect of all the contaminants emerging from highland portion onwards and salt water intrusion from the sea.

Keywords: Physico chemical parameters, Physiography, Saline intrusion, Correlation

INTRODUCTION

Rivers are very important in human progress by providing drinking water, making the earth fertile and serving as a medium for transportation. For centuries, humans have been enjoying the ecosystem services provided by rivers without understanding how the river ecosystem functions and maintains its vitality (Naiman, 1992). Man has changed the nature of rivers by controlling their floods, by constructing large impoundments, by overexploiting their living and non-living resources and by using rivers for disposal of wastes. Such taming of rivers and exploitation of riverine resources have often led to serious decline and causing serious implications on human health and the environment (Carpenter *et al.*, 1998). Global concern for the quality of river water in addition to quantity has been on the increase, in recent years. In India, the river water quality problems are intensified during the last few decades and now the situation has become alarming. Studies on the river ecosystems indicate that the major Indian rivers are grossly polluted, especially beside the cities (Srivastava, 1992). Rivers in Kerala face the problem of pollution caused by municipal wastes which include liquid, solid, industrial effluents and agricultural runoffs. Significance of water as a potent ecological factor can be appreciated only by studying its physico-chemical characteristics.

Neyyar River is one of the important small catchment rivers in the south-western coast of India, where the demand of water is increasing exponentially over the years in tune with increase in population and economic development. The River is extensively used for domestic, recreational, drinking and irrigation purposes in the area. But different municipal, chemical and domestic wastes are being disposed in to the river and people use this river for extensive sand mining without any concern for the life of the river. Therefore there is an urgent need for continuous monitoring of the river water quality so as to safeguard public health threats from using this water. Each water source should be monitored with utmost care and precision for laying down strategies for the effective conservation and management of the pristine water resources. In this perspective, the present study tries to focus on the water quality status along the course of Neyyar River from the upstream stretch to the downstream.

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PROBABILITIES OF SOIL ARTHROPOD ASSOCIATION IN RUBBER PLANTATIONS DURING DIFFERENT SEASONS

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ABSTRACT

The present study aimed to analyze the probabilities of association soil arthropods in rubber plantation habitat during monsoon, pre monsoon, summer and post monsoon seasons. Soil animal groups of various orders like Acari, Araneae, Pseddoscorpionidae, Chilopoda, Diplopoda, Pauropoda, Symphyla, Isopoda, Celeoptera, Collembola, Dermaptera, Dictyoptera, Diplura, Diptera, Hemiptera, Hymenoptera, Isoptera, Lepidoptera, Neuroptera, Notoptera, Orthoptera, Protura, Psocoptera and Thysanoptera were obtained. In pre monsoon season by chance association were more prevalent among soil arthropods groups than negative association. The soil Acari and Collembola showed positive association in all seasons. From the results found that the post monsoon season showed more association probability than that of monsoon, pre monsoon and summer seasons.

Key words: Rubber plantation habital, association probability, isopod, soil arthropods

INTRODUCTION

Soil is an extremely dynamic and complex system that permits the development of an extremely large number of ecological habitats and thus forms home for an array of live organisms (Gardi and Jeffery 2009). Soil is a complex system containing micro-macro fauna, influenced by biotic and abiotic factors (Lavelle and Spain, 2001). Soil arthropods help to maintain the soil food web and thereby balance of the soil ecosystem. Soil arthropods are suitable indication of soil quality. The decomposition process in soil is mostly controlled by the association of soil arthropods. They help in organic matter decomposition, nutrient cycle and enhancement of soil structure (Moore and Walter, 1988). Thus by all means, soil arthropods perform an important role in maintaining soil fertility. This is through the decomposition and humification of all organic matter. The present study was undertaken to assess the seasonal variation in soil micro arthropods associated with a rubber plantation.

MATERIALS AND METHODS

The present investigation was carried out in rubber plantation habitats, in Ranni, Taluk (9°22' 53.24" N, latitude and 76°47' 06.54"E longitude) of Pathanamthitta District, Kerala. Soil samples were collected from ten different rubber plantation habitat of Ranni Taluk, during 2015 June to 2016 May.

Collection of soil arthropods

Soil samples from 5x5cm² area and a depth of 5cm were randomly collected from rubber plantations. The collected soil samples were taken in polytene bags, tied using rubber bands, labeled and carried to the soil laboratory. The collected soil samples were placed in iron trays of 30x40cm² area and large micro arthropod groups were sorted from the extract using needles and fine camel hair brush. The collected soil arthropods were numbered and identified using the key of Sutton (1972). The experimental species *Philoscia javanensis* were isolated from monthly samples using Berlese Tulgreen funnel extraction method. The extracted soil arthropods were preserved in 85% alcohol.

Soil arthropod collection has been carried out and data incorporated into four seasons considering June, July and August as Monsoon season; September, October and November as Post monsoon season; December, January and February as Summer season and March, April and May as Pre monsoon season.

Seasonal Effects of Water Quality Changes in Neyyar River, Kerala, India

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Abstract- The seasonal fluctuations in various physico-chemical parameters in the water were investigated in the six sampling sites namely Neyyar Dam, Kallikkadu, Mandapathinkadavu, Aruvippuram, Neyyattinkara and Poovar of Neyyar River on the basis of their physiographic distribution during north east monsoon and pre-monsoon. Water temperature broadly fluctuated between 27.0°C at Neyyar dam in north east monsoon to 33.2°C at Neyyattinkara in pre-monsoon. Though, seasonal influence was marginal, a lowering in pH was generally visible during north east monsoon. In the station near coast, impact of saline intrusion was obvious in the distribution of EC. TDS varied broadly between 20.4mg/l to 16000mg/l, respectively in the reservoir and the Poovar. Correspondingly the chloride also has been gradually increasing towards downstream. In general turbidity is found to be low except occasional high values at Kallikadu. Our study indicates that alkalinity values are very less all along the river during both seasons and total hardness exceeds the prescribed limits in downstream stretches. The samples in the midland and lowland invariably showed considerable concentrations of the nutrient. Inverse to the distribution of DO, the BOD value was the minimum at reservoir and the maximum at Poovar. Significant correlations between the parameters were observed by using SPSS software.

Index Terms- Neyyar, North east monsoon, Physico-chemical parameters, Physiography, Pre-monsoon.

I. Introduction

Rivers play an important role in human progress by providing drinking water, making the earth fertile and serving as a medium for transport. The ecosystem services provided by rivers have been utilizing by humans without knowing the functions and vitality of river (Naiman, 1992). The nature of many of the rivers around the world are changed due to unscientific construction of bunds across the river, reclamation of water holding and purifying regions, overexploitation of their living and non-living resources and disposal of various waste materials directly in to the river. Indian river system is polluted mainly because of the human impact (Goel *et al*., 2001, Patil *et al*., 2003 and Maity *et al*., 2004) and major rivers are grossly polluted, especially beside the cities (Srivastava, 1992). The river water quality has been greatly influenced not only by such activities but natural and climatic determinants may also contribute. Pollution of river with the seasonal change in water quality is of great environmental concern worldwide.

The Neyyar River is one of the important small catchment rivers in the south-western coast of India, originates from Agasthya malai in the Western Ghat mountain ranges at an elevation of about 1866km above mean sea level. This small river flows through highly varied geologic and physiographic provinces of the area for a length of about 56km. Though, this river ecosystem face severe pollution threats because of the huge disposal of various waste materials, sand mining and agricultural practices at its bank, it is extensively used for domestic, recreational, drinking and irrigation purposes in the area. The water related issues are very critical in the small catchment rivers of developing economies with high incidence of human stress (Padmalal *et al*., 2011). The water quality of a riverine ecosystem can be assessed mostly by studying its physico-chemical characteristics. The seasonal change in surface water quality is an important aspect for evaluating temporal variations of river pollution (Ouyang *et al*., 2006). Under this context, the present study tries to focus on the water quality changes along the course of Neyyar River from the upstream stretch to the downstream during pre-monsoon and north east monsoon.

II. Materials and Methods

Neyyar is the southern-most river of Kerala State having a total basin area of 483sq. km, lies between 8°15′ to 8°40′-N latitudes and 77°00′ to 77°20′-E longitudes (Fig. 1). The river's main tributaries are Chittar, Aruvikod thodu and Maruthur thodu. Six sites located along the upstream to downstream course of the river were sampled. The sampling sites such as Neyyar Dam (S1), Kallikadu (S2), Mandapathinkadavu (S3), Aruvippuram (S4), Neyyattinkara (S5) and Poovar (S6) are fixed along the river considering the physiography (Table 1). The sampling locations at Neyyar dam and Kallikkadu are situated at the highland physiographic area, whereas Mandapathinkadavu station is located at the transition area of highland and midland, Aruvippuram at the midland and Neyyattinkara and Poovar at the lowland.

Water samples were collected from six sampling stations of the river monthly for two seasons namely Northeast monsoon (October to November-2015) and Pre-monsoon (March to April-2016). Water sample is analyzed for physico-chemical parameters such as Water temperature (WT), PH, Electrical Conductivity (EC), TDS, Turbidity (Turb.), Chloride (Cl), Total Alkalinity (T.Alk), Total Hardness (T.H), Nitrate (NO_3-N), Phosphate (PO_4), Sulphate (SO_4), DO and BOD. In-situ determination is done for parameters such as Water temperature, pH and alkalinity and samples of DO and BOD is chemically fixed in the field itself. All the analyses are carried out following standard methods (APHA, 2005). Seasonal average and standard deviation of data on water quality were calculated using

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WATER QUALITY ASSESSMENT OF ASHTAMUDI LAKE WITH SPECIAL REFERENCE TO ENVIRONMENTAL POLLUTION

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ABSTRACT

The present study deals with the water quality of Ashtamudi Lake, which lies in the Kollam district of Kerala, with regard to various physico chemical parameters like water temperature, pH, turbidity, conductivity, total dissolved solids (TDS), total hardness, dissolved oxygen (DO), biological oxygen demand (BOD), nitrate, sulphate and phosphate. The physico chemical characteristic of Ashtamudi Lake was found to be highly fluctuated between the six sampling stations selected during the present investigation. High value of dissolved oxygen obtained in station 2 (Sambranikodi) showed inverse relation with BOD, nitrate and phosphate. The correlation coefficient showed both positive and negative relationships among parameters. The study revealed that the water quality is rich in TDS content, indicating the estuarine property of Ashtamudi Lake. Though, the quality of water is deprived in majority of the sampling stations, comparatively less conductivity, TDS, and hardness were obtained in station 1 (Near-Ashramam). The BOD value was very high in station 3 (Kandachira Kayal), which indicates the severity of pollution in the lake.

Key words: Ashtamudi Lake, Physico chemical parameters, Pollution, Correlation

INTRODUCTION

Backwaters are places where rivers meet the sea or freshwater mixes with sea water and tides influxes occur. However, the water in an estuary is not uniformly brackish. The upper stretches of backwaters are mostly fresh. The backwaters play an important role in the functioning of marine ecosystem. It acts as an interface between land and sea, thus control the movement of terrestrial materials, nutrients and pollutants into the marine environment. Backwaters experience varying degrees of pollution. The pollution of estuarine ecosystem through the human activities has been increasing over the past years. The physico chemical characteristics of the aquatic system indicate the extent of pollution existing there. Water quality is affected mainly by changes in various physico chemical factors (Carr and Neary, 2008). So it is inevitable to check regularly the quality of water, and thereby adopting necessary steps for the protection of the ecosystem by eliminating the factors responsible for pollution.

The present study was undertaken in Ashtamudi Lake (Ashtamudi Kayal), which lies in Kollam District of Kerala state. This is the second largest and the most visited backwater and lake in the state. The lake is also called the gateway to the backwaters of Kerala and is well known for its houseboat and backwater resorts. Ashtamudi Wetland was included in the list of wetlands of international importance in the year 2001, as defined by the Ramsar Convention for the conservation and sustainable utilization of wetlands. Ashtamudi backwater has odd value for its hydrological functions and biodiversity. There are reports on the health of this estuary, which are dependent on the nature and quantity of various contaminants and toxic pollutants received by them. The main contaminants are sewage, synthetic organics, petroleum hydrocarbons, pesticides and toxic heavy metals. This is happening mainly due to rapid industrialization and modernization. The recreational role of the estuarine ecosystem is declining at a faster rate due to pollution. Hence the present work has been taken up to study the water quality characteristics at selected sites of Ashtamudi Lake, which would help to evolve mitigation and control measures.

MATERIALS AND METHODS

Ashtamudi wetland, situated in the Kollam district, Kerala (Lattitude 8°592 N and Longitude 76°362 E), is the second largest wetland in Kerala with a palm shaped outline with eight prominent arms. Kallada River is a major river discharging into the Ashtamudi Lake. The Kallada river, which originates near Ponmudi from the Kulathupuzha hills (Western Ghats) is formed by the confluence of three rivers namely Kulathupuzha, Chenthurnipuzha, and

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Sex Ratio of *Cryptopygus thermophilus* in Rubber Plantations of Chengannur Thaluk of Alappuzha District, Kerala, India

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Abstract: ***Sex ratio of Cryptopygus thermophilus in Rubber plantation of Chengannur Thaluk, Alappuzha district, Kerala state, India, from June 2014 to August 2015 was studied.100 samples were randomly collected every month. Hand sorting and light funnel extraction was adopted to extract Cryptopygus thermophilus. Ovipositer of females and a small protuberance in the third ventral abdominal segment in male were taken in to consideration for sex identification. The study showed that the male female ratio is almost 1:1.5 in all these months. The Length range sex ratio observed showed that 0-1 cm range, males outnumbered females, but 2-3 cm range, females outnumbered males and above 5 cm length range, males were totally absent. In all these cases critical chi-square value was larger than the computed chi-square value with P > 0.01 indicating a deviation of the sex ratio from normal 1:1.Male survivor ship is high in lower length range and female survivor ship is more in upper length range in the studied habitat.***

Keywords: Microarthropods, Collembola, Sex Ratio, Ovipositer

1. Introduction

The soil micro arthropod community is a major component of the soil ecosystem. It depends on decomposing plant and animal material for its basic energy input. Different ways are adopted by the micro arthropods to break down the organic materials. First of all they transform the plant and animal tissues to humic substances by decomposing them. Then through bacterial and fungal activities these humic substances are converted in to organic matter. The activity of soil micro arthropods and micro flora are complementary and intricately interrelated and where soil micro arthropods are very numerous, micro-organisms, especially bacteria, are also abundant. Springtails (Collembola) are among the most abundant soil invertebrates, and among arthropods they are one of the earliest colonizers of terrestrial systems. They play an important role in plant litter decomposition, nutrient cycling, in forming soil micro structures and in modifying plant growth, and thus received considerable attention (Parkinson1988) .In contrast, from an evolutionary biology point of view Collembola received little attention, ie little is known about the sex ratio and parthenogenesis. Based on field studies it is now known that beside bisexual reproduction, parthenogenesis is common in Collembola.

The present work was undertaken to study the sex ratio of *Cryptopygus thermophilus* in Rubber plantations of Chengannur Thaluk of Alappuzha district, Kerala .

2. Materials and Methods

Sex ratio studies were conducted from 2014 June to 2015 August (15 months). Random sampling was adopted for the study of sex ratio.100 samples from Rubber plantations were collected monthly. Each sample is from 5x5x5cm area. Hand sorting followed by light funnel extraction was adopted to extract *cryptopygus thermophilus* from the sample. The extracted animals were transferred to culture bottles for sex identifications. Ovipositor of females was taken in to consideration for identifications. A small protuberance in the third ventral abdominal segment is the distinguishing mark for male. It is light yellow in colour. The presence of ovipositor and protuberance can be easily identified with naked eye in mature animals and with the aid of the dissection microscope in juveniles and sub adults.

3. Results

In Plantation in 2014 June the males were 27.78% and female 72.22%. 26.37% male and 73.63% in July .In August male 27.66% and female 72.34 .In September 27.84% male and 72.16% females.28.57% males and 71.43% females in October.28.97% males and71.03 % % females in November. In December 28.57% males and 71.43% females, in January 30.69% males and 69.31 % females, In February 28.3% males and 71.7% females. In march 29.9%males and 70.1 % females. in April 30.61% males and 69.39% females, in May 31.68% males and 68.325 females, in June 30.61% males and 69.39% females. July 30.21% males and females 69.79% and in August 31.58% males and 68.42 % females were observed. The male female ratio is almost 1: 1.5 in all these months.

Table 1: Sex Ratio of *Cryptopygus thermophilus* in Rubber Plantations

Year	Month	Total no of Animals	No. of Males	% of Males	No of Females	% of females
2014	June	900	250	27.78	650	72.22
	July	910	240	26.37	670	73.63
	August	940	260	27.66	680	72.34
	September	970	270	27.84	700	72.16
	October	1050	300	28.57	750	71.43
	November	1070	310	28.97	760	71.03
	December	980	280	28.57	700	71.43
2015	January	1010	310	30.69	700	69.31
	February	1060	300	28.3	760	71.7

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Study on the variations of Soil Edaphic and Chemical Factors of different forest types of Achencovil Range during Post Monsoon Season

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Abstract- Comparison between the three forest types namely moist deciduous, semi evergreen and evergreen of Achencovil forest in the post monsoon season on the basis of soil edaphic factors like gravel, p^H, Organic carbon content (OC), Exchangeable Acid (EA), Exchangeable Base (EB), sand, silt, clay and soil chemical factors like Nitrogen, Phosphorous, Potassium, Calcium and Magnesium contents. 20 sites from moist deciduous, semi evergreen and Evergreen were randomly selected. Soil samples of 5×5 cm^2 area from a depth of 5 cm were collected from these three habitats. Mean with standard deviation were taken. Habitat wise variation was analyzed by using two way ANOVA. The study shows that the evergreen soil has high nitrogen content (3779.8 ppm). Phosphorous content (5.98 ppm), potassium content (242.45 ppm) and calcium content high in moist deciduous and magnesium (74.75ppm) content high in semi evergreen. The Evergreen soil has high organic carbon content (4.72 %).

Index Terms- Achencovil Forest, Moist deciduous, Semi evergreen, Evergreen, Soil edaphic factors, Post Monsoon

I. INTRODUCTION

Soil is a major component of earth's ecosystem. Soil must be considered as a complex of living and nonliving components which are present in different combinations, with identifiable gross characteristics. As cited by Kuhnelt (1961), 'the soil is the uppermost weathering layer of the solid earth Crust; it consists of broken up and chemically changed parent rock and the remains of the plants and animals. A thin layer of soil covers most of the earth's land surface. This layer is varying from a few centimeters to 2 or 3 meters in thickness. It is in this layer of soil that the plant and animal kingdom meet the mineral world and establishes a dynamic relationship. Early chemist considers soil as a store house of plant nutrients. One gram of soil supports a population of millions or even billions of bacteria and other microorganism. In addition to living components soil also contains nonliving components like rocks, minerals, soil water, soil air etc. Soil is made up of substances existing in solid liquid and gaseous states with colloidal particles of organic and inorganic origin.

Soil contains sand, clay and silt in definite proportions. Besides soil particles, the soil contains mineral nutrients which are important for plant metabolism and growth. These elements are essential for maintaining the osmotic balance and absorbing ions from soil solution. It include macro elements or macronutrients like Carbon, Hydrogen, Oxygen, Calcium, Nitrogen, Phosphorus, Sulphur and Magnesium and microelements or micronutrients like Potassium, Iron, Manganese, Zinc, Boron and molybdenum. The soil also contains organic matter and humus. These organic substances increase soil fertility and acts as a food substrate for microorganism and soil animals. Humus is the dark amorphous portion of the organic matter which has lost its structure through decomposition. The amount of organic carbon in the soil depends on various factors like soil texture, climate, vegetation and land use.

The present study was undertaken for the comparison of soil edaphic and soil chemical factors between the three habitats of the Achencovil forest namely moist deciduous, semi evergreen and evergreen as a part of Western Ghats.

II. METHODOLOGY

The study was conducted in Achencovil forest area of Kollam district lies between latitude 9^0 00 N and 9^0 08 N and longitude 77^0 00 E and 77^0 015 E. This forest area comprises different types of forest ecosystems, including tropical evergreen, semi evergreen and deciduous forests. Hence the study sites were selected evenly based on a primary observation on the forest and soil types in which they belong.

A. *Collection and transportation of sample*

Three forest types, moist deciduous, semi evergreen and evergreen of Achencovil forest range were selected. From each type, 20 sampling sites were identified. Soil samples of 5x5 cm^2 areas from a depth of 5 cm were randomly collected using soil auger during the monsoon period of 2014 (September, October and November). Collected samples were taken to the laboratory in polythene covers.

B. *Soil edaphic factor analysis*

From the sample collected, the soil edaphic factors like gravel content, P^H, organic carbon, Exchangeable acids, Exchangeable base and soil morphology (sand, silt and clay content) were detected using standard procedure. The soil gravel content was measured using standard procedures. The soil P^H was measured using P^H meter. Exchangeable acid and exchangeable bases were measured using the procedure of Trivedy and Goel (1987). Soil organic carbon content was measured by using the procedure of Walkley and Black (1934).

RESEARCH ARTICLE

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STUDY ON HYDROCHEMICAL PARAMETERS OF DIFFERENT AQUATIC ECOSYSTEMS IN AN INDUSTRIAL AREA IN SOUTHERN INDIA

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Abstract: *Studying the physico chemical parameters of a particular water body is an important aspect for understanding the health of that ecosystem. Ponds, streams and backwater are the different aquatic ecosystems included in this study. Different water bodies may present in a particular area but very few information are available based on the water quality of these ecosystems together. Information about various physicochemical parameters of these different water bodies are imperative requirement for many planned conservation strategies. In practice inter-water body comparisons are few in number. The current study focused on streams, ponds and backwater ecosystems within the Chavara industrial area in Kollam in S. India. The physico-chemical parameters include pH, Conductivity, Total Dissolved Solids, Chlorides, Sulphates, Total Hardness, Total Alkalinity, Nitrates, Dissolved Oxygen and COD. The results showed that majority of the values are incompatible with the maximum allowable standards recommended by BIS and WHO guide lines. Results shows that water from these sources are unsuitable for safe drinking and domestic purposes. If the recommendation norms for proper industrial waste disposal are not adhered, then the chance of pollution loading will be increased result in more deterioration of all these water sources.*

Keywords: *Water quality, Physico-chemical parameters, ecosystem*

INTRODUCTION

The earth's water resources are now facing serious pollution problems and have to be managed for human existence. Exact trustworthy information based on water resources is very important for the proper management practices. (Gupta and Deshpande, 2004). According to Linton and Goulder, 2000 conservation strategies adopted for pond ecosystem are very less when compared to other fresh water systems. In most of the national monitoring and protection strategise small water bodies are largely ignored. Streams usually are shallow but are unique ecosystem in basis of biodiversity and water quality parameters. The other important dynamic and complex ecological systems are estuaries. The physico-chemical factors of this aquatic

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Assessment of Heavy Metals in Ashtamudi Lake, Kollam, Kerala

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ABSTRACT

In the present study an attempt has been made on heavy metal analysis on different stations of Ashtamudi Lake namely Near-Ashramam, Sambranikodi, Kandachira Kayal, Thekkumbagam, Pattamthuruthu and Palliyamthuruttu-Vellimon. The metals analyzed include Zinc, Lead, Iron, Cadmium and Chromium. Among the metals analyzed Iron and Chromium showed higher concentrations above the maximum permissible limit. Among the five selected stations, the heavy metal concentration was extremely high in Near-Ashramam, Sambranikodi and Pattamthuruthu. The study revealed that the poor quality of water due to heavy metal contamination in majority of the sampling stations might be due to the discharge of various pollutants associated with the region.

Key words *Ashtamudi Lake, Heavy metals, Pollution*

Heavy metals are environmentally stable and non-biodegradable. Pollution due to heavy metals is dangerous as they tend to accumulate and therefore toxic to the plant, human and animal health. Water quality is affected largely by heavy metal contamination (Carr and Neary, 2008). The major source of metal contamination is industrial effluents. They results in the total destruction of aquatic ecosystems such as rivers, lakes and estuaries. The estuaries are ecologically very important. They are called as Nature's Kidney because they help to clean the polluted water. The pollution of estuarine ecosystem through the human activities has been increasing over the past years. The rate of concentration of these heavy metals will provide a clear picture of the depth of pollution in the estuarine ecosystem. Ashtamudi Lake, which lies in the Kollam district of Kerala, is the second largest and the most visited backwater and lake in the state. Ashtamudi backwater has odd value for its hydrological functions and biodiversity. The health of the estuary is dependent on the nature and quantity of various contaminants and toxic pollutants it receives. The main contaminants are sewage, synthetic organics, petroleum hydrocarbons, pesticides, toxic heavy metals etc. This is happening mainly due to rapid industrialization and modernization. The recreational role of the estuarine ecosystem is declining at a faster rate due to pollution. The present study was mainly designed to understand the pollution status of Ashtamudi Lake by assessing the accumulation of hazardous heavy metals in water. Thereby we can take necessary steps in protecting this ecosystem by eliminating the factors responsible for pollution.

MATERIALS AND METHODS

The present study dealing with heavy metal pollution of the aquatic ecosystem was conducted in Ashtamudi Lake, the Ramsar site (Latitude-8°592 N Longitude-76°362 E). Kallada River is a major river discharging into the Ashtamudi Lake. The Kallada river, which originates near Ponmudi from the Kulathupuzha hills (Western Ghats) is formed by the confluence of three rivers, *viz.*, Kulathupuzha, Cheathurnipuzha, and Kalthuruthipuzha, and after traversing a distance of about 121 km through virgin forests finally debouches into the Ashtamudi wetland at Neendakara (a fishing harbour) near Kollam as it enters the Lakshadweep Sea, part of the Arabian Sea. For the present study, six sites were selected, *viz.*, Near-Ashramam (S1), Sambranikodi (S2), KandachiraKayal (S3), Thekkumbagam (S4), Pattamthuruthu (S5) and Palliyamthuruttu-Vellimon (S6). The study was conducted during the summer month of Kerala viz., March-2017. During the study period the water in the lake was comparatively less and pollution was intense. Surface water samples for heavy metal analysis were collected in uncontaminated polyethylene bottles and samples were acidified with 10% HNO_3, placed in an ice bath and brought to the laboratory. The samples were filtered through a 0.45im micropore membrane filter and kept at minus 20°C until analysis. Content of heavy metal is estimated using Atomic Absorption Spectrophotometer (AAS) as per the procedure prescribe by APHA (1998).

RESULTS AND DISCUSSION

The results of heavy metal analyses of Ashtamudi backwaters are given in Table 1. The variations in heavy metal concentration at different stations of the study area are illustrated in Figure 1.The study conducted at six stations in the study area for various heavy metals revealed significant variations between stations.

Heavy metal Zinc is an essential micronutrient required in traces for plants and animals. The major sources of zinc are industrial process, domestic wastewater and atmospheric fall outs. Results of the present investigation showed that the concentration of zinc in all stations is within the desirable limit (5mg/L) recommended by USEPA (2010). High concentration of zinc content is toxic to aquatic life (Chiani and Yallapragda, 2000). In the present study, the relatively high concentration of zinc in station S1, S5 and S6 may be attributed to industrial effluents. The highest content of zinc was noticed in S1 (0.044mg/L) and lowest in S4 (0.001mg/L) (Fig. 1). The stations S2, S3, S5 & S6 showed Zn values 0.002mg/L, 0.009mg/L, 0.011mg/L & 0.016mg/L respectively (Table 2). At high concentration it is toxic to fish and other aquatic life (Alabaster and Lloyds, 1982). The prolonged consumption of large doses can result in health complications such as fatigue, dizziness and Neuropenia (Hess and Schmid, 2002).

Lead enters into the environment through a large number of natural and anthropogenic activities. The natural sources include forest fire and volcanic emission. On the other hand the anthropogenic sources are mining, wood

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DIVERSITY AND ABUNDANCE OF PHYTOPLANKTON WITH RESPECT TO PHYSICO-CHEMICAL PARAMETERS IN ASHTAMUDI WETLAND, KERALA, INDIA

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BSTRACT

Water quality index (WQI) is one of the reliable tools to examine overall water quality status. It also helps Diversity and abundance of phytoplankton were estimated in the Ashtamudi Lake situated in the Kollam district of Kerala state. 52 species of phytoplankton were recorded from six sampling stations of the lake. The species with highest number of population was *Blue green algae. Oscillatoria and Chatoceras* were the most common species. Phytoplankton are influenced by physico-chemical parameters such as water temperature, pH, turbidity, DO, BOD, nitrate, sulphate and phosphate. The minimum phytoplankton abundance was observed at station S_3 (Kandachira Kayal) having maximum BOD whereas their abundance maximum was at S_1 (Near Ashramam) because of higher concentrations of nutrients such as nitrate and phosphate. Phytoplankton species diversity reaches its maximum at station S_8 (Palliyamthuruttu-Vellimon side), where turbidity was minimum.

Key Words: Ashtamudi Lake, phytoplankton, diversity, abundance, physico-chemical parameters

NTRODUCTION

stuaries form a transition zone between river and maritime nvironments. They are subjected to both marine influences ich as tides, waves, and the influx of saline water and to verine influences such as flows of freshwater and sediment. he mixing of sea and freshwater provide high levels of utrients both in the water column and sediment making stuaries among the most productive natural habitats in the orld (McLusky and Elliott 2004). The productive behaviour f estuaries is because of abundant availability of autotrophs, ie phytoplankton, benthic algae and green rooted plants hich ensure maximum utilization of sunlight for notosynthesis. The estuaries present unique environmental haracteristics that result in high biological productivity ecause of abundance of plankton which are part of the quatic food chain.

hytoplankton are the key primary producers in the estuaries. hese are at the base of the food chain in the aquatic nvironments and are most important among the primary roducers (Chin et al. 1994). They move with the water odies and can be flushed in and out with the tides. Plankton, articularly phytoplankton, has long been used as indicators of water quality. Because of their short life span, plankto responds quickly to environmental changes. Plankton play very important role in organic production in the estuary; the occurrence and abundance indicate water quality, level c pollution and have great significance in the exploration c fisheries. Present study was made to study phytoplankto abundancity with reference to water quality in Ashtamuc wetland which is now under threat of degradation and los of biodiversity due to solid waste dumping, use of mechanize boats, tourism and other anthropogenic activities which ma adversely impact primary producers in the ecosystem an thereby disrupt the entire food chain. This study will help t understand the effect of water quality on the occurrence c phytoplankton.

Study Area

Ashtamudi wetland, situated in the Kollam district, Keral (Lattitude-8°592 N Longitude-76°362 E), is the secon largest wetland in Kerala with a palm shaped extensive wat body and eight prominent arms. For the present study, si sites selected were; Near-Ashramam (S_1), Sambranikod (S_2), Kandachira Kayal (S_3), Thekkumbhagom (S_4 Pattamthuruthu (S_7) and Palliyamthuruttu-Vellimon (S_8).

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Hydro-geochemical properties with respect to landuse in the southernmost river of Kerala

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Abstract

The hydro geochemical features of Neyyar River for a period of one year from May 2015 to April 2016 were analyzed. Six sampling sites were fixed considering physiography and present landuse pattern of the river basin. The residents in the drainage basin are primarily responsible for framing a better landuse and thereby maintain a good water and sediment regime. Geospatial pattern of the present landuse of the study area indicated that the sustainability of this river ecosystem is in danger due to unscientific landuse practices, which is reflected in the river quality as well. The parameters such as hydrogen ion concentration, electrical conductivity, chloride, Biological Oxygen Demand, total hardness and sulphate of river water and Organic Carbon of river bed sediments were analyzed in this study. The overall analysis shows that the highland areas are characterized by better quality of water together with low organic carbon, which is mainly due to better landuse and minimal reclamation. The midland and lowland areas are characterized by poor quality of water with high organic carbon, which is due to high anthropogenic activities and maximum pollutants associated with the region together with the alteration in landuse from a traditional eco-friendly pattern to a severely polluted current pattern.

Keywords: Neyyar, Chemical parameters, Landuse, Correlation

1. Introduction

Rivers are the lifelines of nature and have a great deal of environmental value. Rivers have very low percentage of water present in the earth but have an inevitable role in the mere existence of human by providing fresh water. But the rivers have been subjected to severe degradation due to several pollution activities. They can create severe negative effects on the structure and balance of these ecosystems. River bed sediments are the potential sources of natural geochemical constituents derived principally from rock weathering. The organic carbon plays a crucial role in assessing riverine environment because of its strong interaction with all processes operating there. Accumulation of pollutants in the sediment affects the quality of water due to sediment-water interaction (Birdwell *et al.*, 2007; Cheng *et al.*, 1995). The ecological decline of Indian rivers is mainly due to contaminated sediments (Virendra *et al.*, 2003). The landuse practices prevalent in a particular region are the prime reason for quality fallout in river. The landuse practices such as paddy reclamation, sand and clay mining, quarrying, deforestation, industrialization and unscientific construction

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ASSESSMENT OF HEAVY METAL CONCENTRATION IN ANABAS TESTUDINEUS FROM DIFFERENT FRESH WATER ENVIRONMENTS OF KERAL, SOUTH WEST COAST OF INDIA

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ABSTRACT

The study was conducted to assess the heavy metal concentration in the tissues of *Anabas testudineus* collected from heterogeneous urban ponds of Chavara, Kerala, south-west coast of India. The metal concentration in fish tissue was determined using AAS. Results revealed that in station one (S1) except Mn, the accumulation pattern of heavy metals (Zn, Cu, Fe) were in the pattern liver > gill > muscle. But Mn followed the pattern gill>liver> muscle. In the case of station two (S2), except Zn, all other metals followed same pattern of accumulation as liver > gill > muscle. Highest concentration of Zn was observed in gill followed by liver and muscle. In station three (S3), all the four metals followed the same accumulation pattern (liver > gill > muscle). The present study proved that liver and gill tissues act as major accumulator of heavy metals than muscle tissue. The concentration of Zn, Mn and Fe were above the limits advised by FAO/WHO, IAEA.

Keywords: *Anabas testudineus*, heavy metal, accumulation pattern.

INTRODUCTION

The most important risk of aquatic food chain is metal contamination. Bioaccumulation of heavy metals will evoke serious issues such as biomagnification in the aquatic ecosystems. The particularities of heavy metals such as its toxic nature, long half-life and consistent steadiness in the biological communities make them a threat to the aquatic forms (Domingo et al., 2007; Siddiqui, et al., 2008; Asuquo et al., 2004).

The metal contamination in an aquatic system can be monitored in a way by analyzing the fish tissue associated with the environment (Ambedkar and Muniyan, 2011). Heavy metals can enter the body of the fish, either through diet or gills. The metals then may get accumulated or eliminated from the body (Jayaprakash et al., 2015). According to Maceda-veiga et al., (2012), heavy metals when bio accumulated in muscle tissue will persist for long periods. Thorough and careful observation of aquatic food sources is compulsory for distinguishing the metal components in them (Bervoets *et al.*, 2001).

MATERIAL AND METHODS

Study area and sampling procedure

In the present study, *Anabas testudineus*, a carnivorous fish (McCarthy *et al.*, 1990) of family Anabantidae was collected from freshwater ponds from Chavara taluk, adjacent to the factory of Kerala Minerals and Metals Ltd. Three sampling stations (S1 to S3) were preferred for the study. Specimen samples were obtained from local anglers, from these aquatic systems. Ten specimens of uniform size and weight were selected from each pond during December 2014. After collection, fish samples were kept in ice box and transported to lab and preserved in -10^{0}C further analysis.

Analysis of metal contaminants

Metal accumulation in liver, gills and muscles of the fish *Anabas testudineus* were analyzed using Atomic Absorption Spectrophotometry (AAS). Dried and powdered fish tissue was subjected to acid digestion using nitric acid and perchloric acid (2:1). This was then placed in a hotplate at 50°C, until a clear solution is obtained (APHA, 2012) and analyzed in AAS for

A study on the species association of Cryptopygus thermophilus in [illegible] of Pathanamthitta district, Kerala, India

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Abstract: The soil micro arthropod community is one of the major components of the soil ecosystem. Soil Collembola showed diverse distribution pattern and species assemblage which has been associated with a number of environmental variables. In the present study it was observed that assemblages of Collembola associated species and their seasonal fluctuations in a grass land ecosystem located in Pathanamthitta district, Kerala, India. Collembola and micro arthropods were sampled every month from June 2014 to May 2015. In Grass land ecosystem *Cryptopygus thermophilus* showed positive association with most of the micro arthropods present in these groups during different seasons except post monsoon.

Key words: *Cryptopygus thermophilus*, Grass land ecosystem, Micro arthropods, seasons, Species assemblages.

INTRODUCTION

The soil micro arthropod community is one of the major components of the soil system. Soil microarthropods act as litter transformers and improve the soil quality of the soil (Bird *et al.*, 2004; Culliney, 2013). These microarthropods are taxonomically and ecologically highly diversified group and are unable to survive the variations of the soil caused by agricultural cultivation and trampling (Parisi *et al.*, 2005). Micro arthropods directly involved in humus formation and monitor the soil permitting necessary complexes of soil organisms to exist. Even though their role in comminution and mixing may be small compared with that of large invertebrates, microarthropods exercise an important function in mineral turnover, vegetation succession and decomposition of organic matter.

Collembola is one of the most abundant and widely distributed taxa among terrestrial Hexapoda (Hopkin, 1997). The greatest diversity and abundance of this species were especially found in soil occurs with much organic matter and adjoining habitats (Zeppelini et *al.*, 2008). The potential significance of Collembola is used as biological indicators to assess soil health and ecosystem quality. So the diversity study of Collembola becomes useful in environmental monitoring and development of conservation strategies (Stork and Eggleton 1992; Zeppelini *et al* 2008). Collembolans are numerically abundant group among the soil arthropods rivaling only with mites in this aspect. Several previous studies reported that Collembolans showed clumped or aggregated distribution (Poole, 1961 and Hale, 1966). The present study was mainly focused to assess the species association of *Cryptopygus thermophilus* present in a grass land ecosystem with respect to different seasons.

MATERIALS AND METHODS

For the assessment of species associations 20 samples were collected from grassland habitats during the period from June 2014 to May 2015. Presence or absence data for a pair of groups were considered to assess the association probabilities between different groups. Association coefficients (C) were calculated by the method described by Robert (1974).

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A COMPARATIVE STUDY ON THE ANTIMICROBIAL POTENTIAL OF SELECTED MEDICINAL PLANTS AGAINST THREE PATHOGENIC BACTERIA

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ABSTRACT

Ethanolic extract of ten Indian medicinal plants, *Ayapana triplinervis, Biophytum sensitivum, Boerhaavia diffusa, Catharanthus roseus, Centella asiatica, Chromolaena odorata, Glycosmis pentaphylla, Murraya koenigii, Psidium guajava* and *Punica granatum* and four commonly available antibiotics, ampicillin, amoxy clav, norfloxacin and amikacin were screened for potential antibacterial activity against *Escherichia coli, Klebsiella pneumoniae* and *Pseudomonas aeruginosa*. The antibacterial susceptibility test was done by adopting disc diffusion method. All the ten plants showed inhibitory effect on selected microbes. *Biophytum sensitivum* exhibited strong antibacterial effect on *K .pneumoniae* with mean inhibition zone of 26.7mm and on E.coli with 29.1mm. *Ayapana triplinervis, Catharanthus roseus* and *Chromolaena odorata* also showed good inhibitory effect on *Klebsiella pneumoniae* and *Centella asiatica* and *Punica granatum* showed fair effect on *Escherichia coli*. They can be further considered for usage among alternative therapeutic medicines for antibiotics.

Key words: Medicinal plants, Antibacterial activity, *Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa.*

INTRODUCTION

Microorganisms are found everywhere in our environment as well as on different parts of eukaryotic body system. They are essential for our survival as we share symbiotic relation with them, but at the same time pathogenic microbes are to be focused in research to avoid severe attacks. Both gram negative and gram positive bacteria occur among pathogenic category, but gram negative bacteria are more resistant to antibiotics because of their complex lipopolysaccharide cell wall. The gram positive bacterial genera that cause disease in humans are *Streptococcus, Staphylococcus, Corynebacterium, Listeria, Bacillus* and *Clostridium*. *Pseudomonas aeruginosa, Klebsiella pneumoniae, Neisseria gonorrhoeae, Chlamydia trachomatis* and *Yersinia pestis* are gram negative bacteria that cause disease in humans like nosocomial blood stream infections, respiratory or urinary tract infections, meningitis, etc.

Plants are prospective source of antimicrobial agents in different countries (Alviano and Alviano, 2009). By tradition different types medicinal plants are used for various treatments in humans. So researchers are focusing on natural products to develop better medications against multidrug resistant microbial strains. The antioxidant and antimicrobial properties of most medicinal plants is believed to be due to tannin, saponins, phenolic compounds, essential oils and flavonoids. The effectiveness of plant extract against a particular pathogen is affected by various intrinsic and extrinsic factors. Traditional plants are new sources of antimicrobials with stable, biologically active components that can establish a scientific base for the use of modern medicine (Zwetlana *et al.*, 2014). The present study showed the antimicrobial activity of ten medicinal plant extracts against *Escherichia coli, Klebsiella pneumoniae* and *Pseudomonas aeruginosa*.

METHODOLOGY

Collection and extraction of plant materials:

Ten medicinal plants were selected for the antibacterial susceptibility test (Table 1). Plant materials were collected from different locations of Alappuzha, Pathanamthitta, and Kollam districts of Kerala, India. The cleaned leaves were shade dried and powdered using electric blender. The powder was kept in air tight bottles till extraction. Extraction was done in soxhlet apparatus using air-dried powder of plant leaves with ethanol in the ratio 1:10. Three different concentrations of 10mg/ml, 15mg/ml and 20mg/ml of extract in DMSO were prepared for each selected plant.

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A Study on the Effect of two Agrochemicals on the Fecundity of a Soil Collembolan Cryptopygus Thermophilus

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Abstract

Agrochemicals play a significant role in increasing the productivity of crops but it has very serious effect on the fauna and flora of the soil ecosystem. Soil micro arthropods especially Collembolans help in increasing the soil fertility by decomposing the litter. Collembola is a group that function as a bio- indicator of the soil condition. The normal fecundity of Cryptopygus thermophilus and the effect of a herbicide Glyphosate and the fungicide Indofil on the fecundity was studied. The studies revealed that both the agrochemicals has a profound effect in reducing the fecundity of Cryptopygus thermophilus, but the effect of Glyphosate is high when compared to Indofil.

Key words: Collembola, Fecundity, Agrochemicals, Glyphosate, Indofil

1. Introduction

The ever growing global population leading to the enormous demand in food supply is one of the biggest challenges in agriculture. Agrochemicals have been an indispensable evil of modern industrial agriculture. Pesticides are those substances which are used to destroy, control, repel or attract pest in order to minimize their detrimental effect. The United Nations Environmental Programme (UNEP, 1979) has ranked pesticide resistance as one of the top four environmental problems of the world. In modern agriculture practice the demand for pesticides is frequently increasing and this may lead to the use of new compounds in agriculture. In order to increase crop production varieties of herbicides, insecticides, fungicides, nematicides and other chemical fertilizers are used in high quantities. Even as pesticides have become an important tool for global food security, their undesirable effect is alarmingly increasing in agricultural sector.

Some of these agrochemicals are persistent, toxic, bio accumulating and biomagnifying in animal tissue as well as humans. Most of the agrochemicals used in the agriculture are non-specific and kill the useful organism too. This may affect the trophic structure of the ecosystem. The indiscriminate use of these chemicals may lead to environmental problems and ecological imbalance and consequently affect the flora and fauna and sometimes it may extend up to human beings. The extensive use of agrochemicals in the environment may pose toxic to Human beings. Human beings are exposed to these harmful chemicals through different pathway such as inhalation, ingestion, and dermal contact.

Agrochemicals can contaminate soil, water, turf, and other vegetation. Insecticides are used to kill insects or weeds while they may be toxic to other host organisms including birds, fish, beneficial insects, and non-target plants. Insecticides are generally the most acutely toxic class of pesticides, but herbicides can also cause risks to non-target organisms. Pesticides are hydrophobic, persistent, bio accumulate and are strongly bound to soil. Agrochemicals can reach surface water through runoff and leaching from treated plants and soil. Due to persistent nature, pesticides may bio accumulate and bio

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Comparative study of the disinfection capacity of different floor cleaning solutions on ventilated room floor

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Abstract

Floor cleaning solutions is used to promote floor hygiene. It removes dirt and bacteria and provides a clean walking surface. Most of the cleaning is achieved by the mechanical action of the mop along with the floor cleaning solutions. The present study aimed to analyze the effect of various floor cleaners (Exo, Lysol, Dettol, Lemon grass oil) in the recommended concentration on floor bacteria. The floor cleaners tested in the present study were selected based on the popularity and availability in market. The study was performed using swabbing method for collection of bacteria and pour plate method for bacterial culture. Among the four floor cleaners, Dettol shows maximum antibacterial action, the chloroxylenol containing in Dettol that show higher anti microbial activity. It is obvious that ayurvedic floor cleaner Lemon grass oil exhibit antibacterial action like other selected floor cleaners. Before cleaning, bacterial population of the specific area was 31 CFU and in after cleaning sample with lemon grass oil 9 bacterial colonies were observed. All the variations between the CFU of bacteria before and after treatment was found as significant in student t test performed. An attempt has been done in the present study to screen antimicrobial effect of four selected floor cleaning solutions on floor with an objective to evaluate performance of daily usable floor cleaning solutions, avoiding bacterial contaminations in floor.

Keywords: Antimicrobial effect, Dettol, Exo, Lysol, Lemon grass oil.

1. Introduction

Floor Cleaner is a concentrated biodegradable floor cleaning solution which kills germs, effectively removes tough stains and leaves a pleasant fragrance; but even clean and dry floors can harbour bacteria. There are many floor cleaner manufactures, exporters, suppliers based in India. Good hygiene routines based on cleaning of surfaces are recommended to help control the spread of pathogens. We live in the age of bacteria (Prescott and Klein, 1996). The microbial colonization of all environmentally accessible surfaces of the body begins at birth. Such surfaces are exposed to a wide range of microorganisms derived from the environment and from other persons. This results in the acquisition, selection and natural development of a diverse but characteristic micro flora at distinct sites (Marsh and Martin, 2009).

IAETSD JOU

In Vitro Assessment of Different Concentration of Allopathic and Ayurvedic Medicinal Preparation on Microbial Inhabitants of Eye

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Abstract: Present study is an *in vitro* assessment of the effect of both allopathic and ayurvedic medicinal preparations on the commonly inhabiting bacteria in eyes. The selected ayurvedic medicines were Elaneer Kuzhambu and Himalaya Ophthacare eye drops; allopathic medicines were Ciplox and Catina. For concentration study four different eye drops were taken in three ratios pure form, 1:1 and 1:2. In pure form the eye drops are used directly. For each ocular medicine their 3 different concentrations with three replicas were obtained. By disc diffusion method these eye drops produced inhibition zones on the swab culture of ocular micro flora after 24 hours of incubation. The inhibition zone for each eye drops varied in diameter. The inhibition zone indicates the destruction of microbial population in the culture by the activity of the eye drops. As per the results from the present investigation, among allopathic eye drops, Ciplox produced maximum zone of inhibition than Catina. Among ayurvedic eye drops, Himalaya produced maximum zone of inhibition than Elaneer Kuzhambu.

Key words: Allopathic and ayurvedic ear drops, Catina, Ciplox, Himalaya, Elaneer Kuzhambu

1. INTRODUCTION

The human micro biota is the aggregate of microorganisms that reside on the surface and in deep layers of skin, in the saliva and oral mucosa, in the conjunctiva, and in the gastrointestinal tracts (Lee *et al.*, 1989). Eye is one of the sense organ which is important throughout our life. It has been said that, the eyes are window to the world. The external ocular surface acquires a microbial flora at birth and some of the commensals may become resident flora in the conjunctiva and lids and have a potential to turn into pathogens. Apart from the resident flora any microorganism from the environment can form a transient flora in the eye and given an opportunity invades the ocular tissues. Under normal circumstances the conjunctiva and eyelids support a population of bacteria (Stephen *et al*, 2008).

Normal ocular flora is diverse. They are similar to those found in the upper respiratory tract and on the skin (Osato, 1996). Individual microorganisms within the ocular flora interact with each other as well as with defense mechanisms of the eye and immune system. Tears function as one such antimicrobial defense-they contain the antimicrobial enzyme lysozyme, and also act together with the mechanical action of the eyelids in washing away pathogens. Under normal conditions, this results in a balance preventing the overgrowth of a particular microorganism and therefore infection. Bacteria are the most common agents causing external ocular infections, including conjunctivitis, blepharities, keratitis, dacryocystitis and orbital cellulitis. They are responsible for 70 – 80% of conjunctival morbidity which poses a huge socio-economic burden to the general public (Epling *et al.*, 2012).

Ciprofloxacin is in a class of antibiotics called fluoroquinolones. It is used to treat bacterial infections of the eye including conjunctivitis and corneal ulcers. Ophthacare is a herbal eye drop preparation containing basic principles of different herbs viz *Carum copticum, Terminalia bellerica, Curcuma longa, Ocimum sanctum, Cinnamomum camphora, Rosa damascana,* and *Melde spumapum.* In most cases improvement was observed with the treatment of the herbal eye drop (Burkil, 1966). Honey is an anti-inflammatory agent which soothes the eyes and heals wound quickly.

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Effect of Herbicide (Glyphosate) upon the fecundity and moulting of a terrestrial isopod (Philoscia javanensis) under lab condition

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Abstract

Soil isopods plays critical role to increase soil fertility. Indiscriminate use of Herbicides on agricultural purposes resulted deleterious effects on the biology and species diversity of soil arthropods. The effect of sublethal concentration of a herbicide glyphosate (N-(Phosphonomethyl)glycine), were treated to find out the fecundity and maturation of an edaphic isopod (Philoscia javanensis). The LC 50 and LC 100 values of Philoscia javanensis were calculated. The safe and sublethal concentrations of Glyphosate were very low indicating high vulnerability of these isopods to agrochemicals. The safe level concentration of Glyphosate was 0.6341ppm. The moulting intervals of P.javanensis showed variation between herbicide treated and normal P.javanensis. Herbicide treated P. javanensis showed drastic reduction in fecundity and also their moulting intervals were prolonged.

Key words: Glyphosate, Herbicide, Isopod, *Philoscia javanensis*, Moulting interval and Fecundity.

1. Introduction

Soils are integral part of ecosystems and constitute large number of soil micro arthropods. Soil micro arthropods enhance soil aggregation, porosity and thus increasing infiltration and reducing runoff. Agricultural practices negatively affects on different groups of soil fauna (Ponge *et al.*, 2013) (Paredes and Lebeis 2016). Many pesticides are not easily degradable, they persist in soil, leach to groundwater and runoff can carry pesticides into aquatic environment and also entered into the food chain thereby affecting all living beings. In all parts of the world, farmers are addicted to using agrochemicals indiscriminately (Conway, 1984) Overuse of agrochemicals will hamper soil, environment as well as human health. Glyphosate (N-phosphonomethyl-glycine) base product is the leading non-selective amino phosphonate type herbicide for the annual and perennial weeds control (Piola *et al.*, 2013).

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Research Article

Evaluation of the anti-diabetic potential of aqueous extract of *Clerodendrum infortunatum* L. *in vivo* in streptozotocin-induced diabetic Wistar rats

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Abstract

Diabetes Mellitus, the metabolic syndrome where the body either fails to produce or effectively utilize insulin, is associated with chronic morbidity. While a definitive cure for the disease is lacking, with the modern medicine offering mainly the means to control the extent of the disease, Complementary and Alternative Medicine (CAMs) offers additional/alternate means to tackle the disease. On the other hand, the lack of evidenced medical practices is a lacuna in most of the traditional medical applications. *Clerodendrum infortunatum*.L (Lamiaceae family), a perennial shrub found in the tropics, has been known for its numerous pharmacological properties and is found as a constituent in many Ayurvedic and Siddha drugs, especially for skin and respiratory ailments. The plant has a noted potential as anti-hyperglycemic and has been found to be used in traditional medicine for the treatment of diabetes. However, evidence based evaluations have not been conducted on the anti-hyperglycemic effect of the plant, especially with respect to the general mode of intake, *i.e*, the aqueous form. In the current study, the aqueous extract of *C. infortunatum* (CI), was scientifically assessed for its effect on streptozotocin induced diabetes in Wistar albino rats. The diabetic rats were divided into 5 groups of 6 animals each. For testing the efficacy of extracts, two groups were intra-orally provided with dosages of 200 mg/Kg and 400 mg/Kg of body weight of animals, respectively, of aqueous extracts of CI. Control groups were maintained for evaluation, which included vehicle control as well as with Glibenclamide, a standard anti-diabetic drug. The extracts at a dose of 400 mg/Kg body weight was found to be associated with significant amelioration of many of the diabetes induced conditions, suggesting that the plant extract could be a strong potential CAM candidate for therapeutic management of diabetes.

Keywords

Complementary and alternative medicine; *Clerodendrum infortunatum*; diabetes; streptozotocin

Citation

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Eco Friendly Sorbent for the Removal of Iron and Lead from Industrial Waste Water

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ABSTRACT

Industrial effluents loaded with heavy metals are a cause of hazards to human and other forms of life. Conventional methods such as chemical precipitation, evaporation, electroplating, ion exchange, reverse osmosis etc., used for removal of heavy metals from waste water however, are often cost prohibitive having inadequate efficiencies at low metal ion concentrations. Biosorption can be considered as an alternative technology which has been proved as more efficient and economical for removal of heavy metals from the industrial waste water. In the present study, the adsorption capacity of epicarp of Atrocarpus heterophyllus for the removal of heavy metals, lead and iron were determined by batch adsorption studies. Adsorption of heavy metals were studied till equilibrium was reached. Studies were carried by using different doses of adorbent, varying the conditions of adsorption and contact time. The results obtained shows that, the adsorption of the metal ions is contact time and adsorbent dosage dependent. Adsorption studies obeys both Langmuir isotherm model and Freundlich models. The goal for this work is to develop inexpensive, highly available, effective adsorbents from epicarp of jackfruit as alternative to existing commercial adsorbents.

Keywords : Heavy Metal, Low Cost Adsorbent, Wastewater, Adsorption Isotherm.

I. INTRODUCTION

Water used in industry creates wastewater that has a potential hazard for our environment because of introducing various contaminants such as heavy metals into soil and water resources. Heavy metal ions are nowadays among the most important pollutants in surface and ground water [1]. The safe and effective disposal of industrial wastewater is thus a challenging task for industrialists and environmentalists. Nowadays, with the exponential increase in population, measures for controlling heavy metal emissions into the environment are essential [2]. Lead causes many serious disorders like, anemia, kidney disease, nervous disorders, and even death, it heads the toxic element list of 2008 [3]. New approaches based on the use of natural inexpensive adsorbents for treatment have been reported [4]. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry [5].

To avoid health hazards it is essential to remove toxic heavy metals from waste water before its disposal. Adsorption process is widely used in the removal of heavy metals. Understanding the sorption of metal ions from aqueous solution is important in water pollution control. Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in

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Comparison of photo catalytic and antibacterial activities of zinc oxide and copper oxide nanoparticles synthesised by sol-gel method

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ABSTRACT

In the present work zinc oxide nanoparticles (ZnO) and copper oxide nanoparticles were successfully synthesized by sol-gel method where zinc acetate and cupric acetate were used as the precursor materials. Sodium hydroxide takes care for the homogeneity and pH value of the solution and helps to make a stoichiometric solution to get Zinc oxide nanoparticles and Copper oxide nanoparticles. The ZnO powder and CuO powder obtained from this method were calcined at 400°C temperatures. The samples were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD spectra indicate that the ZnO nanoparticle has a hexagonal wurtzite structure and CuO nanoparticles has a monoclinic structure. The photo catalytic activities of the metal oxide nanoparticles on the degradation of Methylene Blue were studied. The results show that ZnO nanoparticles were far more superior to CuO in degrading methylene blue. The antibacterial activities of the nanoparticles against both Gram positive and Gram negative bacterial strains shows that both ZnO and CuO can be used as effective antibacterials.

KEY WORDS: Nanoparticles, ZnO, CuO, catalytic, antibacterial.

1. INTRODUCTION

Effluents released from textile industries pose a serious threat to environment as these contain organic dyes. Environmental pollution by organic dyes cause severe ecological problem, since most of them is often toxic to microorganisms and have long degradation times in the environment (Pagga, 1984; Parsons, 2006). Advanced oxidation processes using nanoparticles are found to be more efficient and cost effective compared to the conventional methods which include adsorption, coagulation, biological treatment etc. for the treatment of these effluent (Daneshvar, 2007; Nazar Elamin, 2013; Nirmala, 2010, Qu, 1998; Torimoto, 1996; Das, 2013; Zhang, 2011). In this process electrons (in conduction band) and holes (in valence band) are generated using light energy. These holes and electrons interact with H_2O and O_2, respectively, to yield OH and OOH radicals (Behnajady, 2007; Akyol, 2008; Anandan, 2007). These hydroxyl radicals are highly reactive with very high oxidation potential and can oxidize the dyes completely. It is a fast, clean and destructive method of dye degradation in which no secondary waste is generated (Fernandez, 2010). The effectiveness of nanoparrticles as antibacterials have been well established (Horiguchi, 1980; Dusan Zvekic, 2010; Li, 2002). A variety of methods have been developed for the synthesis of metal nanoparticles which include hydrothermal (Zhou, 2007), chemical precipitation method (Wang H, 2007; Wang, 2007), hydrolysis in polyol medium (Poul, 2001), thermal oxidation process (Zhang, 2007) template method (Kou, 2006) and microwave synthesis (Siddiquey, 2008). It is found that the method used for the synthesis affect the size, morphology, crystalline form and photocatalytic activity of the nanostructures (Zhang, 2007).

Here in this paper, we report the synthesis and characterization of ZnO and CuO nanoparticles and their photocatalytic ability for the degradation of Methylene Blue. We also report the antibacterial abilities of these nanoparticles and their activites are compared.

2. MATERIALS AND METHOD

All the chemicals used for the synthesis of metal nanoparticles were of analytical grade. Zinc acetate dehydrate (99%purity), cupric acetate (99% purity) and sodium hydroxide (pellet 99%) were used as the introductory material. The pH measurements of the colloidal solution were carried out using CYBER pH-14L pH metre.

2.1. Synthesis of ZnO and CuO nanoparticles: In a typical procedure, 2.7441 g of zinc acetate dehydrate was dissolved in 250 ml distilled water under vigorous stirring at room temperature. To 50 ml of this solution, aqueous 1.0M NaOH solution was added drop by drop to reach pH about12. It was then placed on a magnetic stirrer for 2 hours. The white precipitate formed after completion of the reaction, was washed thoroughly with distilled water followed by ethanol to remove the impurities. The precipitate was dried in a hot air oven for overnight at 60°C and further calcined at 400°C for 4 hours. Complete conversion of Zinc oxide in to ZnO nanoparticles took place during this period.

CuO nanoparticles were also prepared using the same procedure by taking 1.9965g of cupric acetate dehydrate.

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Bio-active Azo dyes from 3-(Pentadeca-8-enyl)phenol and Ortho Substituted Anilines

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Abstract

Two new azo dyes synthesized from a natural renewable source, 3-(pentadeca-8-enyl)phenol and ortho substituted anilines, o-aminophenol and o-toluidine were characterized using UV-Visible and FTIR spectroscopy. The compounds were evaluated for their antibacterial activity against Staphylococcus aureus and Escherichia coli by disc diffusion method. The screening data revealed that the dyes exhibited potent antibacterial activity against both bacterial strains.

Keywords: azo dyes, 3-(pentadeca-8-enyl) phenol, o-aminophenol, o-toluidine, antibacterial

1. Introduction

Azo dyes are majorly used in textile industry, besides their applications in fields like cosmetics, food industry, medicines, plastics, automobile industry etc[1-4]. Azo dyes were reported to have been synthesised with the coupling reactions 3-(pentadeca-8-enyl)phenol, a meta substituted unsaturated phenol obtained from cashew nut shell liquid a natural renewable source, with the diazotized aniline, *m*-toluidine[5], *p*-anisidine and *p*-sulphanilic acid[6]. Antibacterial activity of azo dyes is also well-known[7]. The dyes synthesized from *p*-anisidine and *p*-sulphanilic acid exhibited potent antibacterial activity against B. cereus and K. pneumonia[6].

In the present study *o*-aminophenol and o-toluidine are diazotized separately and then coupled with 3-(pentadeca-8-enyl) phenol (figure 1) to produce diazotized *o*-aminophenol 3-(pentadeca-8-enyl) phenol dye and diazotized- *o*-toluidine 3-(pentadeca-8-enyl) phenol dye respectively. They are characterized by UV and FT-IR spectroscopic techniques and their antibacterial activity has also been studied.

2.Materials and Method

3-(Pentadeca-8-enyl) phenol was obtained from M/s Golden Cashew Chemicals Ltd, Mangalore. Sodium nitrite, potassium hydroxide, *o*-aminophenol, *o*-toluidine and methanol were received from Loba Chemie. The chemicals were used as received. Ultraviolet spectral analysis was carried out in a SCHIMADZU 1800 UV Spectrophotometer. Infrared spectra were taken in a PERKIN-ELMER Spectrum 400 IR spectrophotometer by KBr pellet method.

2.1 Synthesis of the Dyes

The procedure adopted for the synthesis of dyes was as reported earlier[8]. orthoaminophenol (3g - 27.5 µmol) was dissolved in 25 mL of 1:1 Hydrochloric acid. A solution of sodium nitrite (0.92g - 13.3 µmol) in distilled water (3mL) was prepared and added drop wise to the acidic solution of amine over a period of 10 min and the mixture was stirred at 0 °C for 50 min. The pH of diazonium solution of amines was adjusted to 8 by the addition of appropriate amount sodium bicarbonate (1M) solution. The pre-cooled solution of 3-(pentadeca-8-enyl) phenol (3.2g - 10.7 µmol) in 15 mL ethanol was injected drop wise to the above pH monitored solution at 0 °C. The reaction mixture was stirred at 0 °C for 40 min by which time the product was precipitated. The water insoluble portion was extracted with diethyl ether, the organic layer was washed repeatedly with 50 mL distilled water and solvent was removed under reduced pressure. Resulting dye was dried in vacuum oven. A portion of the dye was recrystallised from hexane –chloroform (8:2) mixture.

Similarly o-toludine-3-(pentadeca-8-enyl) phenol azo dye was synthesised following the same procedure as given above by taking o-toluidine (3g - 28.04 µmol). The dye obtained as reddish brown viscous liquid was purified by column chromatography.

2.2 Antibacterial Studies

Antibacterial activities of the synthesised dyes were carried out against Gram-positive (*Staphylococcus aureus)* and Gram-negative (*Escherichia coli)* bacterial strains using disc diffusion method. Finally their activities were compared. Nutrient agar was used as the medium for the preparation of pure cultures of bacteria for detecting antibacterial activity. Test organisms were collected from Institute of Microbial Technology, microbial type culture collection centre, (IMTECH), Chandigarh.

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Unprecedented Pentacoordination of Di-2-pyridyl ketone *N*(4)-ethyl thiosemicarbazone Ligand with Formation of Trinuclear Cu(II) Complex

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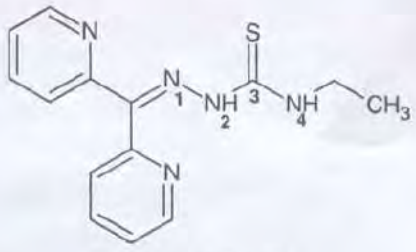
The syntheses and characterization of six copper(II) complexes of di-2-pyridyl ketone *N*(4)-ethylthiosemicarbazone (HDpyETsc) are reported by means of partial elemental analyses, molar conductance measurements, electronic, infrared and EPR spectral studies. The complexes are represented as $[Cu_3(DpyETSc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$ (**1**), $[Cu(DpyETsc)N_3]\cdot H_2O$ (**2**), $[Cu(DpyETsc)Cl]_2\cdot H_2O$ (**3**), $[Cu_2(DpyETsc)_2SO_4]_2\cdot 4H_2O$ (**4**), $[Cu(DpyETsc](ClO_4)_2\cdot H_2O$ (**5**) and $[Cu(DpyETsc)(NCS)]$; (**6**). The compound **1** was found to be a trinuclear copper(II) complex with the ligand showing pentacoordination which is unprecedented for this type of ligand. Two centro-symmetric six membered metallocycles are formed and the terminal copper atoms have distorted square pyramidal geometry.

Keywords: Thiosemicarbazone, Cu(II) complex, Di-2-pyridyl ketone, Crystal structure, EPR spectra.

INTRODUCTION

Thiosemicarbazide and thiosemicarbazone complexes of copper have attracted particular attention over the past decades in the context of their wide spectrum of biological activity and applications as radiopharmaceuticals. Thiosemicarbazones are versatile ligands that can coordinate as neutral ligands or in their deprotonated form [1,2]. The activity of thiosemicarbazones depends very much on the parent aldehyde or ketone and is affected also by *N*(4) substitution [3]. Thiosemicarbazones derived from di-2-pyridyl ketone are potentially tetradentate. However in majority of cases they function as tridentate ligands only.

Thiosemicarbazone is emerging moiety with wide spectrum of biological activity and having sound scope in research and developing process in pharmaceutical and medicinal chemistry [4]. Copper(II) is a biologically active, essential ion; its chelating ability and positive redox potential allow participation in biological transport reactions. Copper(II) also forms the active centers of more than a dozen metalloproteins. Further, copper(II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents. The chemistry of polynuclear copper complexes has become a fascinating area of research in contemporary coordination chemistry following the discovery of multicopper active sites in several blue copper oxidases and development of novel functional materials showing molecular ferromagnetism and specific catalytic properties [5]. Additionally, polynuclear copper compounds have attracted much attention due to their ability to perform DNA strand cleavage [6]. On this basis, the present communication reports on the optimal conditions for synthesis of six copper complexes with the ligand, di-2-pyridyl ketone *N*(4)-ethyl thiosemicarbazone (HDpyETsc) and their characterization by physicochemical methods, together with X-ray crystal structure of one of the copper complexes, *viz.* $[Cu_3(DpyETSc)_2(NO_3)_4(H_2O)_2]\cdot H_2O$.



Structure of HDpyETsc

EXPERIMENTAL

Di-2-pyridyl ketone, *N*(4)-ethyl thiosemicarbazide, copper(II) nitrate trihydrate, copper(II) acetate monohydrate, copper(II) chloride dihydrate, copper(II) sulphate pentahydrate, copper(II) perchlorate hexahydrate, sodium azide and

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EPR Spectral Studies of Dimeric and Monomeric Cu(II) Complexes of di-2-pyridyl Ketone N(4)-methyl Thiosemicarbazone

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ABSTRACT

Four copper(II) complexes, $[Cu_2(DpyMeTsc)_2SO_4]\cdot 3H_2O$ (1), $[Cu(DpyMeTsc)N_3]\cdot H_2O$ (2), $[Cu_2(DpyMeTsc)_2]\cdot(ClO_4)_2\cdot 2H_2O$ (3), and $[Cu(DpyMeTsc)(CH_3COO)]\cdot 2H_2O$ (4) of di-2-pyridyl ketone N(4)-methylthiosemicarbazone (HDpyMeTsc) are studied with electron paramagnetic resonance (EPR) spectroscopy. EPR is the most powerful spectroscopic method to discriminate between monomeric and dimeric Cu(II) complexes in solution. EPR studies indicate dimeric nature of (1) and (3) and monomeric nature of (2) and (4).
Keywords: Thiosemicarbazone; Cu(II) complex; Di-2-pyridyl ketone; EPR spectra.

I. INTRODUCTION

The coordination chemistry of transition metal complexes involving nitrogen and sulfur donor ligands has been the cynosure among chemists during recent years due to the application of these chelates in modelling of biomolecules, in the field of chemical and biological reactivity and nuclear medicine. The potential role played by copper ions, being present in the active sites of a large number of metalloproteins having the CuN_2S_2 chromophore, has stimulated efforts to design new ligand frames having nitrogen sulfur donor sites and characterize copper complexes as models for providing a better understanding of the biological system[1]. The activity of thiosemicarbazones depends very much on the parent aldehyde or ketone and is affected also by N(4) substitution[2]. Thiosemicarbazones derived from di-2-pyridyl ketone are potentially tetradentate. However in majority of cases they function as tridentate ligands only. Literature survey reveals that the presence of a metal ion increases the activity of or mitigate the side effects of the parent organic compounds[3].

Copper(II) is a biologically active, essential ion; its chelating ability and positive redox potential allow participation in biological transport reactions. Also, copper(II) forms the active centers of more than a dozen metalloproteins. Further, copper(II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents[4]. Cu(II) complexes display a wide range of geometric arrangements around the copper ion, from the square planar to deformed tetrahedral geometry. Pseudohalide anions like azides and thiocyanate are found to be versatile ligands in terminal and bridging modes. These phenomena are reflected in their spectral properties. Electron paramagnetic resonance (EPR) is a suitable tool for the study of paramagnetic metal ion complexes and may provide useful information about the oxidation states, modes of coordination, geometry and type of ligand sites[5].

RSC Advances

PAPER

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Investigations on the development of MCM-41 as a potential mesoporous silica based reference material for the analysis of multi-textural properties†

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Investigations on the time dependent analysis of the structural and textural properties of the mesoporous silica material MCM-41 were performed by analyzing the samples at regular intervals for one year by powder X-ray diffraction (PXRD) and nitrogen sorption techniques for samples stored (i) under a dry nitrogen atmosphere in a glove box and (ii) under dry ambient atmospheric conditions. The stability and durability of this high surface area material gave promising results under both storage conditions in terms of its structural and textural properties. Under the typical storage conditions employed, the values of various textural properties, including the surface area (SA, $m^2\ g^{-1}$), pore volume (PV, $cm^3\ g^{-1}$), pore diameter (PD, Å) and wall thickness (WT, Å) determined by nitrogen adsorption were found to be 1030 ± 49, 1.015 ± 0.066, 27.55 ± 0.60 and 17.04 ± 0.61 respectively for the glove box samples. Almost identical values (SA = 1022 ± 45 $m^2\ g^{-1}$), (PV = 0.933 ± 0.065 $cm^3\ g^{-1}$), (PD = 27.54 ± 0.14 Å), (WT = 16.58 ± 0.81 Å) were obtained for the samples under ambient atmospheric conditions. The experimental analysis indicated that this material has potential as a standard reference material for the analysis of the multi-textural characteristics of high surface area mesoporous materials.

1. Introduction

Porous materials are of scientific and technological importance because of the presence of voids of controllable dimensions at the atomic, molecular, and nanometer scales, enabling them to discriminate and interact with molecules and clusters, and interact with atoms, ions and molecules not only at their surfaces but through the bulk of the materials. The distribution of sizes, shapes and volumes of the void spaces in porous materials directly relates to their ability to perform the desired functions of a particular application. The need to create uniform pore sizes, shapes and volumes has steadily increased over recent years because these factors can lead to superior properties which find applications in various fields such as catalysis,[1–5] adsorption,[6] hybrid optics,[7] biomedical devices,[8] sensors,[9] drug delivery[10] separation processes[11] and many more. All of these applications are largely dependent on the textural properties of the materials. This interest in various porous matrices has triggered the need for a new generation of environmentally stable and durable standard reference materials for textural analysis. The characterization of novel and nanoporous films, spheres, fibers and monoliths requires a new standard reference material for textural analysis. Thus, studies on the textural properties are very important for such materials. The surface area (SA), pore volume (PV), pore diameter (PD) and wall thickness (WT) constitute the major textural properties that are of importance to the above applications.

Every instrument and apparatus has to be standardized and calibrated at appropriate intervals to ensure accurate and precise performance and data collection. Many of these instrument techniques need a reference material or standard for calibration. Surface area and pore size analyzers need standard reference materials for calibration. The Institute for Reference Materials and Measurements (IRMM), the Bundesanstalt für Materialforschung und-prüfung (BAM) and the National Institute of Standards and Technology (NIST) are major suppliers of surface area standards,[12–14] and reference standards with surface areas ranging from 0.0686 to 258.0 $m^2\ g^{-1}$ are available. The BAM is the major producer and supplier of reference standards for pore size analysis. CRM BAM-PM-103 and CRM BAM-PM-104 are the standards for pore size analysis. The high surface area standards are activated nanoporous

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Notes

Ru catalyzed formylation of diethylamine with CO_2 and H_2 under moderate pressure condition

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Ru catalyzed formylation of diethylamine (bulky secondary amine) with CO_2 and H_2 has been investigated using a series of phosphine ligands. Significant influence on the catalyst activity and selectivity is observed with bidentate phosphine ligands. The Ru catalyst with the ligand, 1,2-bis(diphenylphosphino)benzene exhibits the highest catalyst performance (TON up to 2475). The high conversion (99%) and high selectivity to the corresponding formamide (up to 90-98%) is achieved at 150 °C and moderate pressure conditions. The effects of temperature, concentration of diethylamine and partial pressure of CO_2 and H_2 on the formylation of diethyl amine catalyzed have been examined in order to improve the catalytic activity and selectivity.

Keywords: Catalysis, Formylation, Diethyl amine, Carbon dioxide, Ruthenium, Bidentate phosphines

C_1 chemistry based on synthesis gas (CO/H_2), methane (CH_4) and carbon dioxide (CO_2) offers many routes to synthesized industrially useful chemicals. Considering the environmental effects of CO_2 and economical concerns, the utilization of CO_2 as a C_1 feedstock to synthesize value-added chemicals has received growing impetus since CO_2 is available in abundance and is cheap, non-toxic, non-flammable and renewable[1–7]. Catalytic hydrogenation of CO_2 is one of the most promising approaches to convert CO_2 to various valuable products such as methanol, ethers, esters, formamides and formic acid[8–12]. The formamides such as dimethylformamide (DMF), diethylformamide are commonly used as a solvent in the plastics, pharmaceutical, paint industries and in many other chemical processes[13]. Conventionally, dialkyl formamide (DAF) is produced by sodium methoxide catalyzed carbonylation of dialkylamine with carbon monoxide (CO) in methanol at 20–100 bar and 353–373 K[14]. Thus, hydrogenation of CO_2 in the presence of secondary alkylamine is an environment friendly alternative route for the production of formamide instead of using toxic compounds. The synthesis of formamides from dialkylamines, CO_2, and H_2 has been studied using various metal based catalysts. It was observed that Ru based catalyst exhibited high conversion and selectivity[15–19]. In pioneering studies in this field, Noyori and co-workers[18] reported formylation of different secondary amines by hydrogenation of supercritical CO_2 (pCO_2 + pH_2 = 210 bar) using $RuH_2[P(CH_3)_3]_4$ and $RuCl_2[P(CH_3)_3]_4$. They achieved high TOF (8000 h^{-1} for formylation of dimethylamine) under supercritical CO_2 condition since $scCO_2$ has rapid diffusion, weak catalyst solvation and the high miscibility with H_2. However, the observed TOFs were considerably low in the case of bulky amines (50–63 h^{-1})[19]. Baiker *et al.*[20] applied Ru complexes with bidentate phosphine ligands, $[RuCl_2L_2]$ [L = $Ph_2P(CH_2)_nPPh_2$ (n = 1–3), $Me_2P(CH_2)_2PMe_2$] for hydrogenation of $scCO_2$ and achieved high TOF and high selectivity for DMF and methyl formate. Formylation of cyclic and aliphatic amines has also been carried out using $RuCl_2(dppe)_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] and Ru/Al_2O_3 modified by dppe as catalysts under $scCO_2$ and H_2 (180 to 220 bar)[21–23]. From the reported literature, it was observed that the formylation of bulky secondary amine using CO_2 usually requires high pressure (180–220 bar) especially supercritical state to achieve high reaction rate and yield due to the high thermodynamic stability and low reactivity of CO_2[15–23]. Literature shows that the major attention is towards formylation of dimethylamine to DMF, while there are only a few reports wherein other derivatives of dialkylamine have been formylated. In the case of dimethylamine, high conversion and selectivity for DMF can be obtained while bulky dialkylamines such as diethylamine, diisopropylamine and dicyclohexylamine are difficult to formylate as they produce ammonium formate salts and the rate of dehydration of such salts to the corresponding formamides is strongly influenced by steric factors[19]. In view of the above, we focused attention on synthesis of formamide from bulky dialkylamine such as diethylamine (as a model substrate) under moderate

Multiple Cycloaddition Reactions of Ketones with a β-Diketiminate Al Compound

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Dedicated to Professor Ramaswamy Murugavel on the occasion of his 50th birthday

Abstract: A β-diketiminate Al compound (**1**) with an exocyclic double bond reacts with two equivalents each of benzophenone and 2-benzoylpyridine in a [4+2] cycloaddition to generate bicyclic and tricyclic compounds **2** and **3**, respectively. Compound **2** consists of six- and eight-membered aluminium rings, whereas **3** has two five- and one eight-membered ring. Compounds **2** and **3** were characterized by a number of analytical tools including single-crystal X-ray diffraction. The quantum mechanical calculations suggest that the dissociation of the solvent molecule from **1** would lead to an active species **1A** having two 1,4-dipolar 4π electron moieties, in which the electrophilic site is the Al atom and the nucleophilic positions are polarized exocyclic and endocyclic C=C π bonds. The detailed mechanistic study shows that the dipolarophiles, benzophenone, and 2-benzoylpyridine undergo double cycloaddition with two 1,4-dipolar 4π electron moieties of **1A**. Herein, the addition of one molecule of the dipolarophile promotes the addition of the second one.

Introduction

Aldehydes and ketones constitute an important class of organic compounds containing carbonyl functional groups, which exhibit versatile reactivity.[1] The polar nature of the C=O bond renders the carbon atom electron deficient, which is thereby prone to nucleophilic attack. Ketones are less reactive compared to aldehydes. Therefore, investigating reactions between ketones and reactive organometallic compounds, such as silylenes, has been a focal area of research.[2] In Diels–Alder reactions, cycloadditions of conjugated dienes with carbonyl compounds are used for the synthesis of six-membered rings containing oxygen atoms. Similarly, the cycloaddition reactions of silylenes with various ketones have resulted in a number of silicon-containing heterocycles. For example, the reaction of an N-heterocyclic silicon(II) compound with benzophenone gave an unusual [4+1] cycloaddition product, which contains a methylenecyclohexadiene.[2e] However, despite the preponderance of silicon-containing heterocycles, aluminium heterocycles are scant, presumably due to the lack of suitable precursors. As a potential precursor of this kind, we previously reported the high-yield synthesis of a C–H-activated aluminium complex, [L^{1}AlMe]·THF (**1**; L^1 = CH[C(CH$_2$)](CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$) from the reaction of the base [Ca{N(SiMe$_3$)$_2$}$_2$]·2THF with LAlCl(Me) (L = CH{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$.[3] Moreover, cycloaddition reactions are catalyzed by Lewis acids, such as aluminium,[4] and therefore, compound **1**, which has a diene moiety in the backbone constitutes two reactive sites: one is the Lewis acidic aluminium center and the other the basic butadiene backbone. In the past, we have successfully employed [L^{1}AlMe]·THF as a building block for the preparation of heterobimetallic compounds.[3] Thus, we anticipated that **1** might be a useful precursor for macrocycles as well. Literature reports on aluminium-containing ring systems by using nitrile insertion into Al–N bonds are available.[5] Synthesis of macrocyclic Al–P compounds were reported by Stephan and co-workers[6] and by Hänisch and co-workers[7] using alkyl aluminium compounds as reactants. Macrocyclic binucleating β-diketiminate ligands were utilized by the Holland group for preparing aluminium complexes.[8] Herein, we describe the striking reactivity of **1** toward ketones, such as benzophenone and 2-benzoylpyridine. The reactions proceeded via aluminium-mediated [4+2] cycloadditions and resulted in the formation of bi- and tricyclic compounds with different structural properties.

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An organic dye-polymer (phenol red-poly (vinyl alcohol)) composite architecture towards tunable -optical and -saturable absorption characteristics

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Herein, we demonstrate that blending an organic dye (guest/filler), with a vinyl polymer (host template), is an inexpensive and simple approach for the fabrication of multifunctional photonic materials which could display an enhancement in the desirable properties of the constituent materials and, at the same time provide novel synergistic properties for the guest-host system. A new guest-host nanocomposite system comprising Phenol Red dye and poly (vinyl alcohol) as guest and host template, respectively, which exhibits tunable optical characteristics and saturable absorption behavior, is introduced. The dependence of local electronic environment provided by the polymer template and the interactions of the polymer molecules with the encapsulated guest molecules on the observed optical/nonlinear absorption behavior is discussed. An understanding of the tunability of the optical/ photophysical processes, with respect to the filler content, as discussed herein could help in the design of improved optical materials for several photonic device applications like organic light emitting diodes and saturable absorbers. *Published by AIP Publishing.*
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I. INTRODUCTION

For several decades, metallic as well as inorganic semiconducting nanoparticles have been the focus of extensive investigations due to their size-tunable optical properties arising from quantum confinement effects. However, it has recently been reported that organic materials which exhibit a large range of structural divergence can form nanometer sized particles (10–250 nm diameter) and their molecular structure, and hence optical/photo physical properties can be tuned either by introducing alterations in the active units of the molecules or by encapsulating them in suitable hosts.[1–6] Materials possessing tunable linear and nonlinear optical (NLO) properties are important prerequisites for photonic device applications like laser mode-locking, optical switching, optical pulse shaping, etc.[7–10]

Organic molecules/nanoparticles are promising choices for optical/NLO investigations owing to a number of reasons.[11–13] Tunable properties can be realized in organic molecules by a variety of ways: introducing structural modifications in the molecules, substitution reactions, adding metallic atoms, developing metal organic frameworks, blending these molecules with inorganic/organic host matrices, etc.[13–17] However, the feasibility of developing homogeneous, patternless solid films of such materials, suitable for device applications, in a cost-effective manner is still an open question. In this context, it remains a challenging field of research to fabricate these photonic materials with tunable optical and NLO properties.

The encapsulation of organic materials/organic dyes in the nano-channels/nanopores of a polymer template as a guest-host system is an efficient strategy to modulate the characteristics of the filler (guest) and polymer (host) molecules and to introduce new synergistic characteristics for the guest-host system.[6,13,18–22] The host polymers provide unique electronic environment and offer appreciable interaction with the embedded guest, which can significantly modify (alter) the physical/spectroscopic properties of the constituent molecules. Modulation of the photophysical properties as well as enhancement in physico-chemical effects like photostability, dye-deaggregation, shifts in PKa values, etc., which occur as a result of complexation or by guest-host interactions, have been reported for both the aqueous solution and solid forms of such materials.[12,13,17,21,23–25]

In this context, the present article features an attempt to design a simple hybrid optical material based on an organic-polymer system which could impart enhancements in the desirable optical properties of the organic chromophores, combining the desirable mechanical, thermal and photochemical properties of the polymer host in which they are stabilized. Herein, we demonstrate solution casting method as a controllable and simple strategy to fabricate the multifunctional hybrid (guest-host) nanostructured material comprising the organic dye (Phenol Red (PR)) impregnated in poly (vinyl alcohol) (PVA) template.

Poly(vinyl alcohol) (PVA) having molecular weight 125,000 g/mol and degree of hydrolysis 86%–89% (partially

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Subpicomolar sensing of hydrogen peroxide with ovalbumin-embedded chitosan/polystyrene sulfonate multilayer membrane

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ABSTRACT

The use of ovalbumin (OVA)-immobilized layer-by-layer-assembled chitosan/polystyrene sulfonate membranes for the detection of hydrogen peroxide (H_2O_2) at subpicomolar levels is reported. The detection of mercuric chloride ($HgCl_2$) and potassium iodide (KI) was also investigated. While the detection limits of $HgCl_2$ and KI remained in the micromolar concentration range, H_2O_2 could be sensed to a remarkably lower range (subpicomolar). Analysis of fluorescence quenching data of OVA by H_2O_2 using Stern–Volmer plots revealed a static quenching mechanism with high Stern–Volmer quenching constant (9.10×10^{12} L mol^{-1}) and k (5.82×10^{21} L mol^{-1} s^{-1}). The possibility of the conformational transition of OVA in the immobilized state is discussed using steady-state and time-resolved spectroscopic techniques. The resulting increased accessibility of tryptophan residues together with the reversibility of the bilayer for the sensing of H_2O_2 is also illustrated.

Polyelectrolyte multilayer buildup is used extensively for the surface functionalization. The surface structure and composition can be well tuned on a nanometer scale by controlling the construction parameters. The buildup is generally realized by sequential adsorption of alternately charged polyelectrolytes from aqueous solution [1]. Biomacromolecules, dyes, and other particles can be immobilized to the film using this versatile film fabrication tool [2,3]. Self-assembled polyelectrolyte multilayer membranes often provide a safe electrostatic cage for the embedded biomolecules wherein their bioactivity is preserved [4,5]. Polyelectrolytes stabilize protein molecules so that their secondary structure is preserved, leading to protein-resistant/adhesive surfaces, paving the way to drug delivery applications [6,7]. The embedded biomolecules can show enhanced properties, as the matrix provides a very high ratio of surface area to volume [8]. This is exactly the desired property in sensing applications, as it would lead to high accessibility to analyte molecules. Biosensing is another area in which the inherent fluorescence property of embedded protein molecules can be utilized [9–11]. The intrinsic fluorescence of proteins arises from the presence of tyrosine, tryptophan, and phenylalanine [12]. Tryptophan is the prominent fluorescent amino acid, with a quantum yield of 0.13 in solution. The fluorescence of proteins is sensitive to the tryptophan microenvironment and can provide information regarding protein structure, dynamics, and protein folding. The immobilization of proteins during physical adsorption is susceptible to defolding [6,13]. This might lead to the exposure of tryptophan residues. So, two main challenges to utilizing protein fluorescence for sensing are to optimize the experimental variables so as to provide access to buried tryptophan residues and to increase the surface area of the immobilized matrix. From this perspective membranes are superior to other solid supports [8]. In addition to this, based on our previous experience working with chitosan/polystyrene sulfonate (CHI/PSS) multilayer membranes, the adsorption/sorption pattern of the protein to the multilayer is entirely based on the experimental variables [14]. So we anticipated that through careful control of the morphology of the CHI/PSS multilayer it may be possible to provide good access of analytes to tryptophan residues.

The detection of hydrogen peroxide at trace levels is important for biodiagnostic applications. Hydrogen peroxide (H_2O_2) is generated enzymatically for the indirect evaluation of clinically relevant molecules such as glucose and cholesterol [15,16]. Although it is involved in many redox processes in the body, an excess percentage always suggests the presence of high-risk-category diseases. Therefore, its detection at trace levels has always been a topic of interest. Traditionally electrochemical detection is the most preferred method [17,18]. The shortcomings of platinum electrodes

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THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

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Exploring the Interaction of Bisphenol-S with Serum Albumins: A Better or Worse Alternative for Bisphenol A?

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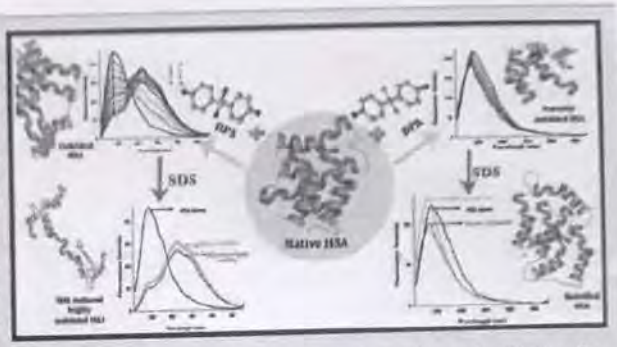
Supporting Information

ABSTRACT: The interaction of bisphenol-S (BPS) with serum albumins using steady-state, synchronous, time-resolved, and circular dichroism spectroscopies has been investigated. The binding interactions have also been investigated in the case of bisphenol A (BPA). The fluorescence quenching pathways are different for both of these endocrine disrupting compounds. Steady-state and time-resolved studies reveal static quenching at lower concentrations of BPS and dynamic quenching at higher concentrations. CD results also maintained the concentration dependent variation with a complete distortion of α-helices at 10^{-5} M BPS. Besides this, addition of sodium dodecyl sulfate (SDS) results in the further unfolding of protein in the case of BPS, whereas time-resolved studies indicated refolding for BPA denatured human serum albumin (HSA). The entire study indicates an irreversible binding of BPS with HSA. Hence, these results reveal the possible involvement of BPS in the physiological pathway raising a health threat as already their presences in body fluids are known.



1. INTRODUCTION

The existence of endocrine disrupting compounds (EDCs), known hormone mimicking chemicals, are not all desired in any of the environmental matrixes. However, to the contrary, their widespread usage as pesticides, industrial chemicals, plastics, plasticizers, and fuels has marked their presence everywhere, including human secretions. Bisphenols, with wide application potential, are also established EDCs. Primarily, BPA was widely applied in the production of epoxy resins, polycarbonate plastics, food cans, thermal printer paper, and dental composites/sealants.[1] BPA is known to leach from these polymers, paving its way to the human body through dermal exposure and dietary intake.[1c,2] The health impacts of BPA have been implicated in many in vivo and in vitro studies.[3] A number of countries banned the usage of products suspected to contain BPA. The efforts were also to replace BPA with its analogues bisphenol B (BPB), bisphenol F (BPF), bisphenol S (BPS), and bisphenol AF (BPAF). Soon these alternatives marked their presence in the human body, showing a negative health impact.

BPS is perhaps one of the analogues, extensively applied in the place of BPA. Now the presence of BPS can be expected in almost all consumer goods where BPA was initially in use. Similar to BPA, dermal, dust ingestion, and dietary exposures are the main pathways to the human body.[4] The presence of BPS at a concentration range of several nanograms per gram is already found in canned food stuffs.[5] One of the major industries that replaced BPA due to its high occurrence (~3–22 g/kg) is thermal paper. And the thermal paper carries BPS to all recycled paper products, making the dermal exposure inevitable. BPA analogues BPS, BPF, and others have similar estrogenic activity and even more environmental persistence. A high concentration (nanogram/gram to milligram/gram) of BPS is reported to be present in thermal receipt papers, indoor dust, and recycled paper products collected from cities in USA, Japan, Korea, and Vietnam.[4b] Such findings point out the possibility of occupational hazards and possibility of high levels of daily exposure. Studies of Chunyang Liao et al. indicate the occurrence of BPS in human urine samples from the United States and Seven Asian Countries.[6] Low doses of this chemical are also found to disrupt nongenomic signaling pathways in cultured pituitary cells.[7] The compounds' relative inability to biodegrade can lead to its bioaccumulation and likely persistence in the environment.[8] Once such toxic compound enters the body, their fate (transport and delivery) is mainly determined by human serum albumin (HSA), the most prominent carrier protein in the circulatory system.[9] This possible protein–pollutant binding can cause alteration in the protein structure and can hence get in the way of its normal functioning.

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Excitation-Dependent Multiple Fluorescence of a Substituted 2-(2′-Hydroxyphenyl)benzoxazole

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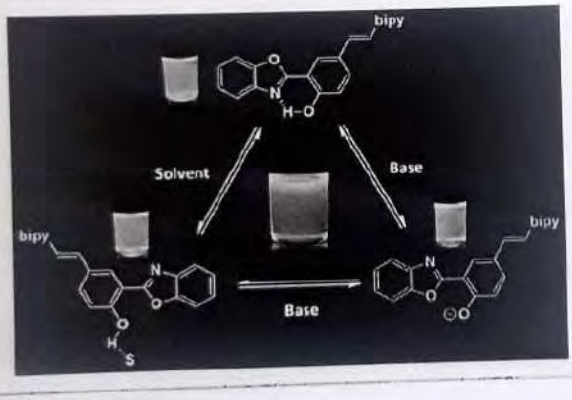
Abstract



capable (ESIPT-capable) HBO component that intersect at the hydroxyphenyl moiety. Therefore, both CT and ESIPT pathways, while spatially mostly separated, are available to the excited state of 1. The ESIPT process offers two emissive isomeric structures (enol and keto) of 1 in the excited state, while the susceptibility of 1 to a base adds another option to tune the composite emission color. In addition to the ground-state acid–base equilibrium that can be harnessed for the control of emission color by excitation energy, compound 1 exhibits excitation-dependent emission that is attributed to solvent-affected ground-state structural changes. Therefore, depending on the medium and excitation wavelength, the emission from the enol, keto, and anion forms could occur simultaneously, which are in the color ranges of blue, green, and orange/red, respectively. A composite color of white with CIE coordinates of (0.33, 0.33) can be materialized through judicious choices of medium and excitation wavelength.

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REVIEW

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Zn(II)-coordination modulated ligand photophysical processes – the development of fluorescent indicators for imaging biological Zn(II) ions

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Molecular photophysics and metal coordination chemistry are the two fundamental pillars that support the development of fluorescent cation indicators. In this article, we describe how Zn(II)-coordination alters various ligand-centered photophysical processes that are pertinent to developing Zn(II) indicators. The main aim is to show how small organic Zn(II) indicators work under the constraints of specific requirements, including Zn(II) detection range, photophysical requirements such as excitation energy and emission color, temporal and spatial resolutions in a heterogeneous intracellular environment, and fluorescence response selectivity between similar cations such as Zn(II) and Cd(II). In the last section, the biological questions that fluorescent Zn(II) indicators help to answer are described, which have been motivating and challenging this field of research.

1. The impact of this line of research

1-1. The impact on chemistry

All molecules in the singlet excited state fluoresce, until non-radiative decay pathways kinetically outcompete fluorescence emission. These pathways (Fig. 1) include internal conversion (IC), intersystem crossing (ISC), and photoisomerization, as well as inter- or intramolecular electron transfer, (e^-T), energy transfer (E_nT), and proton transfer (PT). The fluorescence quantum yield (ϕ_{FL}) and excited state lifetime (τ_{EX}) of a fluorophore are functions of these processes, as shown in eqn (1) and (2), respectively. The rates of these processes are sensitive to environmental factors and specific molecular interactions available to the fluorophore (Fig. 1). Temperature (T), ionic strength (I), dielectric constant (ε), and viscosity (η) are bulk environmental properties. The effects of these factors on the excited and ground state properties reveal the conformational and electronic structural information of a fluorophore. The specific abilities of a molecule to form hydrogen bond with solvent molecules, to form

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Distinguishing Förster resonance energy transfer and solvent-mediated charge-transfer relaxation dynamics in a zinc(II) indicator: a femtosecond time-resolved transient absorption spectroscopic study†

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A bifluorophoric molecule (1) capable of intramolecular Förster Resonance Energy Transfer (FRET) is reported. The emission intensity of the FRET acceptor in 1 depends on the molar absorptivity of the donor, which is a function of zinc(II) complexation. The FRET dynamics of $[Zn(1)](ClO_4)_2$ is characterized by femtosecond time-resolved transient absorption spectroscopy. The solvent-mediated relaxation of the charge-transfer (CT) state of the isolated donor and the FRET process of the donor–acceptor conjugate are on similar time scales (40–50 ps in CH_3CN), but distinguishable by the opposite solvent polarity dependency. As the solvent polarity increases, the efficiency of Columbic-based FRET is reduced, whereas CT relaxation is accelerated. In addition to revealing a method to distinguish CT and FRET dynamics, this work provides a photophysical foundation for developing indicators based on the FRET strategy.

We outline a strategy of developing fluorescent indicators for zinc(II) ions based on Förster Resonance Energy Transfer (FRET).[1] This paper focuses on the characterization of an intramolecular FRET process in a zinc(II) complex by femtosecond time-resolved transient absorption spectroscopy. In particular, a method is reported to distinguish FRET and solvent-mediated relaxation of charge-transfer (CT) state of the FRET donor that have similar time constants. The utility of the indicators developed based on this strategy in fluorescence microscopic imaging will be described in a later report.

The rate of FRET (k_{FRET}) as represented in the Förster formulism (eqn (1))[2] is a function of the distance between the energy donor and acceptor (r), the spectral overlap integral between the donor emission and the acceptor absorption spectra ($J(\lambda)$), the orientation factor (κ) associated with the dipole–dipole interaction between the donor and the acceptor,[3] the fluorescence quantum yield of the donor in the absence of an acceptor (ϕ_D), and the refractive index of the medium (η), which relates to dielectric constant ε as shown in eqn (2). The efficiency of FRET (E) can be determined quantitatively from time-domain measurements (eqn (3)), where τ_D is the lifetime of the donor in the absence of an acceptor, and τ_{DA} is the time constant for energy transfer in the donor–acceptor complex. As a ramification of the Förster formulism, changing the donor–acceptor distance (r)[4,5] or the spectral overlap integral ($J(\lambda)$)[6–8] via analyte binding has been employed in developing fluorescent indicators. Herein, we provide a strategy for an analyte to trigger the enhancement of the acceptor fluorescence, when the values of r and $J(\lambda)$ are relatively *insensitive* to analyte binding. The ultrafast FRET dynamics is characterized by femtosecond time-resolved transient absorption spectroscopy, in which a solvent polarity dependency is shown to distinguish the dynamics of CT and FRET on similar time scales.

$$k_{FRET} = \text{constant} \cdot \frac{\kappa^2 \cdot J(\lambda) \cdot \phi_D}{r^6 \cdot \eta^4 \cdot \tau_D} \quad (1)$$

$$\eta^2 = \varepsilon \quad (2)$$

$$E = 1 - \frac{\tau_{DA}}{\tau_D} \quad (3)$$

When a CT-type fluorophore is selected as the FRET donor in a bifluorophoric molecule, the acceptor emission intensity at a fixed excitation wavelength may become a function of the concentration of an analyte that alters the absorption and/or emission of the donor upon formation of a complex. For example, if the analyte binding increases the molar absorptivity of the donor at the excitation wavelength while r and $J(\lambda)$ are barely altered, the acceptor emission is expected to increase as a function of the analyte concentration.

Compound 1 (Chart 1) is reported herein as an example to illustrate the aforementioned strategy. This compound is a conjugate of zinc(II)-binding arylvinylbipyridyl FRET donor moiety (blue) and BODIPY fluorophore as the FRET acceptor (green). Compound 2 is the isolated FRET donor of the CT type, whose absorption and emission spectra shift bathochromically upon zinc(II) complex formation.[9] Compound 3 is the isolated

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Absorption and Emission Sensitivity of 2-(2'-Hydroxyphenyl)benzoxazole to Solvents and Impurities[†]

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Copper-Catalyzed Oxidation

Dual Role of Acetate in Copper(II) Acetate Catalyzed Dehydrogenation of Chelating Aromatic Secondary Amines: A Kinetic Case Study of Copper-Catalyzed Oxidation Reactions

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Abstract: Copper(II) acetate is a frequent empirical choice of the copper source in copper(II)-mediated redox reactions. The effect of the acetate counterion appears crucial but has not been adequately investigated. Herein, we report that copper(II) acetate catalyzes the aerobic dehydrogenation of chelating aromatic secondary amines. The chemoselectivity of acetate and chelating amines in this reaction provides a unique opportunity for a mechanistic study. The progression of this homogeneous reaction is monitored by using electron paramagnetic resonance spectroscopy, UV/Vis absorption spectroscopy, and manometry. The kinetic dependence on the amine substrate, copper(II), and acetate counterion, together with the results of kinetic isotope and substituent effect experiments, suggests that acetate acts both as a bridging ligand of a dinuclear catalytic center for mediating two-electron transfer steps and as a base in the turnover-limiting C–H bond-cleavage step. Upon including 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a surrogate base, DBU and acetate act in a complementary manner to enable a rapid, catalytic dehydrogenation reaction of a chelating secondary amine substrate. Finally, the contrasting reactivities between copper(II) acetate (promoting two-electron transfer) and copper(II) perchlorate (promoting single-electron transfer) underscores how a counterion could completely alter the mechanistic pathway of a copper-mediated oxidation reaction.

Introduction

The prevalence of +1 and +2 oxidation states of copper ensures that copper salts are effective single-electron transfer mediators in radical-involved organic transformations.[1] The majority of organic redox elementary reactions, on the other hand, entail two-electron transfer processes, of which palladium, an excellent two-electron transfer mediator but a much less-abundant element than copper, has been a major source of catalyst development.[2] The two-electron shuttling between the +1 and +3 oxidation states of a mononuclear copper center is implicated in a growing number of copper-involved reactions,[3] notably in Gilman chemistry,[3b,4] Ullmann cross-coupling,[5] and C–H functionalization reactions.[6] The ability of mononuclear copper to engage in both single- and two-electron transfer reactions was recently described by Stahl, Ribas, and co-workers.[5b,7] However, mononuclear copper(III) species have only been observed in a handful cases in which a stabilizing macrocyclic ligand[6a,6b,8] was often present,[3c,9] which casts doubt on its generality in the rapidly growing number of reported copper-mediated redox reactions.

Dinuclear copper centers are capable of mediating two-electron transfer processes through collective redox switching between the +1 and +2 oxidation states. A dicopper center may lower the activation barrier of two-electron transfer steps, similar to the cases demonstrated in dipalladium[10] and digold chemistry,[11] which would circumvent the relatively unstable mononuclear copper(III) intermediates. The utility of di- or multinuclear copper clusters in catalytic aerobic oxidation has been recognized by the inorganic and bioinorganic communities.[12] As a result, elaborated ligand-supported multinuclear complexes have been created to mimic the functions of copper-dependent oxidases and oxygenases.[13] However, the potential of dinuclear (or multinuclear) copper redox catalysis has not yet been fully materialized in synthetic chemistry development. Furthermore, copper-catalyzed oxidation methods have been developed at a rapid rate;[1b,1c,14] yet, the mechanistic clarifications of these reactions are disproportionally lagging behind.

In our investigation on the mechanism of copper(II) acetate mediated azide–alkyne cycloaddition (CuAAC) reactions,[15] we offered evidence and arguments that the copper(II) acetate dimer $[Cu_2(OAc)_4(H_2O)_2]$ mediates the inducting alkyne oxidative homocoupling (OHC)[16] stoichiometrically and the subsequent CuAAC reaction catalytically. The currently accepted mechanistic models of both OHC[16,17] and CuAAC[15,18] include copper-catalyzed two-electron transfer steps. Copper(II) acetate equilibrates in solution between monomeric and dimeric forms, depending on the solvent and additional ligand structures.[19] Given the frequent empirical choice of copper(II) acetate in copper-mediated oxidation reactions,[1c,7a,14,16,20] it is likely that the acetate-bridged dinuclear copper(II) core acts as a two-electron

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Fluorescence Imaging

A Fluorescent Indicator for Imaging Lysosomal Zinc(II) with Förster Resonance Energy Transfer (FRET)-Enhanced Photostability and a Narrow Band of Emission

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Abstract: We demonstrate a strategy to transfer the zinc(II) sensitivity of a fluoroionophore with low photostability and a broad emission band to a bright and photostable fluorophore with a narrow emission band. The two fluorophores are covalently connected to afford an intramolecular Förster resonance energy transfer (FRET) conjugate. The FRET donor in the conjugate is a zinc(II)-sensitive arylvinylbipyridyl fluoroionophore, the absorption and emission of which undergo bathochromic shifts upon zinc(II) coordination. When the FRET donor is excited, efficient intramolecular energy transfer occurs to result in the emission of the acceptor boron dipyrromethene (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene or BODIPY) as a function of zinc(II) concentration. The broad emission band of the donor/zinc(II) complex is transformed into the strong, narrow emission band of the BODIPY acceptor in the FRET conjugates, which can be captured within the narrow emission window that is preferred for multicolor imaging experiments. In addition to competing with other nonradiative decay processes of the FRET donor, the rapid intramolecular FRET of the excited FRET-conjugate molecule protects the donor fluorophore from photobleaching, thus enhancing the photostability of the indicator. FRET conjugates **3** and **4** contain aliphatic amino groups, which selectively target lysosomes in mammalian cells. This subcellular localization preference was verified by using confocal fluorescence microscopy, which also shows the zinc(II)-enhanced emission of **3** and **4** in lysosomes. It was further shown using two-color structured illumination microscopy (SIM), which is capable of extending the lateral resolution over the Abbe diffraction limit by a factor of two, that the morpholino-functionalized compound **4** localizes in the interior of lysosomes, rather than anchoring on the lysosomal membranes, of live HeLa cells.

Introduction

Motivated by the relevance of zinc(II) biology to human health and driven by the need for tools to follow zinc(II) distribution and dynamics in metabolically active cellular and tissue specimens, many fluorescent indicators for zinc(II) have been developed.[1] Of the large number of the reported molecules that undergo zinc(II)-sensitive fluorescence modulation, a relatively small fraction has been used in biological imaging experiments. Therefore, in addition to having emission characteristics (intensity, quantum yield, lifetime, and so forth) that are functions of zinc(II) concentration under physiologically relevant conditions, there are other benchmarks that need to be met for an indicator molecule to be optimally effective in biological fluorescence imaging experiments.

The two relevant issues that this work aims to address are the broadness of the emission band and the low photostability of certain zinc(II)-sensitive fluorophores. A broad emission band diminishes the usefulness of a dye in multicolor imaging. Low photostability reduces the applicability of the indicator in time-course experiments. These two issues could be addressed by the molecular construct depicted in Figure 1.

The molecular construct in Figure 1 contains two fluorophores, between which zinc(II)-dependent intramolecular Förster resonance energy transfer (FRET) occurs. The arylvinylbipyridyl FRET donor typifies a zinc(II)-sensitive fluoroionophore with a broad emission band and low photostability. A "high-performance" dye by the criteria of biological fluorescence imaging experiments shall be selected as the FRET acceptor, which absorbs the excitation energy of the donor to 1) transform a broad donor emission into a narrow, strong emission of the acceptor, and 2) protect the donor from photo-

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Intense red line emitting phosphor $LuNbO_4:Eu^{3+}$ for white light emitting diode applications

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ABSTRACT

$LuNbO_4:xEu^{3+}$ ($x=0$, 0.03, 0.1 and 0.15) red phosphors were prepared through a conventional solid state method. Powder X-ray diffraction patterns and Raman studies confirm the monoclinic fergusonite phase of Eu^{3+} doped phosphors. In $LuNbO_4:xEu^{3+}$, overlap of host lattice emission spectra with the Eu^{3+} $^7F_0-{}^5L_6$ transitions resulted in strong near UV excitation around 394 nm. Eu^{3+} ions give strong electric dipole transition dominant red emission at ~613 nm ($\lambda_{ex}=394$ nm) as it occupies a non-centrosymmetric site in fergusonite $LuNbO_4$, and the emission intensity is double that of commercial $Y_2O_3:Eu^{3+}$ phosphor.

1. Introduction

Solid state lighting, the next generation lighting technology still requires efficient, stable, intense narrow emitting red phosphors that can be excited under near UV (~395 nm) or blue light (~465 nm) to meet high colour rendering index (CRI) and luminous efficacy [1]. Most of the current red phosphors are based on Eu^{2+} ions in different hosts like nitrides, silicates and oxides whose emission is very broad and strongly depend on the local crystal field of the surrounding ions in the lattice [1,2]. An undesirable consequence of this broad emission is deep red emission to which the eye is insensitive. Tsao et al. have shown that the maximum theoretical efficacy for a solid state lamp with correlated colour temperature (CCT) of 3800 K and CRI of 85 is 400 lm/W [3]. This can be achieved with four monochromatic sources around 459 nm (blue), 535 nm (green), 573 nm (yellow), and 614 nm (red). This requirement generated a lot of interest in Eu^{3+} doped red phosphors as they have sharp intraconfigurational $^5D_0-{}^7F_2$ transitions in ~610 nm red region and have *f–f* excitation peaks in near UV (due to $^7F_0-{}^5L_6$ transitions) and blue (due to $^7F_0-{}^5D_2$ transitions) regions. Once excited, they relax via non-radiative transitions to $^5D_0$ states, from there only radiative return to the ground state is possible (^7F_J). When Eu^{3+} ions locate in a non-centro symmetric site in a host lattice out of various $^5D_0-{}^7F_J$ transitions, $^5D_0-{}^7F_2$ elctric dipole (ED) transition dominates over others [4]. As band gap between $^5D_0$ level and the highest component of the ground state multiplet (^7F_J) is very high, they can then give highly intense narrow red band emissions. So there is immense interest on Eu^{3+} doped red phosphors for which the narrower the red emission, the better will be the CRI [3,5,6].

In scheelite host compounds Eu^{3+} doping usually give intense *4f–4f* transitions. So scheelite based red phosphors have been thoroughly investigated [7,8]. But fergusonite structure which can be treated as a distorted scheelite structure has not yet been well investigated for solid state lighting applications except a few studies in $LnNbO_4:Eu^{3+}$ Ln=Y, La, Gd [9]. Monoclinic fergusonite structure having the general formula ABO_4 can change to a tetragonal scheelite structure depending on the temperature [10]. As in scheelite structure the A-site cation is coordinated to 8 oxygen atoms, but the B-site is not tetrahedrally coordinated to oxygen atoms but have 6 oxygen neighbours [11]. In the isostructural series, Lu^{3+} has the smallest ionic radius and because of this $LuNbO_4$ has a dense packing of NbO_4^{-3} units, which enables them as potential hosts for thermal stability and narrow emission phosphors [12]. However, there is a sparse investigation on their luminescence properties. In the present paper, an attempt has been made to study their luminescence properties under near UV region for their potentiality as a narrow red emission phosphor for the phosphor converted white light emitting diode (pc-WLED) applications.

2. Experimental procedure

The powder samples of $LuNbO_4:xEu^{3+}$ ($x=0$, 0.03, 0.1 and 0.15) were prepared through a conventional solid state method. Stoichiometric amounts of Lu_2O_3, Eu_2O_3 and Nb_2O_5 (All chemicals are from Acros Organics with 99.9% purity) were weighed and thoroughly mixed in an agate mortar using acetone as the mixing medium. The homogeneous mixtures thus obtained were calcined at 1300 °C for 6 h.

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X-Ray powder diffraction (XRD) analysis was performed with a PANalytical X'Pert Pro diffractometer having Ni filtered Cu-Kα radiation with a X-ray tube operating at 40 kV, 30 mA and 2θ varied from 10 to 90° in 0.016° steps. Raman spectra were recorded using a HR800 LabRAM confocal Raman spectrometer operating at 20 mW laser power equipped with a peltier cooled CCD detector. Samples were excited using a He–Ne laser source having an excitation wavelength of 632.8 nm and with an acquisition time of 5 seconds using a 50× microscope objective. The morphology of powder particles was studied by a scanning electron microscope (JEOL, JSM-5600LV) operated at 15 kV. The photoluminescence data of the prepared samples were obtained using a Spex-Fluorolog DM3000F spectrofluorimeter with a 450 W xenon flash lamp as the exciting source.

3. Results and discussion

Structural characterisation: Fig. 1 shows the powder XRD patterns of $LuNbO_4$:xEu^{3+} (x=0, 0.03, 0.1 and 0.15) phosphors. All the peaks can be indexed using the monoclinic fergusonite-type structure with a space group I2/a (space group number 15). As the ionic radius of Nb^{5+} (0.64 Å, CN6) is very low compared with Eu^{3+} (1.066 Å, CN8), Eu^{3+} is expected to replace Lu^{3+} (0.977 Å, CN8) ions. No impurity peaks are observed with increase in doping concentration so Eu^{3+} ions can effectively replace Lu^{3+} ions in $LuNbO_4$:xEu^{3+} phosphors. The morphology of the synthesised particles was characterised by SEM. The SEM images of $LuNbO_4$:xEu^{3+} (Fig. S1 in Supporting information) show good crystalline particles having 1–4 μ size which are suitable for the fabrication of solid state lighting devices.

Raman spectra of the phosphors were recorded to further confirm the crystalline structure as well as any structural differences with Eu^{3+} substitution. Based on the crystal structure data two Nb-O symmetric modes, ν_1 (singlet) and ν_2 (doublet) and two Nb-O antisymmetric modes ν_3 and ν_4 (both triplet) are observed (Fig. S2 in Supporting information). The modes are observed at higher wave numbers than that of the other rare earth ortho-niobates [13]. This observation infers the closer packing of the NbO_4^{3-} units as the reduction of Nb–O distances to yield higher frequencies for smaller rare earth ions. This type of stiff lattice is ideal for phosphor hosts which reduce the nonradiative path ways which improves the efficiency of phosphor.

Photoluminescence studies: Excitation spectra of $LuNbO_4$:xEu^{3+} (x=0.03, 0.1 and 0.15) phosphors shown in Fig. 2 have a broad

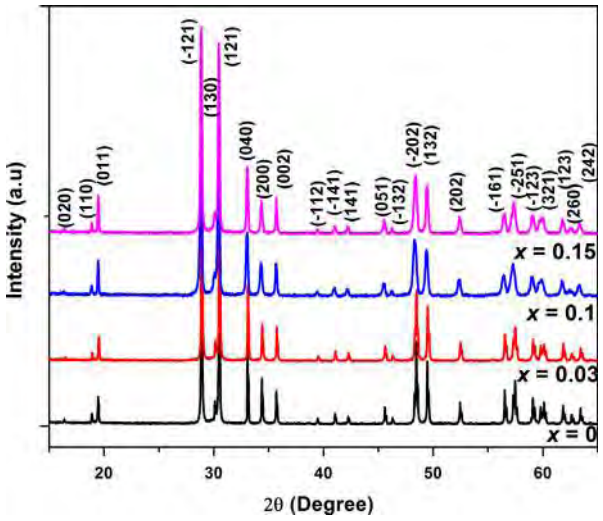

Fig. 1. Powder XRD patterns of $LuNbO_4$:xEu^{3+} (x=0, 0.03, 0.1 and 0.15).

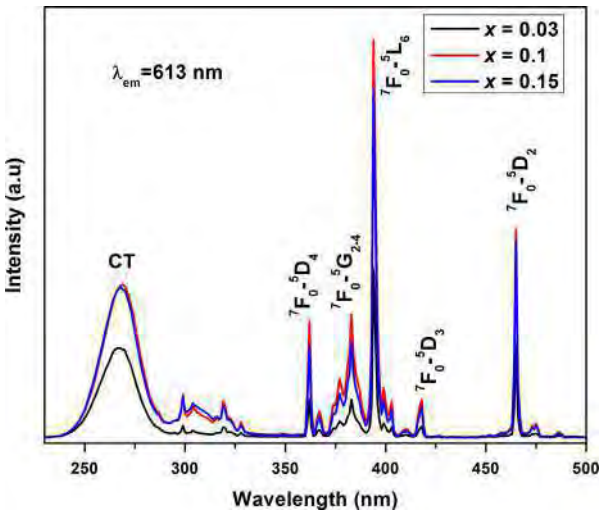

Fig. 2. Excitation (λ_{em}=613 nm) spectra of $LuNbO_4$:xEu^{3+} (x=0.03, 0.1 and 0.15) phosphors.

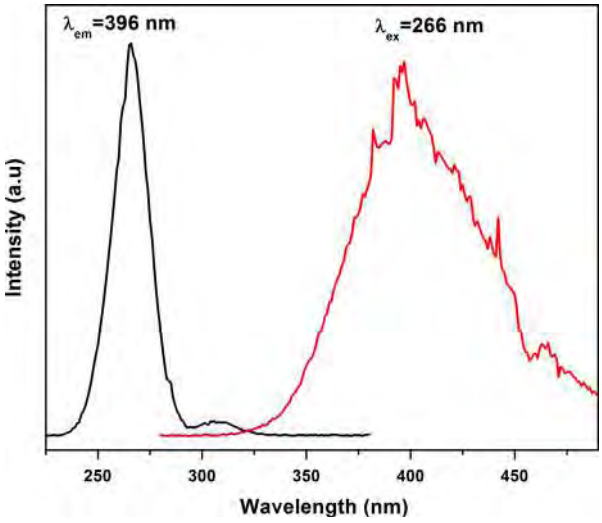

Fig. 3. Excitation (λ_{em}=396 nm) and emission (λ_{ex}=266 nm) spectra of $LuNbO_4$ host lattice.

charge transfer band around 268 nm. This band is due to charge transfer (CT) from 2*p* orbital of oxygen ions to the empty 4*d* orbitals of Nb^{5+} and to the 4*f* orbitals of Eu^{3+} [13]. CT band maximum of reported $LaNbO_4$:Eu^{3+} is at ~271 nm [9]. CT band maxima of $LuNbO_4$:Eu^{3+} phosphors show a small blue shift in comparison with $LaNbO_4$:Eu^{3+} phosphors. The lower ionic radius and higher electronegativity of Lu^{3+} ions in comparison with La^{3+} can lead to stronger binding of oxygen ligand by the A-cations and hence shifted to higher CT band energy [10]. The other sharp peaks in the excitation spectra are due to intra-configurational *f*–*f* transitions [4]. The highly intense $^7F_0-{}^5L_6$ and $^7F_0-{}^5D_2$ transitions in the excitation spectra have much importance as these transitions match with the emission wavelengths of near-UV and blue LED chips of pc-WLEDs. Excitation and emission spectra of neat host lattice $LuNbO_4$ are given in Fig. 3. The NbO_6^{7-} group shows a broad emission around 396 nm under 266 nm excitation. As the emission spectra of host lattice have spectral overlap with the Eu^{3+} $^7F_0-{}^5L_6$ transitions it seems that host lattice can effectively transfer their absorption energy to activator ions and can enhance the luminescence properties. This may be the reason for highly intense $^7F_0-{}^5L_6$ excitation peaks in $LuNbO_4$:xEu^{3+} phosphors.

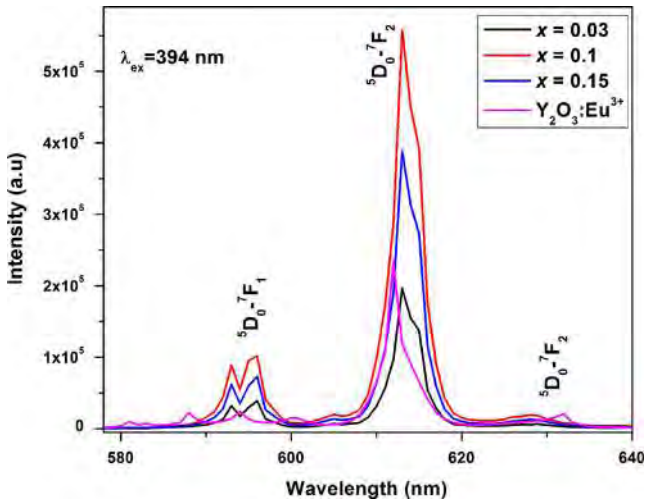

Fig. 4. Emission (λ_{ex}=394 nm) spectra of $LuNbO_4$:xEu^{3+} (x=0.03, 0.1 and 0.15) and commercial Y_2O_3:Eu^{3+} phosphors.

The emission spectra of $LuNbO_4$:xEu^{3+} along with commercial Y_2O_3:Eu^{3+} red phosphors excited under 394 nm are shown in Fig. 4. In $LuNbO_4$:xEu^{3+}, Eu^{3+} is expected to replace smaller Lu^{3+} ions (based on ionic size consideration and charge neutrality) in a C_2 non-centro symmetric site and hence creates a large distortion around Eu^{3+} ions [13]. As a result, ED transition will dominate over MD transition and will result in narrow red emission and the asymmetric ratio (intensity of $^5D_0$-$^7F_2$/intensity of $^5D_0-{}^7F_1$) will be high. For $LuNbO_4$:xEu^{3+} phosphors the asymmetric ratio is ~5. With the increase in Eu^{3+} doping the emission intensity increases and reaches a maximum for 10 mol% doping after that quenching of luminescence is observed. The $LuNbO_4$:0.1 Eu^{3+} red phosphor gives 2.4 times intense red emission than commercial Y_2O_3:Eu^{3+} red phosphor under near-UV excitation. The *fwhm* of $LuNbO_4$:0.1Eu^{3+} phosphor is 3.9 nm which is a very good characteristic for colour purity and improving efficacy of LED. The obtained chromaticity coordinates (0.64, 0.34) are comparable with NTSC standard.

4. Conclusions

In the present work, $LuNbO_4$:xEu^{3+} (x=0.03, 0.1 and 0.15) phosphors were prepared by the solid state reaction at 1300 °C. These phosphors show intense red emission corresponding to $^5D_0-{}^7F_2$ transition of Eu^{3+} ion under 394 nm near-UV excitation. The optimum Eu^{3+} concentration is 10 mol% after that concentration quenching occurs. The emission spectra (λ_{ex}=394 nm) shows intense $^5D_0-{}^7F_2$ transition around 613 nm having full width half maxima ~4 nm. As the present narrow red emission phosphors have better emission intensity in comparison with Y_2O_3:Eu^{3+}, they might be a promising red phosphor for pc-WLEDs.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.01.045.

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Effect of Zr^{4+} and Si^{4+} substitution on the luminescence properties of $CaMoO_4:Eu^{3+}$ red phosphors

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Abstract A series of intense red emitting phosphors, $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4:0.2Eu^{3+}$ ($x = 0.025$, 0.05, 0.075, 0.1) that could be effectively excited in the UV region was prepared by conventional high temperature solid state reaction route. Structural, morphological and photoluminescence properties of the prepared samples were studied in detail. The incorporation of Zr^{4+} and Si^{4+} ions in $CaMoO_4$ lattice maintained the powellite crystal structure. Luminescence properties were optimized for 7.5 mol% of Zr^{4+} and Si^{4+} concentration. Emission intensities improved more than twice in comparison with $CaMoO_4:Eu^{3+}$. Life times of the prepared samples improved and the quantum efficiency enhanced to ~39 %. The improvement in emission intensity and quantum efficiency is explained in terms of the local distortion around the Eu^{3+} ions resulting in improved absorption in the UV region. The CIE color co-ordinates of the red emission were in agreement with the values of the standard red phosphors providing potentiality to be used in phosphor converted (pc) white LEDs.

1 Introduction

A novel red phosphor material that can be effectively excited in the near UV and visible region with good absorption and emission properties, good thermal and chemical stability and high quantum yield is of great demand in the solid state lighting applications particularly in the development of pc-white LEDs [1, 2]. Molybdates with powellite structure are reported as good host lattices under near UV/blue excitation because of high chemical stability, broad and intense charge transfer (CT) band arising from MoO_4 tetrahedron unit in the near UV region and the capability of efficiently capturing radiation from a GaN based LED [3]. Intra configurational f–f transitions of trivalent europium (Eu^{3+}) ions resulting in the red luminescence are of technological importance [4]. $CaMoO_4:Eu^{3+}$ is a potentially attractive candidate as a superior red phosphor because of its efficient absorbtion under near-UV excitation, satisfactory chromaticity coordinates and excellent stability [5]. Many works were reported on the improvement of luminescent properties of $CaMoO_4:Eu^{3+}$ phosphors by various charge compensation using Li^+, K^+, Na^+ etc. and by codoping of ions like Bi^{3+} [6–8]. Quantum efficiency of $CaMoO_4:Eu^{3+}$ was reported to be 12.78 and 21–23 % via hydrothermal synthesis and sol–gel reaction routes respectively [9, 10]. However, its red emission intensity and quantum efficiency still needs to be improved at the application point of view. As the luminescent performance of Eu^{3+} is deeply affected by the crystal field factors such as structural distortion and symmetry, the incorporation of slightly smaller ions like Zr^{4+} and Si^{4+} in place of Ca^{2+} and Mo^{6+} ions may result in some structural adjustment enhancing the red emission. Substitution of the Ca^{2+} site with Eu^{3+} ions results in a net positive charge. In general, the positive charges can be compensated by either cation vacancies or oxygen interstitials [11]. Substitution of Zr^{4+} in the Ca^{2+} site creates a more positive charge effect in the A site which alters the environment around the luminescent Eu^{3+} in turn affecting the luminescence

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behavior [12]. The equivalent substitution of Si^{4+} ion at the Mo^{6+} site compensates the valency of the crystal lattice. In addition literature also shows that SiO_2 groups strongly absorb excitation energy in the UV and near-UV regions [13].

In the present work we made an attempt to enhance the photoluminescence properties by substitution of Zr^{4+} and Si^{4+} in $CaMoO_4$:Eu^{3+} phosphors without altering the crystal structure. In earlier reports Eu^{3+} doping concentration in $CaMoO_4$ system is optimized as 20 mol% [14]. Thus we choose $Ca_{0.8}MoO_4$:$0.2Eu^{3+}$ phosphors and Zr^{4+} and Si^{4+} were substituted in various concentrations and accordingly $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4$:$0.2Eu^{3+}$ ($x = 0.025$, 0.05, 0.075, 0.1) phosphors were synthesized. The structural, morphological and photoluminescence characterizations of the prepared samples were carried out and the results are presented in this paper.

2 Experimental

The phosphors $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4$:$0.2Eu^{3+}$ ($x = 0.025$, 0.05, 0.075, 0.1) were prepared by a high temperature solid state reaction route. $CaCO_3$, ZrO_2, MoO_3, SiO_2 and Eu_2O_3 (Sigma Aldrich, 99.99 %) were used as the starting materials. Chemicals were weighed in the stoichiometric ratio and then finely ground and mixed in an agate mortar. Mixing was carried out in acetone medium with intermittent drying. The procedure of mixing and subsequent drying was repeated three times so as to obtain a homogeneous mixture. This mixture was made into a pellet and then calcined on an alumina plate at 1,200 °C for 6 h. The calcined pellet was ground into fine powder for characterization.

The crystalline structure and phase purity of the samples were examined by recording XRD patterns using a powder X-ray diffractometer (X'Pert Pro PANalytical) operated at 40 kV/30 mA with a Ni filtered Cu-Kα radiation ($\lambda = 0.15406$ nm) in the 2θ range from 10° to 90°. The structure refinement of the XRD patterns was further performed by the Rietveld analysis using the X'pert Highscore plus program. Morphological studies of powder particles were done by a scanning electron microscope (JEOL, JSM-5600LV) operated at 15 kV. EDS spectra was also recorded to identify the elements present. The excitation and emission spectra were recorded on a Fluorolog HORIBA fluorescence spectrophotometer with a Xe lamp (450 W) as the excitation source. Luminescence life time of the phosphors was recorded by the phosphorimeter attached to Fluorolog®3 spectrofluorimeter. CIE chromaticity coordinates was also calculated using software CIE calculator. All the measurements were carried out at room temperature.

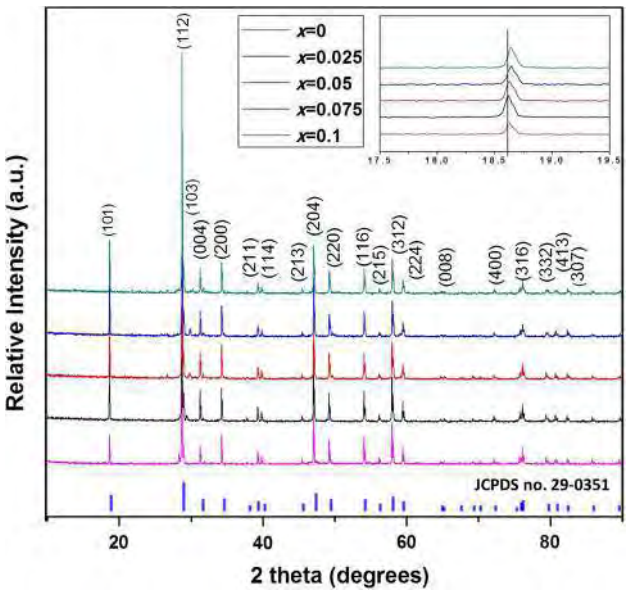

Fig. 1 Powder X-ray diffraction patterns of $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4$:$0.2Eu^{3+}$ ($x = 0.025$, 0.05, 0.075, 0.1) and reference pattern (JCPDS No. 29-0351)

3 Results and discussion

3.1 Structural studies

Powder X-ray diffraction patterns of the samples are given in Fig. 1. All the samples were in good agreement with the reported diffraction pattern of $CaMoO_4$ (JCPDS no. 29-0351; tetragonal powellite; space group $I4_1/a$). No extra peaks from impurities were observed and samples are highly crystalline. The prominent peaks corresponding to (112), (004), (200), (204), (220), (116) and (312) lattice planes are observed.

Rietveld refinement of all the samples was carried out using X'Pert Plus program. The starting model for the refinement of the phases was taken from the reported crystal structure of $CaMoO_4$ [15]. Ca, Eu and Zr are at (4b: 0, 1/4, 5/8) sites, Mo and Si at (4a : 0, 1/4, 1/8) sites and O at (16f : x, y, z). With the increasing Zr^{4+} (Co-ordination number CN = 8, Ionic radius: 0.84 Å) and Si^{4+} (CN = 6, Ionic radius: 0.4 Å) substitution in place of Ca^{2+} (CN = 8, Ionic radius: 1.12 Å) and Mo^{6+} (CN = 6, Ionic radius: 0.59 Å) ions the lattice volume was found to decrease indicating the incorporation of Zr^{4+} and Si^{4+} ions into the lattice [16]. The lattice volume was found to be 313.09, 313.03, 312.96 and 312.9 $[Å]^3$ with increasing Zr^{4+} and Si^{4+} ion substitution for $x = 0.025$–0.1 concentrations. Further the shift in the XRD peaks towards the higher angle side as shown in the inset of Fig. 1 clearly reveals the substitution of smaller Zr^{4+} and Si^{4+} ions into the lattice.

Table 1 Variation of lattice parameters, R-factors, and other parameters obtained from Rietveld analysis

Sample	$x = 0.025$	$x = 0.05$	$x = 0.075$	$x = 0.1$
Flat background	34.6601	35.05621	34.69736	36.93279
Coefficient 1	−14.3386	−14.4442	−13.2699	−14.0883
Coefficient 2	14.05791	14.09839	13.04401	12.48639
Scale Factor	0.00004	0.00004	0.000038	0.00004
Lattice parameters				
a [Å]	5.2328(8)	5.231(1)	5.231(1)	5.230(1)
b [Å]	5.2328(8)	5.231(1)	5.231(1)	5.230(1)
c [Å]	11.434(2)	11.435(2)	11.436(2)	11.437(3)
Caglioti parameters				
U	0.005448	0.010239	0.012526	0.020061
V	0.005642	0.008045	0.005507	0.005478
W	0.000899	0.000375	0.001234	0.000659
Asymmetry parameter	0	0	0	0
Peak Shape 1	0.630373	0.720364	0.669939	0.820141
Peak Shape 2	0.004303	0.001124	0.002733	−0.00072
Residual parameters				
Rexp (%)	13.66	13.65	13.82	13.54
Rp (%)	12.23	12.88	13.52	12.47
Rwp (%)	15.75	16.65	17.40	16.14
GOF	1.32	1.48	1.58	1.41

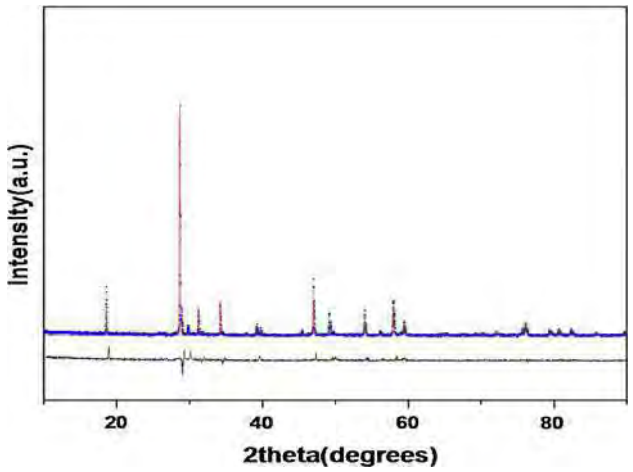

Fig. 2 Observed (*points*), calculated (*continuous line*) and the difference (*bottom line*) powder X-ray diffraction patterns of $Ca_{0.7}Zr_{0.1}Mo_{0.9}Si_{0.1}O_4$:$0.2Eu^{3+}$

Variation of lattice parameters, R-factors, and other parameters obtained from Rietveld analysis of all the samples are given in Table 1. The observed, calculated and the difference powder diffraction profiles of a typical sample is given in Fig. 2.

3.2 Morphological studies

Typical SEM photographs recorded for $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4$:$0.2Eu^{3+}$ ($x = 0.025$, 0.05, 0.075, 0.1) powders are given in Fig. 3. All the samples show particles in 5–8 μ size range. Some aggregation of particles is seen in the SEM micrographs. EDS spectra of typical Zr^{4+} and Si^{4+} substituted and un-substituted $CaMoO_4$:$0.2Eu^{3+}$ samples are given in the Fig. 4. The incorporation of zirconium and silicon ions into the $CaMoO_4$ matrix can be clearly understood from the Fig. 4a when compared to the spectra of un-substituted compound in Fig. 4b.

3.3 Photoluminescence studies

Photoluminescence excitation spectrum of the samples for an emission at 615 nm is given in Fig. 5. The spectrum includes a broad CT band from 250 nm to 350 nm assigned to the redistribution of charge density from 2p orbit of O^{2-} to 4d and 4f molecular orbit of Mo^{6+} and Eu^{3+} [17]. Intense peaks at 395 and 465 nm corresponding to the intra configurational 4f–4f transitions of Eu^{3+} ions in the host lattice, assigned to $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions, respectively [18]. With increasing Zr^{4+} and Si^{4+} concentration, a slight red shift of the CT band and increase in CTB intensity and subsequent increase in the intensity of $^7F_0 \rightarrow {}^5L_6$ transition is observed.

The emission spectra of $Ca_{0.725}Zr_{0.075}Mo_{0.925}Si_{0.075}O_4$:$0.2Eu^{3+}$ phosphor under 395 nm excitation is shown in Fig. 6. The spectrum includes weak orange emission located at around 591 nm owing to the magnetic dipole transition $^5D_0$–$^7F_1$ which is usually insensitive to site

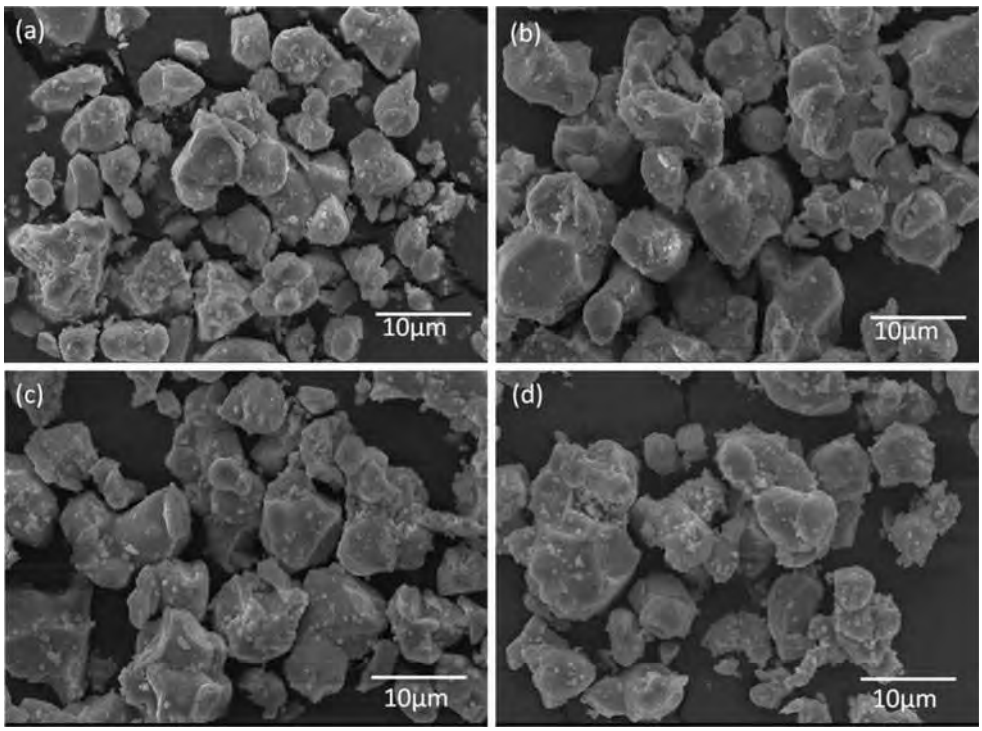

Fig. 3 Scanning electron micrographs of $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4$:0.2$Eu^{3+}$ *a* $x = 0.025$, *b* $x = 0.05$, *c* $x = 0.075$, *d* $x = 0.1$

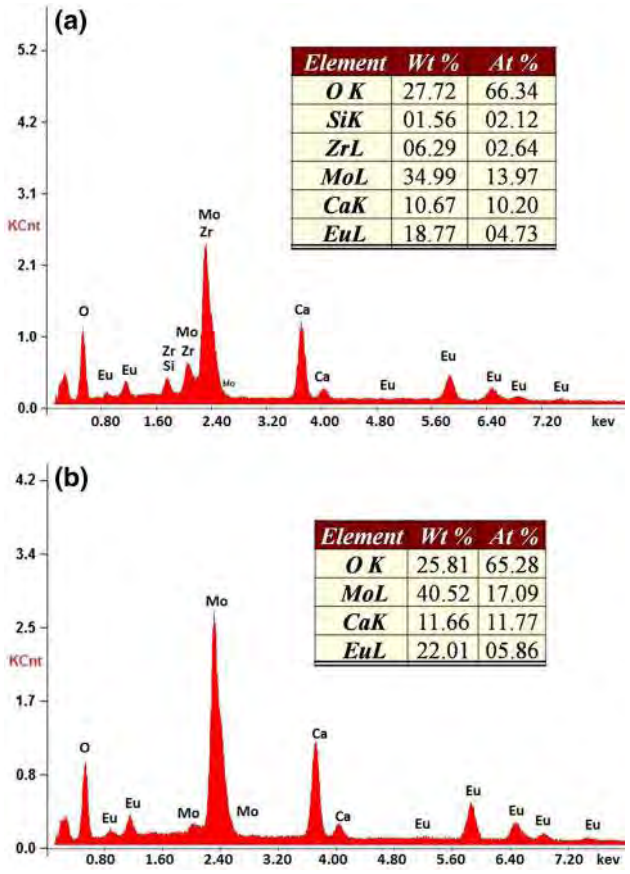

Fig. 4 EDS spectra of the representative samples. **a** $Ca_{0.7}Zr_{0.1}Mo_{0.9}Si_{0.1}O_4$:0.2$Eu^{3+}$, **b** $Ca_{0.8}MoO_4$:0.2Eu^{3+}

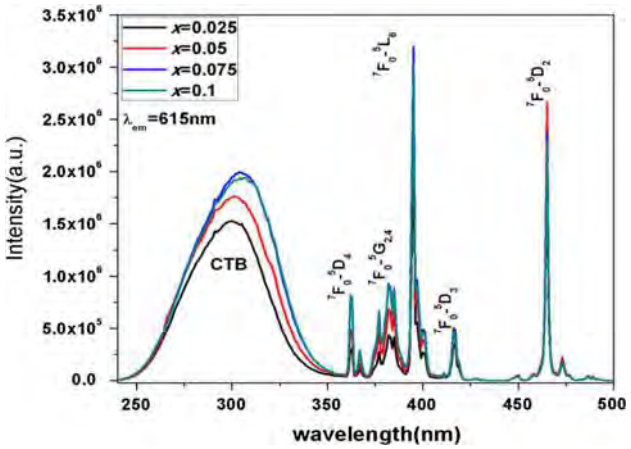

Fig. 5 Photoluminescence excitation spectra of $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4$:0.2$Eu^{3+}$ ($x = 0.025, 0.05, 0.075, 0.1$) for 615 nm emission

symmetries. Strong emission lines observed at 612 and 615 nm results from electric dipole transition $^5D_0$–$^7F_2$. Since these transitions are usually parity forbidden, those emission lines explains the occupancy of Eu^{3+} ions in an non centrosymmetric site [19]. High values of asymmetric ratios (ratio of electric dipole to magnetic dipole transition intensities) of about 12 show high color purity and better occupancy of Eu^{3+} ions in a more non centro symmetric site. The inset of Fig. 6 shows the variation of emission intensities with Zr^{4+} and Si^{4+} concentration. The increasing emission intensity with increasing doping concentration of

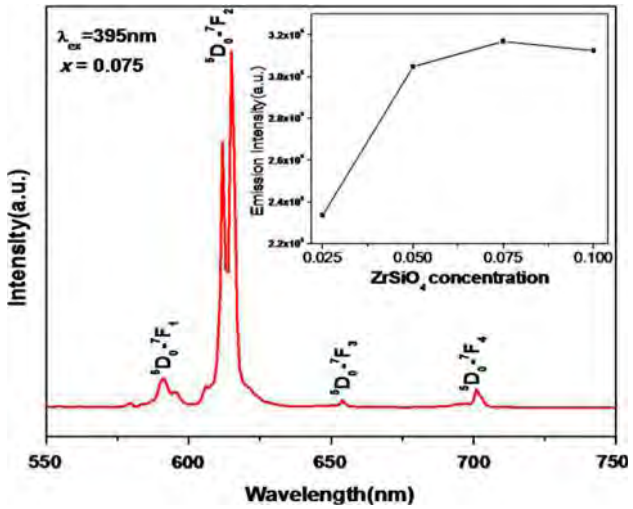

Fig. 6 Photoluminescence emission spectra of $Ca_{0.725}Zr_{0.725}Mo_{0.925}Si_{0.725}O_4{:}0.2Eu^{3+}$ under 395 nm excitation (*Inset*: variation in luminescent intensities with Zr^{4+} and Si^{4+} substitution)

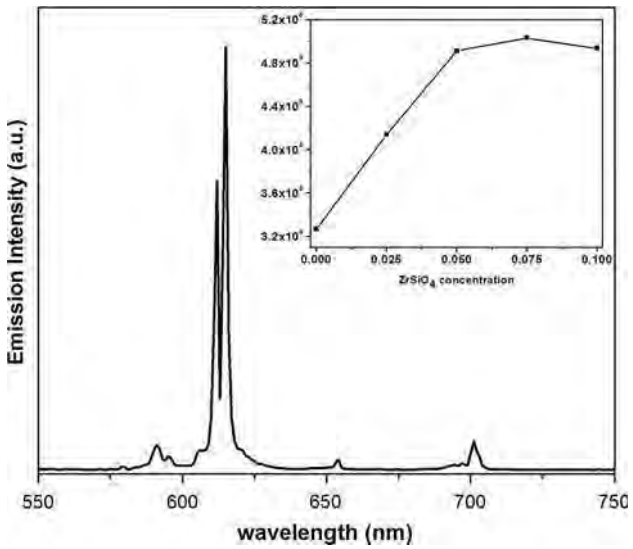

Fig. 7 Photoluminescence emission spectra of $Ca_{0.725}Zr_{0.725}Mo_{0.925}Si_{0.725}O_4{:}0.2Eu^{3+}$ under 300 nm excitation (*Inset*: variation in luminescent intensities with Zr^{4+} and Si^{4+} substitution)

Zr^{4+} and Si^{4+} is due to the local distortion around the luminescent Eu^{3+} ions which is able to lift the parity selection rule. Maximum intensity was observed for $x = 0.075$ concentration. With the substitution level greater than $x = 0.075$ the Eu^{3+} ions becomes closer to each other due to contraction in the lattice thereby quenching the emission. Variation of emission intensity with Zr^{4+} and Si^{4+} substitutions and their emisson profiles under 300 nm excitation was also recorded (Fig. 7) to understand the influence of the host lattice on the Eu^{3+} emission. Increase in the emission

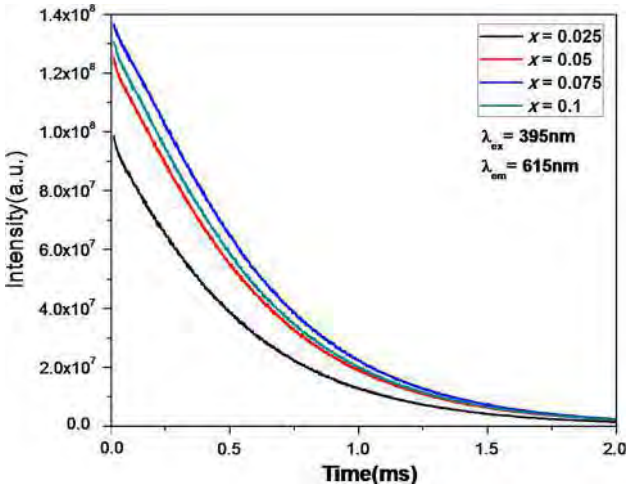

Fig. 8 *Decay curves* of Eu^{3+} emission at 615 nm in $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4{:}0.2Eu^{3+}$($x = 0.025,\ 0.05,\ 0.075,\ 0.1$) and $Ca_{0.8}MoO_4{:}0.2Eu^{3+}$ under 395 nm excitation

intensity with substituition shows that the host acts as a sensitizer for the emisssion.

The decay curves for $^5D_0$–$^7F_2$ transition (615 nm) of the prepared phosphors under near-UV excitation are shown in Fig. 8. All the decay curves can be fitted well with a single exponential function given as;

$$I = A \exp(-t/\tau)$$

where I, τ and A are intensity, decay time and fitting parameter respectively.

Assuming that only radiative and non radiative processes are essentially involved in the depopulation of $^5D_0$ states of Eu^{3+} ion, the quantum efficiency (η) can be expressed as;

$$\eta = A_{rad}/(A_{rad} + A_{nrad}) \quad (1)$$

where A_{rad} and A_{nrad} are radiative and non radiative transition probabilities respectively. The emission intensity (I) can be taken as the integrated (S) of $^5D_0$–$^7F_{0-4}$ emission curves as;

$$I_{i-j} = \hbar\omega_{i-j}A_{i-j}N_i \sim S_{i-j} \quad (2)$$

where i and j are initial ($^5D_0$) and final ($^7F_{0-4}$) levels respectively; $\hbar\omega_{i-j}$ is the transition energy, A_{i-j} is the Einstein's coefficients of spontaneous emission and N_i the population of $^5D_0$ emitting level.

The experimental coefficient of spontaneous emission (A_{0j}) can be calculated based on the relation

$$A_{0j} = A_{01}(I_{0j}/I_{01})(\upsilon_{01}/\upsilon_{0j}) \quad (3)$$

υ_{01} and υ_{0j} are the energy baricenters of the $^5D_0$–$^7F_1$ and $^5D_0$–^7F_j energy levels determined from the emission peaks of Eu^{3+} ion.

Table 2 Life time and quantum efficiency of the samples

Sample	Lifetime (ms)	Efficiency (%)
$x = 0.025$	0.4911	32.35
$x = 0.05$	0.5482	37.30
$x = 0.075$	0.5835	39.02
$x = 0.1$	0.5548	32.57
$CaMoO_4$:0.2Eu^{3+}	–	12.78 [ref 9]

A_{01} is the Einstein's coefficients of spontaneous emission between $^5D_0$ and $^7F_1$ energy levels.

In vacuum, the average refractive index (n) is 1.506 and $(A_{0-1})_{vac} = 14.65\ s^{-1}$ is considered. Then;

$$A_{0-1} = n^3(A_{0-1})vac \sim 50s^{-1} \quad (4)$$

The lifetime (τ) of the $^5D_0$ states, A_{rad}, A_{nrad} are related as;

$$A_{tot} = 1/\tau = A_{rad} + A_{nrad} \quad (5)$$

Using equations (1, 2, 3, 4, 5) [20–24] quantum efficiency values can be calculated. Lifetimes and the efficiencies of the phosphors were calculated and tabulated (Table 2).

The observation is that the luminescence decay time and quantum efficiencies of red emission increases up to a doping level $x = 0.075$ and further decreases. This trend in variation of life time is in accordance with the trend in the variation of the emission intensities. The optimized sample showed high quantum efficiency of about 39 % which is much higher than the reported values [9, 10]. Improvement in the efficiency is attributed to the reducing lattice defects decreasing the non radiative transitions which occurs mainly due to the multiphonon relaxations [25].

The excitation and emission spectra of as prepared $Ca_{0.725}Zr_{0.075}Mo_{0.925}Si_{0.075}O_4$:0.2$Eu^{3+}$ and $Ca_{0.8}MoO_4$:0.2 Eu^{3+} are shown in Fig. 9. The as prepared samples show broader CT bands and more intense f–f transition peaks than $Ca_{0.8}MoO_4$:0.2Eu^{3+}. With the substitution of the Zr^{4+} and Si^{4+} the bond length decreases and thus the covalency of the bond increases resulting in the lowering of the CT energy. This nephelauxetic (covalency) effect may be the reason for the slight red shift in the excitation spectrum [26]. The excitation intesity of the CTB as well as f–f transition is improved as the Zr^{4+} substituion creates a positive charge effect in the A site. [12]. Simultaneous substitution of Si^{4+} ions maintains the charge neutrality of the lattice. The absorption in the UV region is improved by the substitution of Zr^{4+} and Si^{4+} ions into the lattice. Thus the distortion in the A site symmetry and the red shift in the CTB leads to intense red emission under 395 nm excitation. Our samples showed enhanced emission intensities about two times than that of $Ca_{0.8}MoO_4$:0.2Eu^{3+} phosphor with high asymmetric ratios. The enhancement of photoluminescence in these phosphors is mainly attributed to combined effect of both increased absorption strengths and the increased efficiency.

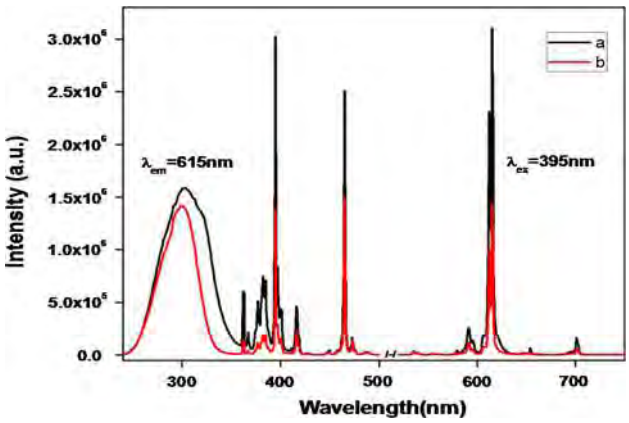

Fig. 9 Excitation and the emission spectra of *a* $Ca_{0.725}Zr_{0.075}Mo_{0.925}Si_{0.075}O_4$:0.2$Eu^{3+}$ *b* $Ca_{0.8}MoO_4$:0.2Eu^{3+}

The CIE color coordinates of all four samples were calculated to be (0.65, 0.34) using the software CIE Calculator which is close to the NTSC standard values (0.67, 0.33) for a potential red phosphors. Thus with improved luminescence intensities, high efficiencies and high asymmetric ratio the developed phosphors are better candidates as a potential red phosphor.

4 Conclusions

A series $Ca_{0.8-x}Zr_xMo_{1-x}Si_xO_4$:0.2$Eu^{3+}$ ($x = 0.025$, 0.05, 0.075, 0.1) phosphors which showed higher red luminescence intensity and better quantum efficiency than the $CaMoO_4$:Eu^{3+} phosphors was prepared. The samples exhibited strong absorption in the UV/blue regions matching well with the output wavelengths of the UV and blue LED chips. By Zr^{4+} and Si^{4+} substitution in the $CaMoO_4$ system the emission intensity was found to enhance for more than 2 times with high asymmetric ratio of $\sim$12 showing high color purity. Variation of emission intensity with respect to Zr^{4+} and Si^{4+} concentrations was also studied and a concentration quenching was observed at a substitution level of $x = 0.075$. The developed phosphors could be better candidates for use in pc-white LEDs.

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Characterization and anticorrosion studies of spray coated nickel oxide (NiO) thin films

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Abstract

In the present work, nanostructured thin films of NiO were synthesized using spray coating technique. The morphology and composition of the film were analyzed. The UV Visible absorption, micro Raman, and Photoluminescence spectrum of the NiO thin films were recorded and analyzed. The electrochemical behaviour of the nickel oxide thin film was examined by means of Electrochemical Impedance Spectroscopy (EIS) analysis, Tafel analysis and Open Circuit Potential (OCP) measurements. Salt spray corrosion test was applied to assess the stability of the NiO thin film over the steel substrate in the corrosive salt environment. The electrochemical impedance spectroscopy (EIS) analysis, Open Circuit Potential measurements (OCP), Tafel analysis revealed the enhanced protection of the substrate by nickel oxide thin film. The salt spray test carried out for 390 h, the thin film exposed to salt spray confirmed that the NiO films provides effective protection against corrosion of the stainless steel SS 304L compared with the substrate without nanoparticle deposition. Electrochemical Impedance Spectroscopy (EIS) analysis, Tafel analysis, Open Circuit Potential measurements (OCP) were repeated after the salt spray corrosion test and the result were again recorded, analyzed and compared with previous results which infers the effective protection of the nickel oxide thin film against corrosion in a corrosive environment..

Previous Next

Keywords

SApray coating; Electrochemical properties; Optical properties; Corrosion studies; Polarization curve

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Original research article

Influence of Ag doping on the structural, optical, morphological and conductivity characteristics of ZnO nanorods

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ABSTRACT

This article reports systematic study of Silver doping on ZnO nanorods synthesized by a simple chemical precipitation method. The prepared samples were characterized for structural, morphological, constitutional, optical and dielectric analysis. The XRD spectra confirmed the hexagonal wurtzite phase of the synthesized samples. The lattice parameter variation revealed the formation of nano inclusions at the boundaries. This was reaffirmed using the peak profile analyses of all samples using W-H analysis. The morphological and compositional analysis was done using SEM & EDAX. The quenching of visible (green) observed from PL spectra along with doping is not being much reported is also been studied. FTIR data confirmed the formation of Ag doped ZnO nanorods by chemical composition analysis. The dielectric and ac conductivity modification studies as a function of frequency and composition was performed using LCR meter which also showed a clear influence of Ag doping.

1. Introduction

Among the various metal oxides Zinc Oxide in the recent past that has attracted the attention of researchers and is regarded one of the most promising metal oxide semiconductor as it posses a wide band gap (3.27 ev) and high exciton stability [1]. This property makes it largely harvested for the applications in the field of opto- electronic devices [2]. Along with being a transparent metal oxide it possess good electron mobility [1] and strong room temperature luminescence [3]. Thus ZnO has applications in technology in the form of transparent electrodes for liquid crystal displays, energy-saving devices, solar control windows, thin-film transistors and light-emitting diodes [4–6]. Grain size variance resulting in the alteration of material properties at nano regime, which is mainly due to decrease of surface to volume ratio, results in the shift of the electronic state of the material compared with its bulk counterpart [7]. ZnO mostly occurring in stablest form as wurtzite structure [8], possess extra zinc which makes it a non-stoichiometric compound and n-type semiconductor [1,9]. This nature of conductivity of ZnO confines its application and hence fabrication of '*p*-type' conductive ZnO is a difficult one. Therefore the focus in research on ZnO has been mainly pivoted on the simple synthesis of intrinsic ZnO having insulating properties, by various techniques and studying its property variation while doping [10]. The investigations in the feasibility of 'p-type' doping in Zinc Oxide has been studied with elements belonging group V, I, and IB [11] whereas group-III and group-VII elements are studied for n type doping [12]. Silver(Ag), as a group IB element has been reported as the best candidate for doping in ZnO [13] owing to its high solubility, ionic size, and also the possibility of incorporation in substitutional Zn sites hence acting as

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PAPER

Investigation of anticorrosion properties of nanocomposites of spray coated zinc oxide and titanium dioxide thin films on stainless steel (304L SS) in saline environment

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Keywords: nanocomposite thin film, spray coating, corrosion studies, electrochemical workstation, Tafel analysis

Abstract

The present study reports the anticorrosive nature of nanocomposite thin films of zinc oxide and titanium dioxide on steel substrate (304L SS) using spray coating method. The morphology and chemical constituents of the nanocomposite thin film were characterized by field effect scanning electron microscopy and energy dispersive analysis of x-ray (EDAX) studies. From the EDAX studies, it was observed that nanocomposite coatings of desired stoichiometry can be synthesized using present coating technique. The cyclic voltametric techniques such as Tafel analysis and electrochemical impedance spectroscopy (EIS) analysis were conducted to study the anticorrosion properties of the coatings. The E_{corr} values obtained from Tafel polarization curves of the sample coated with nanocomposites of ZnO and TiO_2 in different ratios (5:1, 1:1 and 1:5) indicated that the corrosion resistance was improved compared to bare steel. The coating resistance values obtained from the Nyquist plot after fitting with equivalent circuit confirmed the improved anticorrosion performance of the coated samples. The sample coated with ZnO: TiO_2 in the ratio 1:5 showed better corrosion resistance compared to other ratios. The Tafel and EIS studies were repeated after exposure to 5% NaCl for 390 h and the results indicated the anticorrosive nature of the coating in the aggressive environment. The root mean square deviation of surface roughness values calculated from the AFM images before and after salt spray indicated the stability of coating in the saline environment.

1. Introduction

The product manufacturing industry has exploited steel due to its excellent durability and greater recyclability. The strenuous effort had been made in the past few decades to improve better wear and corrosion resistance of steel. Corrosion in steel cannot be completely bunged but can be eradicated up to a limit by adopting various corrosion mitigation technologies such as design improvement, coatings, corrosion resistant alloys or composites, catholic and anodic protection, corrosion inhibitors etc. Various materials such as nitrides, transition metal oxides, polymers, nanoparticles incorporated matrices; organic metals, etc have been used as protective coatings on metal surfaces to prevent corrosion [1–8]. Among these materials, thin films of TiO_2 have been widely used, as they provide improved wear resistance, hardness and high corrosion resistance [9–13]. Nanocomposites of titania such as CeO_2/TiO_2, TiO_2/CuO, TiO_2/SiO_2, titanium incorporated polymers etc have been attempted in the past [14–17]. Nanocomposites of ZnO/TiO_2 find a wide range of applications in the field of photo catalysis, dye-sensitized solar cells, humidity and gas sensors etc [18–21]. However, a detailed survey on literature suggests that anticorrosion study of nanocomposites of TiO_2 and ZnO has been scarcely attempted. Thin films of zinc oxide and titanium dioxide have been deposited by a variety of techniques such as anodic deposition, chemical vapor deposition, RF magnetron sputtering, atomic gel epitaxy, electron beam

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Research article

Enhancement of anticorrosion properties of stainless steel 304L using nanostructured ZnO thin films

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Abstract: Nanostructured ZnO thin films were coated on stainless steel specimen (304L SS) by depositing nanoparticles of zinc oxide. The morphology and optical properties of the thin films were epitomized using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive Analysis of X ray (EDAX), Atomic Force Microscopy (AFM) and Photoluminescence spectroscopy (PL) techniques. FESEM and AFM images revealed that the present depositing procedure is extremely proficient to synthesize uniform and homogeneous nanostructured thin films. The presence of excitonic peak in the PL emission spectrum confirmed the nanocrystalline nature of the thin films. The anticorrosion nature of the zinc oxide coated stainless substrate in the brackish environment was studied using Tafel, Electrochemical Impedance Spectroscopy analysis and Open Circuit Potential studies (OCP) methods. The E_{corr}, I_{corr}, corrosion rate before and after salt spray were calculated from Tafel plot. These parameters indicated that the anticorrosion properties of coated thin films are substantially higher to that of bare steel. The Nyquist plot before and after salt spray was fitted using an equivalent circuit and the coating resistance R_{ct} was calculated. The different mechanisms involved in the corrosion behavior of the thin films were discussed on the basis of equivalent circuit. The physical stability of the coated samples in saline surroundings was studied by AFM assisted nanoindentation techniques. The absence of the cracks and blisters in the sample after nanoindentation before and after salt spray revealed the adherent nature of the nanostructured thin films.

Optical and Corrosion Studies of Spray Pyrolysis Coated Titanium Dioxide Thin Films

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In the present work, nanostructured thin films of titanium dioxide (TiO_2) have been coated on the stainless steel (SS 304L) substrate by spray pyrolysis coating technique. The surface morphology and chemical constituents of the thin film have recorded using Field Effect Scanning Electron Microscopy (FESEM) and Energy Dispersive Analysis of X-rays (EDAX) respectively. The structural and optical properties of the films of as deposited were examined by Micro Raman, Photoluminescence Spectroscopy (PL) and UV-Vis absorption method. The FESEM micrograph showed the microporous nature of the film. EDAX spectrum illustrated the presence of Ti and O on the coated surface of the steel substrate. The peaks in the micro Raman spectrum indicated that the TiO_2 samples of present study are in rutile phase of titanium dioxide. A strong emission peak around 350 nm was observed in the Photoluminescence spectrum of the samples. The anti-corrosion properties of the TiO_2 coated samples were investigated by neutral salt spray test for 390 h. Electrochemical Impedance Spectroscopy (EIS) analysis and Tafel analysis were performed before and after salt spray test and the results suggested an increase of corrosion resistance of the titanium dioxide thin film in a corrosive environment. The positive shift of equilibrium corrosion potential (E_{corr}) of bare stainless steel to thin film coated stainless steel (from −0.96 V to −0.38 V) in the electrochemical Tafel analysis implied the significant increase of corrosion resistance.

Keywords: Corrosion Studies; Optical Properties; Spray Pyrolysis Coated; TiO2 Thin Film

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Optical and dielectric characterisation of Ceria nanocrystals synthesized by an auto-igniting combustion technique

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Abstract Nanocrystalline Ceria (CeO_2) was synthesized through auto-ignited combustion technique. The X-ray diffraction studies of CeO_2 nanoparticles have shown that the as-prepared powder was single phase, crystalline and has a face centred cubic structure. The phase purity of the powder was further examined using Fourier Transform Infrared and Raman spectroscopic techniques. The transmission electron microscopic studies have shown that the particle size of the as prepared powder was in the range of 30–40 nm. The band gap of nanoparticles as calculated from the absorption spectrum was found to be 3.51 eV. The photoluminescent spectrum of the samples exhibited a number of emission peaks which forms a broad band emission between 400 and 500 nm originating from $^2T_{2g}(5d)$–$^2F_{7/2}$, $^2F_{5/2}(4f)$ transition of Ce^{3+} ion due to spin–orbit coupling under the influence of O_h crystal field. The nanopowders were sintered to about 95 % of the theoretical density at 1450 °C for 2 h. The microstructure of the sintered surface was examined using scanning electron microscopy. The dielectric constant (ε_r) and loss tangent ($\tan\delta$) at 5 MHz are found to be about 25.1 and 0.0118 respectively. The complex impedance plots show semicircular arcs resolving at high temperature which confirms the existence of the non-Debye type of relaxation in the sintered CeO_2 samples.

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1 Introduction

Synthesis of advanced ceramics and allied materials in nanosize is gaining widespread interest due to the attractive properties of nanocrystals [1–4]. The superior phase homogeneity, improved sinterability and microstructure of nanocrystalline materials result in the unique electrical, mechanical, optical, dielectric, magnetic properties, suitable for different applications. Cerium oxide (CeO_2) is one of the highly stable, high-temperature ceramic materials, with a melting point of about 2600 °C [5]. Ce^{4+} has an f^0 configuration have with no unpaired electron and is hence diamagnetic in nature. Lanthanide-doped CeO_2 is a good oxygen ion conductor at intermediate temperatures [6]. Cerium oxide finds applications as electrochemical pumps [7], fluorescent materials [8], solid electrolyte for SOFC [9], catalyst for automotive exhaust treatment [10], polishing materials [11] and so on. The unique UV absorption ability, high hardness, reactivity and high stability at improved temperatures make them interesting among materials scientists [12, 13]. X. Liu et al. [14] reported that CeO_2 can be used as a potential host material for lanthanide luminescence. Reports are also available on the luminescent properties of ceria itself [15, 16]. It is widely used for the stabilization of ZrO_2 which is suitable for biomedical applications especially as colouring additives in dental implants [17, 18]. Recently, there was an increasing interest in the ceria nanoparticles for their biological activities such as drug delivery, bio analysis, biomedicine and bio scaffolding [19–22]. The high defect densities and mobilities at grain boundaries influence the electrical

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A Simple Chemical Precipitation Method of Titanium Dioxide Nanoparticles Using Polyvinyl Pyrrolidone as a Capping Agent and Their Characterization

V. P. Muhamed Shajudheen, K. Viswanathan, K. Anitha Rani, A. Uma Maheswari, S. Saravana Kumar

***Abstract*—**In this paper, a simple chemical precipitation route for the preparation of titanium dioxide nanoparticles, synthesized by using titanium tetra isopropoxide as a precursor and polyvinyl pyrrolidone (PVP) as a capping agent, is reported. The Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) of the samples were recorded and the phase transformation temperature of titanium hydroxide, $Ti(OH)_4$ to titanium oxide, TiO_2 was investigated. The as-prepared $Ti(OH)_4$ precipitate was annealed at 800°C to obtain TiO_2 nanoparticles. The thermal, structural, morphological and textural characterizations of the TiO_2 nanoparticle samples were carried out by different techniques such as DSC-TGA, X-Ray Diffraction (XRD), Fourier Transform Infra-Red spectroscopy (FTIR), Micro Raman spectroscopy, UV-Visible absorption spectroscopy (UV-Vis), Photoluminescence spectroscopy (PL) and Field Effect Scanning Electron Microscopy (FESEM) techniques. The as-prepared precipitate was characterized using DSC-TGA and confirmed the mass loss of around 30%. XRD results exhibited no diffraction peaks attributable to anatase phase, for the reaction products, after the solvent removal. The results indicate that the product is purely rutile. The vibrational frequencies of two main absorption bands of prepared samples are discussed from the results of the FTIR analysis. The formation of nanosphere of diameter of the order of 10 nm, has been confirmed by FESEM. The optical band gap was found by using UV-Visible spectrum. From photoluminescence spectra, a strong emission was observed. The obtained results suggest that this method provides a simple, efficient and versatile technique for preparing TiO_2 nanoparticles and it has the potential to be applied to other systems for photocatalytic activity.

***Keywords*—**TiO_2 nanoparticles, chemical precipitation route, phase transition, Fourier Transform Infra-Red spectroscopy, micro Raman spectroscopy, UV-Visible absorption spectroscopy, Photoluminescence spectroscopy, Field Effect Scanning Electron Microscopy.

I. Introduction

AMONG many semiconducting transition metal oxides, TiO_2 nanoparticles in different phases have become standard in environmental applications because they proved to be efficient, biologically and chemically inert, inexpensive, resistant to photo corrosion and chemical corrosion, nontoxic, highly photoactive, recyclable and have suitable band gap (E_g = 3.2 eV) in which its redox potential of the $H_2O/•OH$ couple (-2.8 eV) lies. These properties make TiO_2 a main candidate for broad applications in photochemical solar cells, photocatalysis, chemical sensors, dielectric material of ultrathin-film capacitors, as pigments, self-cleaning surfaces and environmental purification applications [1]. TiO_2 nanoparticles exist in several forms, such as amorphous, anatase and rutile depending on fabricating conditions and further heat treatment [2], [3].

Until now, TiO_2 nanoparticles are prepared by various methods like sol-gel method [4], solid state reaction method [5], reverse microemulsion method [6], chemical vapour deposition method [7], hydrothermal method, solvothermal method, physical vapour deposition method, microwave method and sonochemical method [8]-[10]. Among the synthetic approaches co-precipitate method is considered to be one of the best techniques and potentially advantageous in comparison to other method to produce pure phase formation of compounds, low temperature preparation, highly purity and yield nanopowders [11], [12]. The present work is an attempt to prepare pure rutile phase of TiO_2 nanoparticles. The obtained results are sleeved for their thermal analysis, structure, chemical analysis, morphology and optical characterization.

II. Procedure

All the chemicals reagents used in our experiments were of analytical grade, commercially purchased from Merck used as received without further purification. Nanoparticles of TiO_2were prepared using the precursor titanium isopropoxide and isopropyl alcohol. 100 ml of isopropyl alcohol was added to 15 ml of titanium isopropoxide and stirred for 30 minutes. To this solution 0.1 gm of PVP was added and stirred for 20 minutes. For hydrolysis reaction 10 ml of deionised water was added dropwise to the mixed solution. The resulting white precipitate of $Ti(OH)_4$ is refluxed for 2 hours and then it is stirred continuously for one day. Finally, the precipitate is centrifuged with deionized water and ethanol to remove impurities. After centrifuging, the white precipitate is dried at 80 °C for one day. Finally, the as-prepared $Ti(OH)_4$ precipitate was annealed at 800 °C to obtain TiO_2 nanoparticles. The oxidation mechanism of $Ti(OH)_4$ from ambient up to 1400 °C was investigated by thermogravimetric (TG) and Differential scanning calorimeter (DSC) using Perkin Elmer, Diamond

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Advance Physics Letter

Low temperature Synthesis of Zinc Oxide nanoparticles and their characterization

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Abstract: We report, a simple and low cost chemical precipitation method adopted to prepare zinc oxide nanoparticles (ZnO) using polyvinyl pyrrolidone (PVP) as a capping agent. The thermal, structural, morphologicaland optical properties have been characterized by different techniques such as DSC-TGA, X-Ray Diffraction (XRD), Micro Raman spectroscopy, Fourier Transform Infra-Red spectroscopy (FTIR), Field Effect Scanning Electron Microscopy (FESEM), UV-Visible absorption spectroscopy (UV-Vis) and Photoluminescence spectroscopy (PL). From, DSC-TGA result, above 900°C it become stable with no further weight loss is obtained. X-ray diffraction results confirmed the wurtzite hexagonal structure of ZnO nanoparticles. The two intensive peaks at 162 and 432 cm^{-1}in the Raman Spectrum are attributed to the first order modes of the wurtzite ZnO nanoparticles. The mixed shapes of grapes, sphere, hexagonal and rocks like structures have been noticed in FESEM.The band gap obtained from the UV-Vis absorption spectra, shows a blue shift, which is attributed to increase in carrier concentration (Burstein Moss Effect). Photoluminescence studies of the single crystalline ZnOnanoparticlesshowa strong peak centered at 385 nm, corresponding to the near band edge emission in ultraviolet range.

Keywords: ZnOnanoparticles, simple chemical precipitation route, mixed shape morphology

I. INTRODUCTION

In recent years, there was grown in interest to synthesis nanoparticles, which have been different from bulk materials by a reduction in volume and an increase in the specific surface area [1-4]. Nanoparticles of ZnO have been drawn great interest in research due to their unique electronic, optical, mechanical, magnetic and chemical properties and have broad attention due to its wide range of applications in ultraviolet (UV) lasers, power generators, solar cells, gas sensors, field emission devices, capacitors, transparent UV resistance coating, electrochemical and electromechanical nanodevices, sun screen lotion (cream), cosmetic and medicated creams etc[5-14]. Several physical and chemical methods have been developed to obtain ZnO nanoparticles which include, reverse micelles process, solid state reaction, sol-gel method, ultrasonic irradiation, combustion method, solvothermal synthesis, electrochemical synthesis and chemical precipitation method etc [15-24].

We report a simple low temperature method to synthesize ZnO nanoparticles. The samples were characterized using X-Ray Diffraction (XRD),Micro Raman spectroscopy, UV-Visible absorption spectroscopy (UV-Vis), Fourier Transform Infra-Red spectroscopy (FTIR), Photoluminescence spectroscopy (PL) and Field Effect Scanning Electron Microscopy (FESEM).

II. EXPERIMENTAL

All the chemicals reagents used in our experiments were of analytical grade, commercially purchased from Merck used as received without further purification. 250ml deionized water is taken in a beaker and 0.05gm PVP is added. The solution is stirred 10 minutes using magnetic stirrer and then added 22.43 gm of $ZnSO_4H_2O$ to the solution and stirred continuously for 2 hours. To this solution 15.5ml of 2M NH_4OH added dropwise while the reactants are continuously stirred till the pH becomes 5.5. After 1hour reflexing the precipitate formed is centrifuged, washed several times with water and finally with ethanol, and then air dried to obtain nano powders of zinc hydroxide. The oxidation mechanism of zinc hydroxide from ambient temperature upto 1000°C was investigated by thermogravimetric (TG) and Differential scanning calorimeter (DSC) using Perkin Elmer, Diamond DSC-TGA set up.

X-ray Diffraction patterns of the zinc oxide sample were recorded using a Philips Xpert pro Diffractometer and using CuKα radiation over the diffraction angles (2θ) from 30 to 80°.

The micro Raman spectra of ZnO nanoparticles were recorded using Horiba Labram-HR, in the range of 100-1500 cm^{-1}. The Nd:YAG laser operating at 200mW, 150nm as the excitation wavelength, and a liquid nitrogen cooled Ge detector was used to record the spectrum. The room temperature FT-IR spectrum of ZnO nanoparticles was recorded in the range of 400-

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Structural and Optical Properties of NiS Nanoparticles Synthesized by Chemical Precipitation Method

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ABSTRACT: In the present work, orthorhombic NiS nanoparticles were obtained by chemical precipitation method using tri ethanol ammine (TEA) as a capping agent. The nickel sulfide nanoparticles were characterized by X-ray diffraction (XRD), UV-visible spectrophotometry (UV-vis), photoluminescence (PL) and micro Raman techniques. The X-ray diffraction pattern of the sample indicated the formation of orthorhombic structure of NiS. Absorption due to band edge and defect levels was observed in the absorption spectrum of nickel sulphide nanoparticles.Emission peaks due to defect levels was observed in the photoluminescence spectrum.

KEYWORDS: Nickel Sulfide nanoparticle, micro Raman, UV Visible absorption, Photoluminescence.

I. INTRODUCTION

In the recent years, transition metal sulfide nanoparticles are being studied extensively owing to their unique electrical, optical and catalytic properties.These materials find applicationsin fields of research interest such as fluorescence devices, solar energy conversion devices, electroluminescence devices, super conductors, flat panel displays, semiconductor and optical devices, etc. [1-6]. Nickel sulfide proves to be a promising material for application as cathode material for the rechargeable lithium battery and catalyst in the degradation of organic dyes and different magnetic devices and certain non-linear optical devices. [7-12]. NiS films have been used as catalyst and coatings in photovoltaic cells [13&14]. Catalysts have applications in the oil industry for the separation of elements with hydrocompounds from insulators [15]. Due to the various applications, different synthesis methods were employed for the preparations of the nanoparticles such as sol-gel method, laser ablation, solvothermalprocess, UV irradiation, colloidal microemulsion method [16&17]. Nickel sulfide exhibits complicated compositional, strucutural, optical, electrical and magnetic phase behaviour. Depending on the preparation method, a number of binary nickel sulphides such as Ni3S2, Ni3+xS2, Ni4S3+x, Ni6S5, Ni7S6, Ni3S4 and NiS have been reported [18-22]. To the knowledge of present authors, only few reports are available on the synthesis, photoluminescence and micro Raman study of nickel sulphide nanoparticles

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Recent Advances In Nano Science And Technology 2015 (RAINSAT-2015)

Synthesis and characterization of NiO nanoparticles by thermal oxidation of nickel sulfide nanoparticles

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Abstract

In the present work, nanoparticles of nickel sulfide were synthesized using chemical precipitation method with tri ethanol ammine (TEA) as a capping agent. The nickel sulfide nanoparticles were characterized using X-ray diffraction technique and were found to be in orthorhombic Ni_9S_8 phase. The thermogravimetric (TG) and differential thermal curves of the samples were recorded and the phase transformation temperature of nickel sulfide (Ni_9S_8) to NiO was found to be at 600°C. The as prepared nickel sulfide nanoparticles were annealed at 700°C to obtain NiO nanoparticles. The grain size of nanoparticles of NiO was obtained from XRD pattern and was found to be approximately 10 nm. The micro raman, UV-Visible absorption and photoluminescence spectrum of NiO nanoparticles were recorded and analyzed.

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Keywords:nickel sulfide nanoparticles: nickel oxide nanoparticles;micro raman, UV Visible absorption, Photoluminescence

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Tweaking Electrical and Dielectric Properties of Nickel Oxide Nanocrystals by Varying the Surfactant

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The influence of cationic cetyltrimethylammonium bromide (CTAB) and neutral polymeric polyvinylpyrrolidone (PVP) surfactants on electrical and dielectric properties of NiO nanocrystals is investigated. It is demonstrated that, compressive strain of nanocrystals is higher with PVP than that of CTAB. Consequently surfactant type has significant influence on intrinsic defects of nanocrystals. This is attributed to the difference in stabilization of metallic ions against agglomeration that leads to variation in rate of hydrolysis. Particularly, in the case of PVP assisted synthesis, higher stabilization leads to slow nucleation rate with lower defect density. As a result the hopping time of charge carriers decreases which in turn enhances the conductivity of nanocrystals as evidenced from the shifting of dielectric loss peak to higher frequency.

Keywords: NiO Nanocrystals, Surfactant, Dielectric Constant, Microstrain.

1. INTRODUCTION

Science and technology of nanomaterials have rapidly progresses.[1–5] Among them, nickel oxide (NiO) nanostructures have been studied extensively due to their exceptional optical, electronic, magnetic, thermal, mechanical and catalytic properties. For instance, a better performance of nanocrystalline thin film coated heterojunction organic photovoltaic cells is observed due to increase in the open circuit voltage. This is on account of favourable energy band levels, interface passivation, *p*-type character, crystallinity, smooth surface, and optical transparency.[6] Bulk NiO is an antiferromagnetic insulator with Neel temperature of 523 K.[7] Instead, NiO nanostructures are paramagnetic and their improved antioxidant property that is useful for biosystems applications.[8] Further corrosion and wear resistance of mild steel is increased by using NiO based nanocomposite coatings.[9] The superior catalytic activity of NiO nanocrystals which depends on their size and morphology, find applications in batteries and fuel cells,[10] chemical synthesis[11] and electrochemical based sensors.[12] In addition, a range of NiO based electrochemical sensors are developed to identify biological compounds like H_2O_2,[13] glucose,[14] methanol,[15] amoxicillin,[16] and insulin.[17] Studies have demonstrated that physical, chemical, electrical and dielectric properties of nanostructures synthesized through chemical methods can be modified by suitable choice of precursor,[18] solvent typel,[19] surfactants,[20] precipitating agent,[21,22] doping,[23–25] processing condition[26,27] and calcination temperature.[28] This can cause a significant change in the microstructure of nanostructures which strongly influence their physical and chemical properties. Further, the nature of surfactants used for the synthesis of nanomaterials by bottom-up technique can tailor their properties by reducing the surface energy and preventing the agglomeration between the nanoparticles through either steric hindrance or repulsive electrostatic forces.[10,29] Recently we have investigated the role of surfactant and mineralizer type on phase stabilization of un-doped zirconia nanocrystals produced by chemical precipitation.[21,22] Although studies pertaining to electrical and dielectric properties of NiO nanocrystals have been reported, the influence of surfactant type on these properties is not well understood. In this context, the present work is aimed to study the influence of neutral polymeric polyvinylpyrrolidone (PVP) and cationic surfactant cetyltrimethylammonium bromide (CTAB) on electrical and dielectric properties of NiO nanocrystals synthesized through chemical precipitation method.

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Synthesis, characterization and photoluminescent properties of $BaZr_xNd_{1-x}O_3$ perovskites

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ABSTRACT

$BaZr_xNd_{1-x}O_3$ perovskites were prepared by the conventional solid state ceramic route for $x = 0.85$, 0.9, 0.95, 0.99, 0.995 and 0.999. The powders were calcined at 1250 °C. X-ray diffraction patterns of the samples confirmed the cubic phase formation and no considerable additional peaks were found. The absorption spectra of doped samples showed strong absorption around 225 nm, a shoulder at 250 nm and a broad peak around 330 nm. The samples with higher concentrations of neodymium show peaks around 750 and 800 nm. The absorption at 250 nm was due to the absorption by the host $BaZrO_3$ and others can be attributed to that of Nd^{3+}. The emission spectra of the samples were recorded for different excitations and strong emissions were observed around 344 nm, 360 nm, 401 nm, 527 nm and 901 nm. Chromaticity values of the samples measured using CIE chromaticity diagram were also discussed.

1. Introduction

The recent development of materials with optical properties such as electroluminescence and photoluminescence can lead to new high performance optoelectronic devices [1]. The study of luminescence properties of rare earth elements hosted in several crystalline matrices such as metal oxides, phosphors, metal-organo complexes and variety of semiconductor materials is strongly motivated because of their applications in optoelectronic devices and flat panel displays such as electroluminescent displays, field emission displays, plasma display panels, and vacuum fluorescent displays [2]. The requirement of phosphors for each application is different and the searches for new materials with improved properties are in progress. The photoluminescent properties of Bi, Ga, In and Al materials doped with various lanthanides such as Ce, Pr, Nd, Sm, Gd, Tb, Eu, Yb, and Er are reported. Depending upon the dopants and host materials used, luminescent spectra can be obtained in different regions of electromagnetic spectra.

Among various lanthanides, neodymium (Nd^{3+}) is of technological importance due to its various applications in commercial red phosphors and active laser components [3]. Nd^{3+} possesses intense luminescence at 1.06 μm [4–6]. A number of reports are available on the up-conversion properties of Nd^{3+} [7–10]. Due to the low luminescent efficiency, very little reports are available on the luminescence properties of Nd doped crystals in the visible region, most of the reports are concentrated in the 1.06 μm region. The photoluminescent emission of Nd^{3+} strongly depends on the host materials used. It was reported that choosing appropriate host materials for Nd^{3+} activators, allow the occurrence of visible transitions under ultra violet excitation conditions [11,12]. Mizoguchi et al. [13] reported that on changing the host environment, the emission from Sn^{2+} ion in $BaSnO_3$ shifts from NIR region further into the infrared region. In the case of neodymium, the emission was observed around 1070 nm in Nd:YAG [14], 876 nm and 1070 nm in $BaTiO_3$ host [15], 900 nm and 1060 nm in $LaGaO_3$ [16] and ZrO_2 host [17]. Besides the above mentioned emissions of Nd^{3+}, Yamanoi et al. [18] reported the vacuum ultraviolet (VUV) fluorescence of Nd^{3+} in APLF glass host around 185 nm due to the $4f^25d$ to $4f^3$ transitions of Nd^{3+}. Only a few reports are available on the emission properties of Nd^{3+} based materials in the visible region. Liu and Kuang [19] reported intense visible luminescence from Nd^{3+} in Yttrium oxysulfide host. They observed strong emission in blue region with 261 nm pumping and is attributed to the $^2P_{1/2}$ to $^4I_{9/2}$ transitions of Nd^{3+}. A bright red luminescence at 613 nm is reported for $Nd_x(Ca_{1-x-y-z}Ba_ySr_z)TiO_3$ system under excitation at 335 nm [20].

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Optical properties of nanocrystalline HfO_2 synthesized by an auto-igniting combustion synthesis

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ABSTRACT

The optical properties of nanocrystalline HfO_2 synthesized using a single-step auto-igniting combustion technique is reported. Nanocrystalline hafnium oxide having particle size of the order 10–15 nm were obtained in the present method. The nanopowder was characterized using X-ray diffraction, Fourier transform infrared and Fourier transform Raman spectroscopic studies. All these studies confirm that the phase formation is complete in the combustion synthesis and monoclinic phase [$P2_1/c(14)$] of HfO_2 is obtained without the presence of any impurities or additional phases. The powder morphology of the as-prepared sample was studied using transmission electron microscopy and the results were in good agreement with that of the X-ray diffraction studies. The optical constants such as refractive index, extinction coefficient, optical conductivity and the band gap were estimated from UV–vis spectroscopic techniques. The band gap of nanocrystalline HfO_2 was found to be 5.1 eV and the sample shows a broad PL emission at 628 nm. It is concluded that the transitions between intermediate energy levels in the band gap are responsible for the interesting photoluminescent properties of nanocrystalline HfO_2.

1. Introduction

Hafnium oxide (HfO_2) is an important ceramic material due to its high dielectric constant ($\varepsilon_r \sim 30$), high melting point (2758 °C) and greater chemical stability [1]. HfO_2 and its solid solutions with SiO_2 are promising replacements for SiO_2 for their potential applications as gate dielectrics [2]. Recently the optical applications of HfO_2 are gaining widespread interest. Due to its transparency over a wide range from ultraviolet to mid-infrared, it is used as materials for heat resistant, reflective and protective optical coating [3–5]. HfO_2 found promising optical coating applications such as filters, beam splitters, anti-reflection coating, high reflectivity mirrors, etc. [6,7].

Hafnium in bulk can adopt three different crystal structures at ambient temperatures. At room temperature it is stable in monoclinic structure, transforms to tetragonal at about 1720 °C and becomes cubic at about 2600 °C [8]. Synthesis of advanced ceramics and specialty materials as nanocrystals is one of the major challenges in the development of material processing technology [9]. The advantages of nanocrystalline materials are superior phase homogeneity, sinterability and microstructure leading to unique mechanical, electrical, dielectric, magnetic, optical and catalytic properties [10]. There have been increasing interests in the use of nanoparticles to optical systems because of their enhanced optical properties due to their smaller size [11]. Because of its high chemical stability, high cost and high processing temperatures, hafnium oxide is less studied in the form of nanomaterials than other simple oxides. Recently the synthesis of nanocrystalline hafnia by a sol–gel method was reported [12–14]. The synthesis of nanocrystalline HfO_2 by the hydrolysis of hafnium oxychloride in ethanol was reported [15]. The preparation of nanocrystalline HfO_2 by ultrasonically assisted hydrothermal treatment has also been reported [16].

Recently combustion synthesis technique has been reported as an easy, economical and time-saving method to synthesize advanced ceramic powders and functional materials [17–19]. Since solution mixing is generally used in combustion synthesis, it results in relatively ultra-phase homogeneity than in any other techniques. Generally in combustion synthesis, which uses PVA as a complexing agent and urea as fuel, it requires post-annealing or calcination of the precursor to get phase purity. Recently, with the use of citric

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Phase tuning of zirconia nanocrystals by varying the surfactant and alkaline mineralizer

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Abstract

The influence of cationic (CTAB)/neutral polymeric (PVP) surfactants and strong (NaOH)/weak (NH_4OH) alkaline mineralizers on phase stabilization of zirconia nanocrystals synthesized by chemical precipitation is investigated. X-ray diffraction and micro-Raman analysis of the as-prepared samples show that tetragonal zirconia is predominant as compared to monoclinic using PVP with NH_4OH. The phases are also evident from lattice fringes of TEM images and the corresponding SAED pattern. Photoluminescence spectra of samples reveal oxygen vacancies present in the zirconia nanocrystals. The group H Raman vibration modes identified are attributed to surface defects and quantum size effects of nanocrystals. The phase stabilization of zirconia nanocrystals is explained using the polymerization rate of tetramers during synthesis. The rate can be varied by proper selection of the surfactant and the mineralizer. A slow polymerization rate with PVP and NH_4OH favors the formation of tetragonal zirconia. Thus, a simple method for phase stabilization of zirconia nanocrystals at room temperature using chemical precipitation by varying the surfactant and the mineralizer is demonstrated.

Keywords: Chemical precipitation; Tetragonal Zirconia; Phase stabilization; Cationic and Neutral Polymeric Surfactants; Mineralizer

1. Introduction

Recently there has been a renewed interest in exploring phase dependent properties of zirconia nanocrystals due to their technological importance. Generally zirconia exists in three temperature dependent polymorphs namely thermodynamically stable monoclinic (below 1170 °C), metastable tetragonal (between 1170 and 2370 °C) and cubic (above 2370 °C) [1]. Among these, tetragonal zirconia has high strength and fracture toughness which makes it suitable for the fabrication of structural ceramics [2] and functional materials [3]. Its excellent mechanical properties are due to stress induced martensitic tetragonal-to-monoclinic transformation which results in toughening [4]. In addition, tetragonal zirconia has high chemical and dimensional stability and hence used as a ceramic biomaterial for dental restorations [5]. Tetragonal zirconia coatings enhance stainless steel's resistance to corrosion and wear [6]. It is also used in thermal barrier coatings of gas turbine parts owing to its low thermal conductivity/high thermal expansion coefficient when compared to monoclinic zirconia [1]. Thin films of tetragonal zirconia are used as gate for microelectronic devices due to their high dielectric constant [7]. The ionic conductivity of tetragonal/cubic zirconia is high due to the presence of oxygen vacancies at grain boundaries and hence they are used as solid electrolytes for oxygen sensors [8] and oxide fuel cells [9]. Zirconia modified with sulphate anions is well suited for catalytic reactions like hydrogenation and isomerisation [10]. The presence of acidic, basic hydroxyl groups and coordinatively unsaturated Lewis acidic-base $Zr^{4+}O^{2-}$ pairs can enhance its phase dependent catalytic reactions. For instance, sulfated tetragonal zirconia can act as an active catalyst for *n*-butane isomerization [11] whereas monoclinic zirconia is used for selective hydrogenation of CO_2 to produce methanol [12]. Zirconia nanocrystals exhibit phase dependent luminescence and used for the fabrication of eco-friendly photonic systems [13].

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Impact of carbon nanotube geometrical volume on nonlinear absorption and scattering properties

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ABSTRACT

Nonlinear optical (NLO) properties of carbon nanostructures are of great interest due to their broadband spectral response. As carbon nanotubes (CNTs) can be synthesized with various lengths, thicknesses, and numbers of layers, their optical properties can also be different. We have performed side-by-side comparative studies of the relationship between the geometrical volume and NLO properties of CNTs. The real and imaginary components of the third order optical nonlinearity are obtained using well-known Z-scan technique. While the transmission and scattered light are detected using photodiodes, the generated photoacoustic signal is recorded simultaneously using an ultrasonic transducer. Results show an inverse relationship between the volume of CNTs and their NLO properties. This can be attributed to the availability of more nanoparticles within the laser beam profile and concurrent generation of scattering sites upon the absorption of incident radiation.

1. Introduction

Recent developments in the design and fabrication of nanoscale photonic devices have attracted significant attention to synthesis and characterization of a variety of nanomaterials such as graphene, carbon nanotubes, semiconductor nanoparticles, metal/dielectric nanocomposites, nanodiamonds, and organic nanostructures [1–6]. In particular, since their discovery by Iijima in 1991 [7], carbon nanotubes (CNTs) have been the subject of many experimental and theoretical studies [8–13]. CNTs are all-carbon nanomaterials with lengths ranging from several hundred nanometers to a few micrometers and diameters of less than 1 nm to tens of nanometers. Their high aspect ratio as well as their excellent mechanical, thermal, and electrical properties have been exploited for applications such as bio-chemical sensors [14], field emitters [15], solar cells [16], optical switches [17], broadband optical limiting, saturable absorbers in a mode-locking element [18–21], and molecular photoacoustic contrast agents for optical imaging [22–25]. Wu et al. reported the effect of aspect ratio on the network structure of CNT/polymer composites and their physical and mechanical properties [26]. Pötschke et al. [27] and Cipiriano et al. [28] observed that CNTs with large aspect ratios impart much higher storage moduli and viscosities compared to those with low aspect ratios. The aspect ratio of CNTs also effects the dielectric behaviour, electric percolation behaviour, and shielding effectiveness of the CNTs and CNT/Polymer composites [29,30].

Due to their wide-band absorption from π-plasmon excitation [31–33], CNTs are considered effective optical power limiting materials and have been extensively investigated both in suspensions and thin films [34–37]. Previous observation of carbon particle heating by laser irradiation lead to the conclusion that the NLO response is due to light scattering from a vapour shell generated around the particle [4,38–40]. Although past studies have demonstrated the influence of structural properties of CNTs such as shape, bundling effects, etc. on their nonlinear optical properties, a side-by-side comparison of CNT length, diameter, and volume with their NLO response is still a motivating topic. Such a systematic study can be extended to other types and shapes of nonlinear materials and may help in identifying practical material for power limiting applications.

We report the impact of dimension (length and diameter) of CNTs on their third order nonlinear optical properties. Optical and photoacoustic (PA) Z-scan techniques were used to study the nonlinear optical properties and photoacoustic response

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Structural and Optical Characterization of Copper Selenide ($Cu_{2-X}Se$) Nanoparticles

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ABSTRACT

The stoichiometric Cu_2Se and non-stoichiometric $Cu_{1.98}Se$ nanoparticles were prepared by a simple chemical method at room temperature The X-ray diffraction patterns revealed the formation of single phase nanostructured Cu_2Se and $Cu_{1.98}Se$ particles with cubic lattice for different deposition conditions and the particle size is 17.45 nm, 26.85 nm respectively for Cu_2Se and $Cu_{2-x}Se$. Fourier transform infrared spectroscopy (FTIR) confirmed the formation of single phase Cu_2Se and $Cu_{1.98}Se$ nanoparticles, with characteristic vibrational modes of Cu and Se ions. Scanning electron microscopy (SEM) studies revealed that the Cu_2Se particle surface is found to be textured with grains of irregular shapes while for $Cu_{1.98}Se$, a mesh like structure which is loosely packed than Cu_2Se is observed. This distinction may be due to variations in Cu content as seen from EDAX analysis. UV-Vis Studies specify blue shift from the bulk copper selenide as observed from the absorption shoulders occurs at 281 nm for Cu_2Se and 276 nm for $Cu_{1.98}Se$ samples. The Optical band gap obtained for Cu_2Se and $Cu_{2-x}Se$ nanoparticles are 4.41 eV and 4.52 eV respectively.

1. Introduction

Nano crystalline copper chalcogenides have attracted an extensive attention due to their interesting properties and their great potential applications in many different fields. Copper selenide (Cu_2Se) belongs to II-VI group, which has received considerable attention in the past two decades because of its application in solar cell, optical filter, super ionic conductors, thermo electric converters, etc., [1]. Copper selenides are well known as a p-type semiconductor possessing a direct band gap, as well as an indirect band gap [2]. However, their band gap value (E_g) varies with the change of their stoichiometries or phases. Hong-Liang Li *et al.* [3] have employed a sonochemical-assisted approach to prepare α-CuSe crystals and the size and the shape of the products can be affected by changing the reaction time. Copper selenide can exist in a wide range of stoichiometric compositions (CuSe, Cu_2Se, $CuSe_2$, Cu_3Se_2, Cu_5Se_4, Cu_7Se_4, etc.) and non-stoichiometric compositions ($Cu_{2-x}Se$) and can be constructed into several crystallographic forms (monoclinic, cubic, tetragonal, hexagonal, etc. The special constitutions and properties of these compositions make copper selenide an ideal candidate for scientific research [1]. Pushpendra Kumar and Kedar Singh [4] have reported on successful synthesis of luminescent and crystalline copper selenide QDs in aqueous solution of hydrazine hydrate and ethylene glycol. They have found that from the absorption and photoluminescence studies display large blue shift and due to the quantum confinement effect copper selenide QDs could be potential building blocks to construct functional devices and solar cell. Pengfei Hu and Yali Cao [5] have reported a precipitation reaction route for the tuned preparation of different copper selenides ($Cu_{2-x}Se$ and CuSe) nanocrystals at room temperature. Yan Zhang [6] have synthesized via a modified composite hydroxide mediated method to prepare single crystalline $Cu_{2-x}Se$ nanowires with lengths up to 50 μm and from the UV-visible-near-infrared reflection spectrum demonstrates the absorption edges of the $Cu_{2-x}Se$ nano wires in the ultraviolet and near-infrared region, which could be interpreted in terms of direct transitions and indirect transitions respectively. Arokiya Mary and Joe Jesudurai [7] have synthesized Cu_2Se particles by the hydrothermal method at a temperature of 200 °C. Peranantham et al. [8] were prepared copper selenide and indium telluride thin films at different substrate temperatures by a vacuum evaporation technique and the optical transmittance measurements indicated the existence of direct and indirect transitions in copper selenide films. Chrissafis et al. [9] have studied the thermal effect accompanying the transition of $Cu_{2-x}Se$ into a superionic conduction state was studied by non-isothermal measurements at different heating and cooling rates and the phase transformation occurs at a peak temperature 136.8 °C for Cu_2Se and 133.3 °C for $Cu_{1.99}Se$. Arellano tanori et al. [10] have prepared the copper-selenide (CuSe)) copper-telluride (CuTe) and studied their optical properties. Fengxia Rong et al [11] have studied cuprous selenide (Cu_2Se) nanoparicles at room temperature. Ying Chyl Liew et al. [12] have prepared thin films of copper selenide and the structural, electrical properties are discussed. Gosavi et al. [13] have reported the physical, optical and electrical properties of CuSe thin films deposited by solution growth technique at room temperature. Hamzic et al. [14] have studied the magnetic transitions in $Cu_{2-x}Se$ below room temperature and found that on heating above 170 K it becomes completely diamagnetic. X-ray diffraction and Raman studies on $Cu_{2-x}Se$ prepared in non-vacuum process are carried out by Ara Cho et al. [15].

2. Experimental Methods

The $Cu_{2-x}Se$ nanoparticles were prepared at room temperature synthesis reported in the literature [16]. Copper nanocrystalline chlcogenides $Cu_{2-x}Se$ has been successfully synthesized in a mixture of ethlenediamine and hydrazine hydrate as a solvent at room temperature. All reagents were of analytical grade or better and used without further purification. A suitable proportion of powered copper oxide and Se were put into a conical flask with a capacity of 100 mL, and then mixed with solvent consisting of ethylenediamine and hydrazine hydrate.

$$4CuO+2N_2H_4.H_2O+3Se \longrightarrow 2Cu_2Se+4NH_4+3H_2O+2OH^-+Se^{2-}{}_3+2N_2.$$

The flask was maintained at room temperature with a constant electromagnetic stirring for 24 hours. The mixture initially changed to a dark greenish black color and finally to dark green with a black precipitate.

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Studies on the photoluminescent properties of a single phase white light emitting phosphor $CaLa_{1-x}NbMoO_8$: x Dy^{3+} for pc-white LED applications

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Dy^{3+} doped $CaLa_{1-x}NbMoO_8$ (x=0.02, 0.025, 0.03, 0.035, 0.05, 0.075) phosphors were synthesized using a high temperature solid state method. Powder XRD results confirm the tetragonal phase and detailed investigations on the photoluminescence properties indicated that Dy^{3+} doped $CaLaNbMoO_8$ phosphors has a strong absorption in near UV region and two sharp emission peaks in the visible region. The yellow (575 nm) and blue emissions (487 nm) upon UV excitation resulted from the forced electric dipole transition of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and the magnetic dipole transition of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ respectively. The emission colors of all the doped samples are located in the white light region. Therefore, Dy^{3+} doped $CaLaNbMoO_8$ can serve as a promising candidate for single-phase white-light emitting phosphor under near UV excitation.

1. Introduction

In recent years, with the advancement in the materials technology, there is a growing interest in developing inorganic phosphors that produce white light when doped with lanthanides. Solid state lighting offers high luminous efficiency, low power consumption, reliability, superior life time and environmental friendliness [1]. White light emitting diodes are regarded as the next generation solid state lighting sources as they offer advantages over conventional lighting technologies like incandescent and fluorescent lamps. Exploring novel luminescent materials for WLEDs with high luminous efficacy, high quantum efficiency, high chromatic stability, brilliant color rendering properties, low correlated color temperature, thermal and chemical stability and price competitiveness has been a major challenge to material researchers [2,3]. There is a great demand for developing novel, stable and efficient single phase white light emitting phosphor that can be effectively excited in the near UV/blue region and has attracted much attention for white LED applications. The currently used methods for realizing white light emission in a single phase host involves doping of a single rare earth ion (Dy^{3+}, Eu^{2+}) into an appropriate host matrix, or by co-doping of suitable activators like Tm^{3+}, Tb^{3+}, Eu^{3+}, Ce^{3+} simultaneously along with Dy^{3+} in hosts, by co-doping of different activator ions to control emission color via energy transfer processes, and also by controlling the defect concentrations and reaction conditions for defect-related luminescent materials [4].

Dysprosium (Dy^{3+}) ions exhibits two main emissions in the visible region, the yellow (570–600 nm) and blue (470–500 nm) emissions which are attributed to the forced electric dipole transition of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and the magnetic dipole transition of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ respectively [5]. The hypersensitive $^4F_{9/2} \rightarrow {}^6H_{13/2}$ ($\Delta L=2$, $\Delta J=2$) transition of Dy^{3+} is strongly influenced by the crystal field environment of Dy^{3+}, hence Dy^{3+} ions can be used to probe the local structure of luminescent centers in a definite host lattice whereas the magnetic dipole transition hardly varies with the local symmetry. The emission has a white color which turns to yellow in host lattices where hypersensitivity is pronounced [6]. The emission from Dy^{3+} ions has great dependence on the site symmetry and the chemical nature of the surrounding ions and the luminescent centers [7].

Rare earth doped molybdates and tungstates with scheelite structure are considered as good host lattices under near-UV or blue excitation due to its MoO_4 tetrahedron unit and also for the luminescence of Dy^{3+} ions because of their excellent thermal and chemical stability [8]. The MoO_4^{2-} complex has a strong absorption in the ultraviolet (UV) region due to the charge transfer from the oxygen to metal, resulting in the energy transfer from the MoO_4^{2-} group to the rare earth ions, thereby greatly enhancing the quantum efficiency of rare earth activated phosphors. $CaMoO_4$: Dy^{3+} phosphors codoped with K^+, as a charge compensator prepared by hydrothermal method have been reported [9] and white

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Effect of host structure on the photoluminescence properties of $Ln_3TaO_7:Eu^{3+}$ red phosphors

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ABSTRACT

Eu^{3+} doped Ln_3TaO_7 (Ln = La, Gd, Y, Lu) red phosphors were prepared using a solid state route. The Ln^{3+} substitution induces variation of crystalline structure from a defect fluorite to weberite types with increased ordering of the cations from Lu to La. These phosphors show strong absorptions at near UV wavelength and emit orange–red luminescence. The increased trend in luminescence lifetime further surmises uniform distribution of Eu^{3+} ions from Lu to La. The luminescence intensity and quantum efficiency are closely related to the degree of ordering of the cations in the lattice. The Eu^{3+} luminescence in La_3TaO_7 embodies the structural variation through intense multiband $^5D_0 \rightarrow {}^7F_{0,1,2,4}$ transitions to only dominant hypersensitive electric dipole $^5D_0 \rightarrow {}^7F_2$ transition. All the Eu^{3+} emission transitions ($^5D_0 \rightarrow {}^7F_{0,1,2,4}$) are more intense in La_3TaO_7 host due to increased polarizability and covalent nature of Eu^{3+} bonding environment with the surrounding.

1. Introduction

In view of the great importance of red phosphors towards the development of white LEDs in the lighting industry, the study of Eu^{3+} luminescence in various host systems gains attraction [1]. It is well known that the emission characteristics of Eu^{3+} highly depend on the crystal structure of the host lattice, doping site, doping concentration, ordering of the host lattice, uniformity in the activator distribution and various other factors [2,3]. The probability of electronic transitions from the lowest $^5D_0$ excited state to the $^7F_{0-6}$ ground states differs depending on site symmetries. According to Judd–Ofelt theory, when Eu^{3+} ion occupies a crystallographic site that does not coincide with a center of symmetry, odd crystal field terms lifts the parity prohibition in the electric dipole (ED) transition. The hypersensitive forced ED $^5D_0 \rightarrow {}^7F_2$ transition results in the emissions in the red wavelength region (~612 nm) along with the allowed magnetic dipole (MD) $^5D_0 \rightarrow {}^7F_1$ transition in the orange wavelength region (~590 nm). On the other hand, when Eu^{3+} ion is located at a site with inversion symmetry, only allowed MD transitions are possible [4,5]. Spherical symmetry of the Eu^{3+} ions are broken when placed in a crystalline environment and $2J + 1$ degeneracy of a $^{2s+1}L_J$ multiplet is partially or totally removed. The multiplet is thus split into different crystal field levels. The number of these split levels can be determined from the symmetry of the site [6]. Thus, it is a tricky task to find out the suitable host lattice for the Eu^{3+} ions to have better emission characteristics.

Rare earth niobates and tantalates with a general formula, Ln_3MO_7 have great compositional diversity and gained great attraction as functional materials due to their magnetic, conductive and optoelectronic behavior [7–11]. These kind of compounds which contain both lanthanides (4f metals) and transition metals (4d or 5d) can adopt diverse structures with different site symmetries; ranging from cubic (space groups: Fm-3m, Fd-3m, Ia-3, etc.) to its many orthorhombic super structures (space groups (SG): Cmcm, Ccmm, $C222_1$, etc.) [12–14]. These types of closely related structures offer ample opportunity to understand the factors that influence the Eu^{3+} luminescence. In lanthanides, the 4f atomic orbitals are lying deeply inside the atom and well shielded from its external environment by the valence electrons giving rise to a number of discrete energy levels. Thus the chemistry of the lanthanides is largely determined by their atomic radii. There is considerable amount of literature on the crystal structure of Ln_3MO_7 (Ln = La, Gd, Eu, Dy, Y, Lu; M = Nb, Sb, Ta, Ir, etc.) type compounds [7,15–21]. Most of the such compounds of general formula Ln_3MO_7 are derived from the basic fluorite MO_2 (M_4O_8) structure by creating oxygen vacancies in the lattice. Cubic pyrochlore and C-type structures are formed by removing 1/8th and 1/4th of the oxygen atoms respectively in an orderly manner. The reduction in the number of anions leads to a decrease in the coordination number of M cations. Thus there will be VI and VIII coordinated cationic

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Structural influence on the photoluminescence properties of Eu^{3+} doped Gd_3MO_7 (M = Nb, Sb, and Ta) red phosphors†

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New red phosphor materials of general formula $Gd_{3-x}MO_7:xEu^{3+}$ (M = Nb, Sb, and Ta) were prepared using a high temperature solid state reaction route. Detailed structural studies using XRD, FT-IR and Raman spectroscopic techniques showed that niobate and tantalate samples crystallized in the weberite type structure whereas the antimonate sample in the fluorite structure. Photoluminescence properties of the three compositions are correlated with their crystal structures. It was observed that more ordering occurs in the lattice when an M site is doped from Sb to Nb to Ta. Although niobate and tantalate samples possess similar structures more distortions were noticed in the tantalate sample increasing the radiative transition probabilities. Due to the more ordered structure of the Gd_3TaO_7 host lattice resulting in a more uniform distribution of Eu^{3+} ions, the tantalate system showed better luminescence properties. The variation in the luminescence intensity with various Eu^{3+} concentrations in the Gd_3TaO_7 host lattice was also studied to calculate the optimum doping concentration.

Introduction

Luminescence properties of the various phosphor materials highly depend on the crystallographic structures of the host lattice and the nature of the activator ion.[1,2] Thus choosing the host lattice and the activator ions as well as understanding the chemistry and the structure plays a crucial role in phosphor synthesis. The fluorite structure (AO_2) is considered to be one of the most flexible structures because of its ability to construct superstructures or derivatives. Pyrochlore and weberite, which are anion-deficient fluorite-related structures ($A_2B_2O_7$), also maintain the closed-packed cation layers as in the fluorite structure.[3] If the four tetravalent metal ions in the A and B sites are replaced by three trivalent ions (Ln) and one pentavalent ion (M), one oxide vacancy is formed per fluorite cell. Due to the significant differences in radii between the Ln^{3+} and M^{5+} ions, cation ordering occurs on the metal sites and the oxide-vacancy ordering on the anion sites.[4] Depending on the Ln^{3+} and M^{5+} ions there is a wide possibility of almost similar structures with different ordering and defect formation.

The most widely used activators for red luminescence in the phosphor materials are europium ions (Eu^{3+}) due to their high lumen equivalence, quantum efficiency, and photostability at the same time.[5,6] It is known that the probability of electronic transitions from the lowest $^5D_0$ excited state to the $^7F_{0-6}$ ground state differs depending on site symmetries.[7] Despite extensive studies on various phosphor systems there is limited understanding of the dependence of luminescence properties on the local structures and distributions of activator ions in the host lattice. However the photoluminescence spectra provide invaluable information about the nature of the doping sites and dopant locations in the host lattice.[8] The asymmetric ratio which is the ratio of the integrated intensities of the electric dipole and magnetic dipole transitions provides an estimation of the degree of local distortion and the nature of the doping sites.[9] Another informative spectral feature for assessing the local environment of Eu^{3+} ions is the $^5D_0 \rightarrow {}^7F_0$ transition which occurs between these non-degenerate levels in the 577–584 nm range. Splitting in this transition points out the dual or more non-equivalent site occupancy of Eu^{3+} ions.[10] The distribution of Eu^{3+} ions in bulk compounds has been a subject of experimental and theoretical interest. Reports clearly reveal the fact that the luminescence emission intensity is higher for the more ordered structures due to the more uniform distribution of the activator ions and due to the reduced non-radiative decay pathways.

Crystallographic investigation of Ln_3MO_7 structures can be found dating as far back as 1964.[11] Since then, there have been

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Biomedical Optics EXPRESS

Miniature *in vivo* MEMS-based line-scanned dual-axis confocal microscope for point-of-care pathology

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Abstract: There is a need for miniature optical-sectioning microscopes to enable *in vivo* interrogation of tissues as a real-time and noninvasive alternative to gold-standard histopathology. Such devices could have a transformative impact for the early detection of cancer as well as for guiding tumor-resection procedures. Miniature confocal microscopes have been developed by various researchers and corporations to enable optical sectioning of highly scattering tissues, all of which have necessitated various trade-offs in size, speed, depth selectivity, field of view, resolution, image contrast, and sensitivity. In this study, a miniature line-scanned (LS) dual-axis confocal (DAC) microscope, with a 12-mm diameter distal tip, has been developed for clinical point-of-care pathology. The dual-axis architecture has demonstrated an advantage over the conventional single-axis confocal configuration for reducing background noise from out-of-focus and multiply scattered light. The use of line scanning enables fast frame rates (16 frames/sec is demonstrated here, but faster rates are possible), which mitigates motion artifacts of a hand-held device during clinical use. We have developed a method to actively align the illumination and collection beams in a DAC microscope through the use of a pair of rotatable alignment mirrors. Incorporation of a custom objective lens, with a small form factor for *in vivo* clinical use, enables our device to achieve an optical-sectioning thickness and lateral resolution of 2.0 and 1.1 microns respectively. Validation measurements with reflective targets, as well as *in vivo* and *ex vivo* images of tissues, demonstrate the clinical potential of this high-speed optical-sectioning microscopy device.

OCIS codes: (170.1790) Confocal microscopy; (170.2520) Fluorescence microscopy; (170.5810) Scanning microscopy; (170.3880) Medical and biological imaging; (230.4685) Optical microelectromechanical devices.

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Detection and quantification of dental plaque based on laser-induced autofluorescence intensity ratio values

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Abstract. The aim of this study was to evaluate the applicability of laser-induced autofluorescence (LIAF) spectroscopy to detect and quantify dental plaque. LIAF spectra were recorded *in situ* from dental plaque (0–3 grades of plaque index) in 300 patients with 404 nm diode laser excitation. The fluorescence intensity ratio of the emission peaks was calculated from the LIAF spectral data following which their scatter plots were drawn and the area under the receiver operating characteristics were calculated. The LIAF spectrum of clinically invisible grade-1 plaque showed a prominent emission peak at 510 nm with a satellite peak around 630 nm in contrast to grade 0 that has a single peak around 500 nm. The fluorescence intensity ratio ($F510/F630$) has a decreasing trend with increase in plaque grade and the ratio values show statistically significant differences ($p < 0.01$) between different grades. An overall sensitivity and specificity of 100% each was achieved for discrimination between grade-0 and grade-1 plaque. The clinical significance of this study is that the diagnostic algorithm developed based on fluorescence spectral intensity ratio ($F510/F630$) would be useful to precisely identify minute amounts of plaque without the need for disclosing solutions and to convince patients of the need for proper oral hygiene and homecare practices. [DOI: 10.1117/1.JBO.20.4.048001]

Keywords: laser-induced autofluorescence spectroscopy; quantification; dental plaque; clinically invisible plaque detection.

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1 Introduction

Periodontal disease is the most common cause of tooth loss among adults and its primary etiologic factor is dental plaque. Studies have shown that as early as 2 to 4 h after oral prophylaxis or tooth brushing, the pioneer bacteria (*Streptococci*) cover about 30% of the enamel.[1] Therefore, early identification and meticulous removal of plaque are essential for preventing periodontal disease and maintaining periodontal health.

However, identification of dental plaque is difficult for both patient and dentist because the tooth and dental plaque often look alike, especially if plaque is present in scanty amounts. Traditionally, dental plaque is often detected by clinicians either directly using an explorer[2] or with the help of a disclosing solution[3] and is quantified using indices based on the area of tooth covered or its thickness. But these assessment methods have the limitation of being subjective, therefore, results may vary from clinician to clinician, especially when the plaque is scanty. Recording indices may also need extensive calibration among examiners for high precision and reliability, which could be quite time consuming and costly.[4] On the other hand, disclosing agents used to stain mature and newly formed plaques differently lack specificity. It can stain oral mucosa and lip, though temporarily, which is a major esthetic issue. Fluorescent dyes,[5] automated techniques using computers,[6,7] and plaque quantification using three-dimensional co-ordinates[8] have also been described in the literature but the complexity of the methods, cost of equipment, standardization of the techniques, etc., are some of the major drawbacks in the popularization of these methods. Thus, there is a need to develop a cost-effective and noninvasive technique to more objectively detect and quantify dental plaque accumulation, especially during early stages of plaque formation.

Laser-induced autofluorescence (LIAF) spectroscopy is evolving as a powerful tool to detect and characterize biochemical and morphological changes occurring in the human body based on the changes in the fluorescence signatures.[9] In dentistry, LIAF spectroscopy has been effectively used for early detection of oral cancer[10–12] and tooth caries.[13–15] Mature dental plaque has been identified by the red fluorescence emission caused by the bacteria porphyrins in a few *in vitro* studies.[16,17] Few imaging systems such as plakScope home plaque tester and Vistacam intraoral camera are available on the market to visualize plaque, but may not be useful to visualize plaque accumulation in relatively inaccessible areas such as the palatal aspect of upper anterior teeth or the buccal aspect of posterior teeth due to the curvature of the dental arch. Although the SopraCare imaging system was used very recently to discriminate plaque and gingival inflammation,[18] the sample size was not large enough

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Antimicrobial Photodynamic Efficiency of Novel Cationic Porphyrins towards Periodontal Gram-positive and Gram-negative Pathogenic Bacteria

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ABSTRACT

The Gram-negative *Aggregatibacter actinomycetemcomitans* and *Fusobacterium nucleatum* are major causative agents of aggressive periodontal disease. Due to increase in the number of antibiotic-resistant bacteria, antimicrobial Photodynamic therapy (aPDT) seems to be a plausible alternative. In this work, photosensitization was performed on Gram-positive and Gram-negative bacteria in pure culture using new-age cationic porphyrins, namely mesoimidazolium-substituted porphyrin derivative (ImP) and pyridinium-substituted porphyrin derivative (PyP). The photophysical properties of both the sensitizers including absorption, fluorescence emission, quantum yields of the triplet excited states and singlet oxygen generation efficiencies were evaluated in the context of aPDT application. The studied porphyrins exhibited high ability to accumulate into bacterial cells with complete penetration into early stage biofilms. As compared with ImP, PyP was found to be more effective for photoinactivation of bacterial strains associated with periodontitis, without any signs of dark toxicity, owing to its high photocytotoxicity.

Abbreviations: ImP, 5,10,15,20-Tetrakis[4-(1-methyl-1H-imidazol-3-ium)phenyl]porphyrin tetrabromide; PyP, 5,10,15,20-Tetrakis[4-(8-pyridiniooctyloxy)phenyl]porphyrin tetrabromide; aPDT, antimicrobial photodynamic therapy; PDT, photodynamic therapy; PS, photosensitizer; ROS, reactive oxygen species; DPBF, 1,3-diphenylisobenzofuran; *m*-THPP, meta-tetrahydroxyporphyrin; CSLM, confocal scanning fluorescence microscopy; HpD, hematoporphyrin derivative ; EDTA, Ethylenediaminetetraacetic acid; TLC, Thin layer chromatography.

INTRODUCTION

The photodestruction study of Oscar Raab (1) on Paramecia predates the first anticancer reports. Tappeiner and Jessionek (2) performed the first photodynamic therapy (PDT) on skin cancer using eosin as photosensitizer. Photodynamic antimicrobial agents assumed significance in the beginning of twenty-first century due to the growing resistance of pathogenic microorganisms against the conventional therapy with antibiotics (3). Although a broad spectrum of antibiotics are available, various pathogenic microorganisms are gaining resistance as a result of chromosomal mutation, inductive expression of latent chromosomal genes, exchange of genetic material via transformation, bacteriophage transduction and plasmid conjugation (4). Thus, there is an emergent need to develop and evolve alternate methodologies against the pathogenic microbes.

Photodynamic therapy is a promising and effective alternative to conventional therapeutic methods (5–10). In PDT, the photosensitizer (PS) gets activated by light of suitable wavelength and this in turn reacts with molecular oxygen in ground state to produce excited singlet state oxygen (11,12), which is very reactive and has the ability to oxidize bio-organic molecules (13). Thus, antimicrobial PDT (aPDT) has significant advantages over other therapeutic modalities of treatment owing to its ability to get attached directly to the membranes of pathogenic cells and the possibility for accurate delivery of light to the affected tissue (14).

The cell wall of Gram-negative bacteria is more extensive and complex than that of Gram-positive species (3). Anionic and neutral photosensitizers bind efficiently on Gram-positive bacteria to induce photoinactivation by irradiation in the visible light region with a suitable wavelength, whereas Gram-negative bacteria appear resistant to the same treatment. Growth inhibition of certain Gram-negatives by porphyrin photosensitization occurs only in the presence of cell membrane disorganizing substances, such as EDTA, nitrilotriacetic acid and sodium hexametaphosphate (15). Recent studies (16–20) reveal that different chemical classes of

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Efficacy of antimicrobial photodynamic therapy in the management of chronic periodontitis: a randomized controlled clinical trial

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Abstract

Aim: To evaluate the potential of antimicrobial photodynamic therapy (aPDT) as an adjunct to scaling and root planing (SRP) in the treatment of chronic periodontitis.

Material and Methods: In a single-centred randomized and controlled clinical trial, 90 patients (51 females and 39 males) with untreated chronic periodontitis were randomly assigned to receive SRP with aPDT (test group) or SRP alone (control group). Clinical parameters and halitosis were recorded for 6 months after treatment by a periodontist who was blinded to the procedure.

Results: Inter-group and intra-group statistical analyses were performed. Significant difference between the two groups with respect to each variable was assessed using non-parametric Rank Order ANCOVA. Probing pocket depth and clinical attachment levels showed statistically significant reduction in the test group on evaluation at 3 months and 6 months as compared to the control group ($p < 0.05$). A statistically significant improvement in gingival index and gingival bleeding index was seen for the test group after 2 weeks and 1 month of aPDT ($p < 0.01$), whereas the improvement in gingival index and gingival bleeding index at 3 months and in plaque index at 2 weeks after aPDT was less ($p < 0.05$). Also, a significant difference was detected for the test group at 1 month in terms of halitosis ($p < 0.05$), which did not persist for long.

Conclusions: Antimicrobial photodynamic therapy acts as a beneficial adjunct to SRP in non-surgical treatment and management of chronic periodontitis in short-term. Further studies are required to assess the long-term effectiveness of aPDT.

Key words: adjunctive periodontal treatment; halitosis; methylene blue; periodontal disease; photodynamic therapy; randomized controlled trial

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Conflict of interest and source of funding statement

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The gold standard for the non-surgical treatment of periodontal disease is scaling and root planing (SRP). Although SRP has shown significant improvements in a large number of cases, it was observed to be not very effective in completely eliminating subgingival periodontal pathogens and calculus (Adriaens & Adriaens 2004, Umeda et al. 2004). Alternatively, antibiotics are widely used now-a-days to suppress periodontal pathogens and augment the effect of conventional mechanical treatment.

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Effect of trivalent rare-element doping on structural and optical properties of SnO_2 thin films deposited by dip coating deposition technique

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Abstract Erbium doped tin oxide thin films (SnO_2:Er) were prepared by the sol–gel method using dip coating technique. X-ray diffraction patterns showed a decrease of crystallinity in the films with increase in erbium doping concentration (0–5 mol%). Scanning electron microscopy analysis revealed an inhibition of grain growth with increase in erbium doping concentration. The film surfaces were uniform with crack free appearance. X-ray photoelectron spectroscopy revealed the presence of erbium, oxygen, tin oxide in the SnO_2:Er films. The resistivity of the SnO_2:Er films decreased and then increased with the increase in erbium doping concentration. The optical properties of the films have been studied from transmission spectra. An average transmittance of 80 % in ultraviolet–visible region was observed for all the films. Optical band gap energy (E_{gap}) of SnO_2:Er films were observed to increase with the increase in doping concentration. Photoluminescence spectra of the films exhibited an increase in the emission intensity for (0–3 mol%) and decreased for 5 mol% erbium doping film. Such SnO_2:Er films with wide band gap and luminescence efficiency are applicable in blue and ultraviolet optical devices, such as light-emitting diodes and laser diodes.

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1 Introduction

Tin dioxide (SnO_2) is a wide band gap semiconductor with increasing use as a matrix in phosphorescent materials [1, 2]. This conducting oxide is a well known functional material, sensor, transparent conducting electrode, solar cells, special coating for energy-conversion, low-emissivity windows, and nanoelectronic devices [3]. The technological interest in rare earth luminescence reaches beyond telecommunications to displays, laser materials, data storage, radiation detection, and medical applications. Recently, most of the interests in luminescent rare earth ions have concentrated on Er^{3+} due to its unique electronic and optical properties.

Among the RE, Er^{3+} has high technological potential, because this ion presents several emission ranges, from visible to the infrared. In its threefold oxidation state, rare-earth ions (RE^{3+}) exhibit luminescence due to 4f core transition, which is practically independent of host matrix [4]. The combination of Er^{3+} with wide band gap semiconductors like SnO_2 can contribute for technological innovation, leading to the creation of new opto-electronic devices, such as electroluminescent mechanisms, solar cells and posses very significant applications in optical communication [5]. SnO_2:Er films can also be used in optical amplifiers and electroluminescent devices where electron–hole energy is transferred to Er^{3+} ion.

However, the optical cross-sections for the intra-4f transitions of Er in metal-oxide semiconductor are rather small, typically on the order of 10^{-21} cm^2. For this reason, there is considerable interest in sensitising the Er^{3+} ions by adding into metal-oxide semiconductors like SnO_2. Particle size distribution plays a very important role in different layers of solar cells. The ionic radius of Sn^{4+} is 0.690 and Er^{3+} is 0.890 Å in the same coordination. The difference

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between radius and charge of the Er^{3+} and Sn^{4+} lattice ions makes difficult the ion incorporation into the SnO_2 lattice, which leads to a low quantum efficiency in the luminescence process [6]. To avoid this problem the matrix has been used in the shape of nanoparticles, produced by the sol–gel method.

Sol–gel fabrication has gained much interest because of its simplicity, low processing temperature, stoichiometry control and its ability to produce uniform, homogenous films over large areas that can provide integration with other circuit elements [3]. In SnO_2, oxygen vacancies act as donors centers. Two donor levels associated with this center have been reported, a shallow level at 30 meV below the conduction band and a deep level about 150 meV. Er^{3+} is incorporated into SnO_2 lattice substitutional in Sn^{4+} sites and exhibits an acceptor like behavior in SnO_2, leading to electrical charge compensation, and resistive films [7].

In this study, we present the influence of different Er doping concentration in SnO_2 films. The structural, electrical and optical properties of SnO_2:Er thin films were examined in relationship with the variation in erbium doping concentrations.

2 Experimental procedure

The SnO_2 solution was prepared by dissolving 8.37 g of $SnCl_2{:}2H_2O$ in 100 ml of absolute ethanol. This mixture was stirred and heated at 83 °C for 2 h in a closed vessel. Then the vessel was opened, and the solution was again stirred and heated until the solvent was completely evaporated. The final result was a powder, to which 50 ml of absolute ethanol was added. The final SnO_2 solution was then stirred and heated for 2 h at 50 °C. An appropriate quantity of erbium trichloride hexahydrate ($ErCl_3{\cdot}6H_2O$) was dissolved in the prepared SnO_2 solution. The doped mixture was finally stirred and heated at 50 °C for 2 h. SnO_2:Er films were deposited on quartz substrate and was prepared using the sol–gel dip-coating technique. The deposited layer was then dried in air at 150 °C for 30 min after each dipping. Then, the SnO_2:Er films were annealed at 450 °C for 30 min to assure the crystallization of SnO_2 and then to 500 °C for 120 min in order to activate the Er^{3+} ions in the matrix. To obtain a satisfactory film thickness for practical application, the above cycle (dipping–drying–heating) was repeated several times (eight coatings).

Crystallization phase of the SnO_2:Er films were characterized by X-ray diffraction using X-ray diffractometer (Model—PW 1710 PHILIPS). The surface morphology of the films was investigated by using scanning electron microscope (Model—JSM 5600LV JEOL). XPS spectra was recorded using a monochromatic Al Kα (1486.6 eV) source and a MAC-2 electron analyzer (RIBER system model-FCX 700). The electrical property of SnO_2:Er films were determined by four-point probe measurements with a Keithley 6200 source meter and a cylindrical four-point probe head. The spectral transmittance of the films was recorded as a function of wavelength (300–900 nm) using JASCO V-550 UV–Vis spectrophotometer. The film thickness and optical band gap values were determined using Swanepoel's envelope method [Swanepoel 1983]. Photoluminescence (PL) spectra were recorded by using SPEX—Fluorolog F112X spectrometer.

3 Results and discussion

3.1 X-ray diffraction studies

The X-ray diffraction pattern of sol–gel derived SnO_2:Er films deposited on quartz substrates annealed in air at 500 °C are shown in Fig. 1. The XRD patterns revealed that all the SnO_2:Er films posses tetragonal structure with orientation along (110), (101) and (211) reflections (JCPDS No. 41-1445). In addition to these planes, the planes such as (200), (220), (002), (310), (112) were observed in the undoped SnO_2 film. No characteristic peaks of impurities, such as erbium oxide or other mixed tin oxide phases were observed.

The crystallite size 'D' of SnO_2:Er films were calculated using Scherer's formula [8].

$$D = \frac{k\lambda}{\beta \, Cos\, \theta} \tag{1}$$

where D is the crystallite size, β is the full width at half-maximum (FWHM) of the most intense diffraction peak, λ

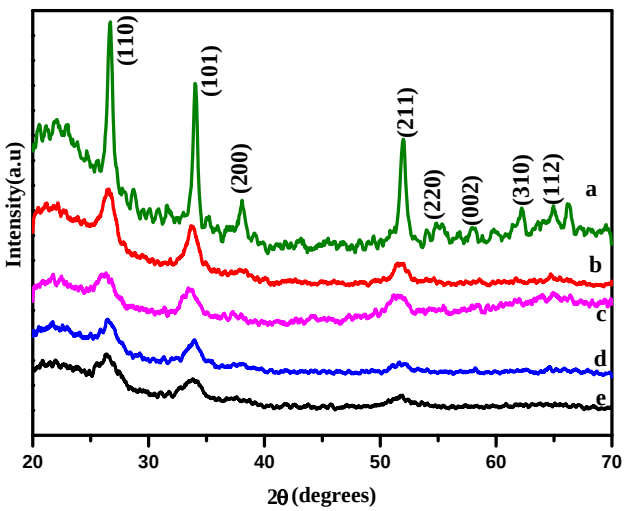

Fig. 1 XRD patterns of SnO_2:Er films for different erbium concentrations. (*a*) 0 mol% (*b*) 1 mol% (*c*) 2 mol% (*d*) 3 mol% (*e*) 5 mol% Er

is the X-ray wavelength (1.5406 Å) and θ is the Bragg angle. The grain size in SnO_2 film (22.27 nm) decreased to 6.98 nm for 5 mol% SnO_2:Er film. Table 1 shows the FWHM, crystalline size, band gap energy and thickness of SnO_2:Er thin films. The lower grain size increase the efficiency of solar cells like dye based solar cells. The reflections in the XRD pattern became broader and the intensity decreased with increasing the Er concentration. This indicates reduced grain size and a lower extent of crystallisation in the SnO_2:Er films (Fig. 1). Broadened peaks indicate the nanosizing of the grains. This may be due to the disorder caused by the substitution of Er^{3+} having an ionic radius (0.890 Å) greater than Sn^{4+} (0.690 Å). It can also be observed (Fig. 1) that the intensity of the diffraction peaks decreased, the corresponding FWHM of the peaks increased with increase in the Er concentration. This indicates deterioration of crystallinity in the films with increase in the doping concentration.

From the XRD spectra, interplanar spacing (d) was calculated. All the d-values are slightly smaller or higher than those of the bulk, which indicates a distortion in the unit cell structure compared to that of bulk materials. The distortion in samples is evaluated as,

$$\Delta d = \frac{d - d_o}{d_o} \times 100 \tag{2}$$

where d and d_o are the d-spacing values of the film and bulk, respectively [3]. This lattice distortion contributes to lattice strain. The values of lattice distortion in the samples are given in Table 2. The lattice parameters are calculated using the equation

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{3}$$

where'd' is the interplanar distance, (*hkl*) are the miller indices, *a* and *c* are the lattice constants. The calculated values are given in the Table 2. The lattice constants for tetragonal SnO_2 film are reported in JCPDS standard data $a = 4.7382$ Å and $c = 3.1871$ Å (JCPDS card no: 041-1445). The lattice parameters increased with erbium doping concentration. The distorted structure and charge imbalance in SnO_2:Er films can result in the formation of internal strain and oxygen vacancy [9].

3.2 Surface morphology studies

Figure 2 shows SEM micrographs of SnO_2:Er thin films for different erbium doping concentrations (0–5 mol%) annealed at 500 °C. The surface of all films are continuous, smooth, uniform and without micro-cracks. The PL properties of the films depend on the surface morphology. The micrograph of undoped SnO_2 film shows bigger grains compared to that of SnO_2:Er films. The micrographs indicate nearly spherical structures. When erbium was added as a dopant, the micrograph shows a different appearance, showing the effect of dopant in the host matrix. The images reveal the formation of nanocrystalline materials and show the randomly oriented nanoparticles with variable sizes. In 1 mol% SnO_2:Er films, large number of particles can be observed in the micrographs. When the erbium doping concentration increased (5 mol%), it was observed that the particle size decreased and small pores were observed. This shows the effect of increasing erbium doping concentration on the SnO_2 film. The presence of pores directly affects the optical properties, since pore size and particle distribution can significantly contribute to increasing optical losses due to scattered light in the inter-grain region. This result agrees well with the XRD analysis mentioned above. Hence, the surface morphology of the films, strongly depend on the concentration of doping ions.

3.3 XPS studies

X-ray photoelectron spectroscopy is a surface analysis technique that can be used for compositional and chemical states analysis. Figure 3 shows XPS spectrum of undoped SnO_2 and Figs. 4, 5, and 6 shows the XPS spectra of SnO_2 :Er films (1–5 mol%). XPS spectrum of undoped SnO_2 confirms the presence of Sn 3d, O 1S and C 1S states with binding energies (BE) at 484.13 & 493.9, 530 and 284 eV respectively. The BE analysis of SnO_2:Er films revealed that Er 4d, Sn 3d, C 1s and O 1s signals were observed near 169, 487 & 494, 284 and 531 eV, respectively.

Carbon is ubiquitous and is present on all surfaces for XPS analysis. It is common practice to use the carbon C 1s peak at 285.0 eV as a reference for charge correction

Table 1 FWHM (β rad), crystallite size (nm), band gap (eV) and thickness (nm) of SnO_2:Er films for different erbium concentrations

Erbium concentration (mol%)	FWHM (β rad)	Crystallite size D (nm)	Band gap (eV)	Thickness (nm)
0	0.0061 ± 0.0078	22.2 ± 0.023	3.921 ± 0.064	468 ± 1.49
1	0.0113 ± 0.0113	14.19 ± 0.031	3.99 ± 0.0219	602 ± 0.73
2	0.0141 ± 0.0141	10.07 ± 0.027	4.04 ± 0.0272	606 ± 0.89
3	0.0181 ± −0.0181	7.85 ± 0.0149	4.09 ± 0.058	627 ± 1.12
5	0.0203 ± −0.0203	6.98 ± 0.0817	4.175 ± 0.0745	690 ± 0.58

Table 2 d- spacing, lattice parameters of SnO_2:Er films for different erbium concentrations

Er concentration (mol%)	$\Delta d_{(110)}$	$\Delta d_{(101)}$	$\Delta d_{(211)}$	Lattice parameters (nm)	
				a	*c*
0	0.0031	0.0159	−0.123	4.731	3.196
1	0.4408	0.0073	0.3880	4.717	3.197
2	0.0037	0.0082	0.2530	4.734	3.184
3	0.2802	0.3371	0.0174	4.740	3.202
5	0.0079	−0.013	0.0018	4.749	3.204

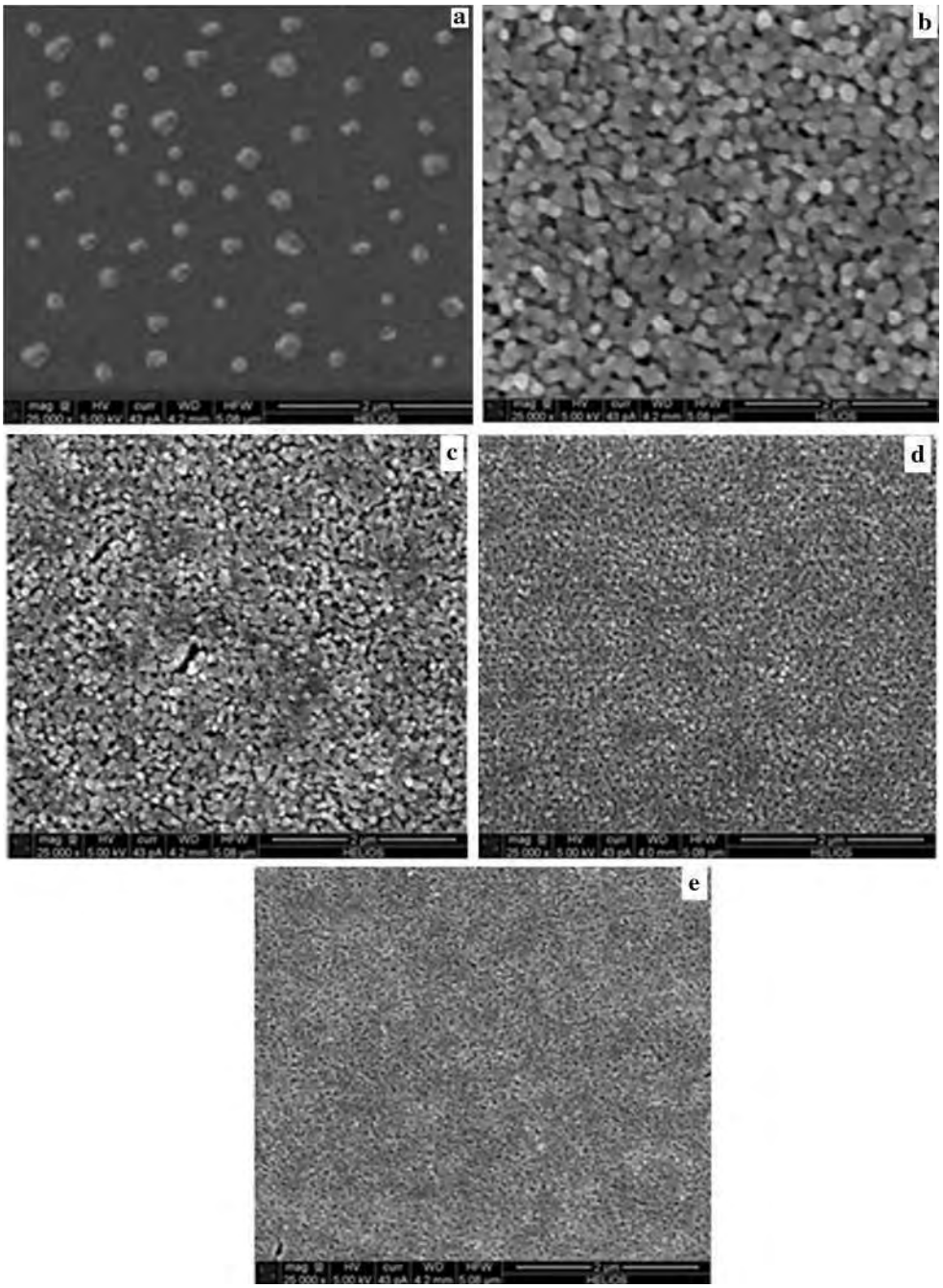

Fig. 2 SEM micrographs of SnO_2:Er for different erbium doping concentrations. (**a**) 0 mol% (**b**) 1 mol% (**c**) 2 mol% (**d**) 3 mol% (**e**) 5 mol% Er

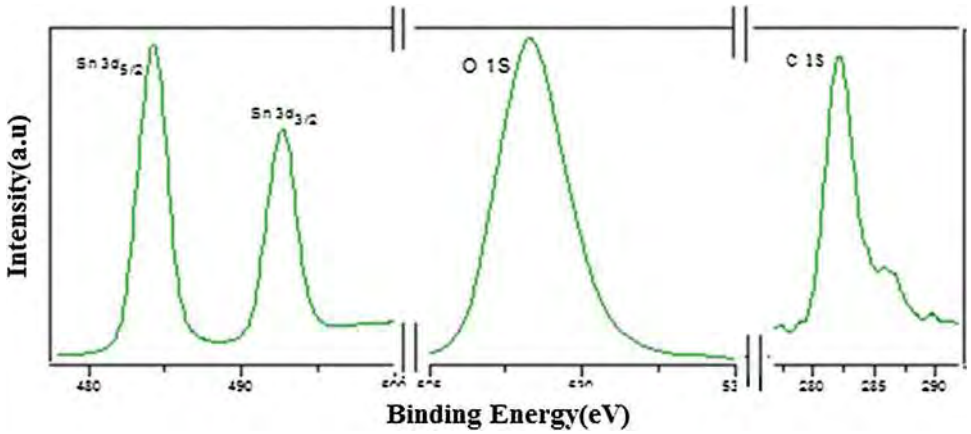

Fig. 3 XPS spectra of undoped SnO_2 film

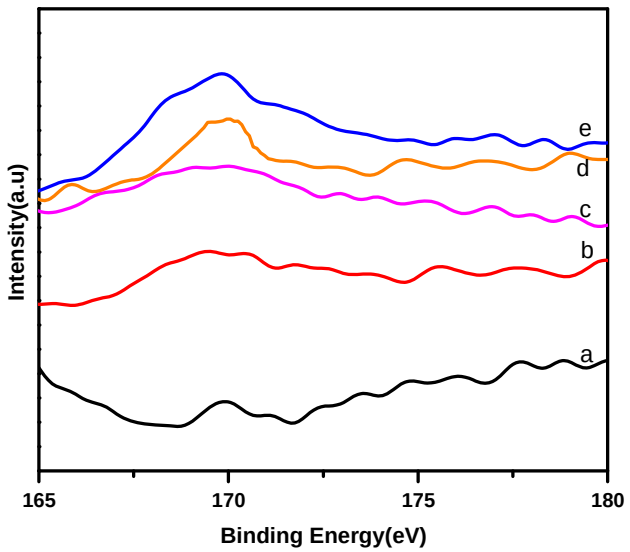

Fig. 4 XPS spectra of Er 4d in SnO_2:Er films for different erbium doping concentration. (*a*) 1 mol% (*b*) 2 mol% (*c*) 3 mol% (*d*) 4 mol% (*e*) 5 mol% Er

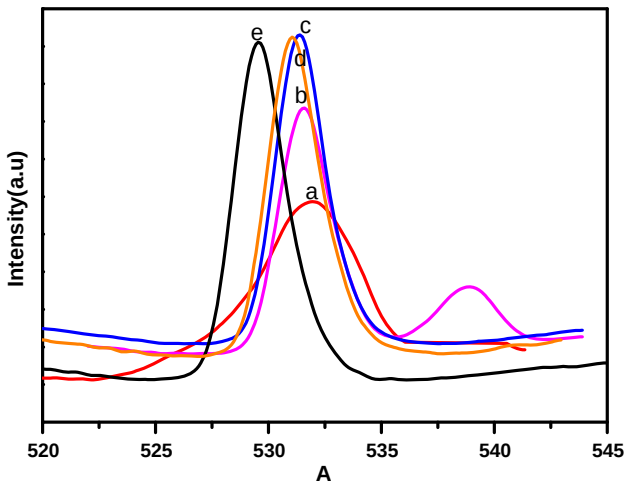

Fig. 5 XPS spectra of O 1S of SnO_2:Er films for different Er doping concentrations. (*a*) 1 mol% (*b*) 2 mol% (*c*) 3 mol% (*d*) 4 mol% (*e*) 5 mol% Er

(Fig. 4). The peak of C 1s spectra at 285.0 eV is assigned to C–C and C–H hydrocarbon bonds.

The normalized 4d spectra of Er (1–5 mol%) in SnO_2:Er films are given in Fig. 5, showing a characteristic spectral feature near 169 eV. Such feature is attributed to the 4d levels in Er^{3+} forming peaks through an interaction with the unfilled shell [10]. The shape of the BE spectra of erbium is an indicative of the oxidation state of Er in the material. The existence of the peak near 169 eV for all the cases, suggests that the oxidation state of Er in SnO_2:Er films did not change markedly during the dip coating process. In SnO_2:Er films, all the samples show the binding energy of Er 4d (Fig. 5) in the region of 169.2–169.7 eV, indicating that all erbium detected was in a trivalent state (Er^{3+}). The BE slightly shift to higher value for 5 mol% Er in SnO_2:Er films. Report suggest that this shifting to higher binding energies may be due to the presence of

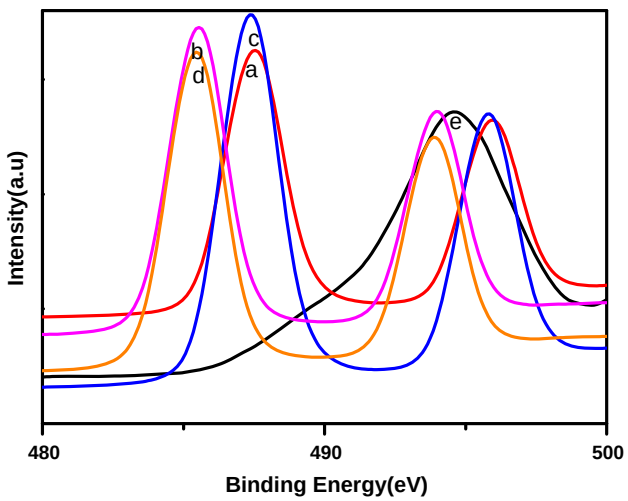

Fig. 6 XPS spectra of Sn 3d in SnO_2:Er films for different Er doping concentrations. (*a*) 1 mol% (*b*) 2 mol% (*c*) 3 mol% (*d*) 3 mol% (*e*) 5 mol%

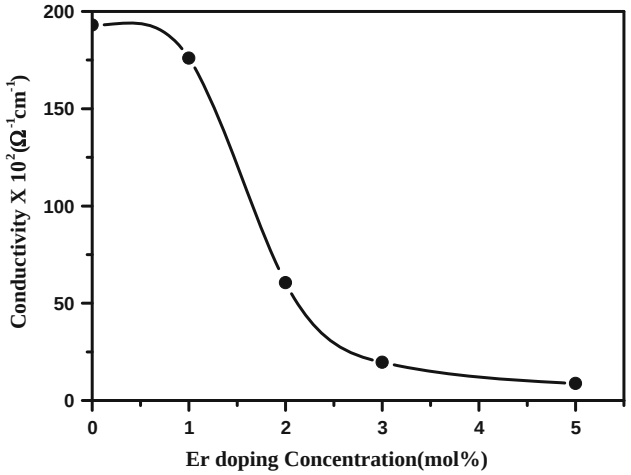

Fig. 7 Variation in conductivity with different erbium concentrations in SnO_2:Er films

nanoparticles with smaller sizes (<10 nm) [11]. These results are in good agreement with the results obtained from XRD. The peak energy and peak shape of Er 4d, Sn 3d and O 1s peaks are consistent with other studies [12, 13]. We, therefore, conclude that the incorporation of Er into SnO_2 samples essentially preserves the Er^{3+} state, forming efficient emission centers. At a low doping concentration of Er, we observe the lower intensity peak of the Er 4d state. Spectral multiplets at ~169 eV with essentially the same features as shown in Fig. 5 were observed in the 4d photoemission spectra obtained from the erbium state of $4f_{11}$/Er^{3+} [10]. Hence, we suggest that the SnO_2:Er films grown by sol gel dip coating method are basically stoichiometric, which is one of basic requirements for a solar cell, where these materials act as a metallization mask to electroless metal plating solutions.

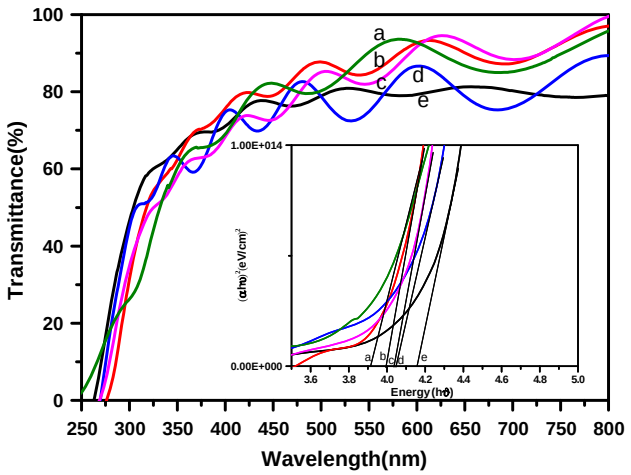

Fig. 8 Transmittance spectra of (*a*) 0 mol% (*b*) 1 mol% (*c*) 2 mol% (*d*) 3 mol% (*e*) 5 mol% Er thin films (*inset* hν vs. $(\alpha h\nu)^2$ graph)

Figure 6 shows the narrow scan XPS spectra of the O 1s state for samples deposited with different Er concentrations. The binding energies of O 1s are 531.8, 531.4, 531.3 and 529.5 eV for SnO_2:Er films (1–5 mol%) respectively. Generally, the O 1s peak observed in the region 529–531 eV has been attributed to lattice oxygen. Ghuang et al. [14] attributed the peak around 530.7–531.6 eV to oxygen in non-stoichiometric oxides in the surface region. They observed chemisorbed O_2 on the metal surface in 530–530.9 eV and surface oxides and hydroxides in 529.6–531.0 and 533.3 eV binding energy regions, respectively. On the basis of these observations, the O 1s peak observed in the region 529.5–531.8 eV for SnO_2:Er thin films can be attributed to lattice oxygen and chemisorbed oxygen. The intensity of oxygen peak increased for 1–3 mol% Er doping. This shows the presence of oxygen vacancies in the film, which can enhance the PL emission. When the doping concentration increased to 5 mol% Er, the intensity of oxygen peak decreased and the peak shifted towards low binding energy region. This can be due to Er doping in SnO_2 lattice, which can lead to change in oxygen vacancy, formation of tin interstitials, lattice strains etc.

Figure 6 shows the narrow scan XPS spectra of Sn 3d states for the samples deposited with various Er concentrations. The spectra show well-resolved doublets due to the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ components corresponding to binding energies of 487.6, 485.57, 487.41 eV & 495.9, 494.01, 495.7 and 494.7 eV for SnO_2:Er films (1–5 mol%) respectively. The binding energy of Sn $3d_{5/2}$ is attributed to the Sn^{4+} bonding state, which agrees well with the previous report [15]. When the doping concentration increased to 5 mol% Er in SnO_2:Er films, only one peak at 494.7 eV was visible in the spectra. *The shift in binding energy curve of SnO_2 is due to the change in its chemical bonding. The binding energy of Sn $3d_{3/2}$ shifted with respect to the other samples. This is an indication that the chemical environment was changing due to the incorporation of more dopant concentration* (5 mol% *Er) in SnO_2 compared to that with* 0–4 mol% *Er. Similar studies have shown that the chemical bonding and surface states of the SnO_2 gets modified due to the effect of incorporation of more dopant* [16, 17]. The gap between the Sn $3d_{3/2}$ and Sn $3d_{5/2}$ levels (8.4 eV) closely corresponds to the O in SnO_2 and Sn in SnO_2, respectively [18].

3.4 Electrical property

Figure 7 shows the variation in conductivity of SnO_2:Er films with increase in Er doping concentration. It was observed that the conductivity decreased with increase in Er doping concentration. This behaviour may be related to grain boundary scattering and charge compensation in SnO_2:Er films with the increase in erbium doping concentration. An decrease in crystalline size would be

strongly related to a increase in resistance for free electrons, because of higher grain and grain-boundary scattering. The presence of Er^{3+} and Sn^{4+} in SnO_2:Er films were confirmed from the XPS results. The difference in valence state of the ions leads for the charge compensation. The undoped SnO_2 presents n-type conduction and the increase in Er-doping concentration induces more electron trapping in the material, which increases the film resistivity. Electrical conductivity of SnO_2:Er films may become low due to the presence of a large amount of small grains. This is evident from the SEM micrographs. Besides, XRD studies have shown that the introduction of the dopant inhibits the grain growth. This decreases the electronic mobility affecting conductivity in films [9]. Also, it must be mentioned that the solubility-limit has been overcome, creating scattering centers inside the nanocrystallites which decrease the mobility. Being a wide band gap SnO_2:Er films, posses band gap in the range 4.00–4.18 eV, is transparent to radiation with the wave length for the region of maximum solar intensity. The conductivity could be changed within wide limits, from 10^4 up to 10^1 ohm^{-1} cm^{-1}. This property permits SnO_2:Er films to be used in solar cell fabrication as frontal layer in SIS structures [19].

3.5 Optical properties

The optical transmission spectra of SnO_2:Er thin films annealed in air at 500 °C are shown in Fig. 8. The average transmittance of the films decreased from 95 to 80 %, when the doping level increased from 0 to 5 mol%. The interference pattern seen in the transmittance spectra is the evidence for homogeneous and uniform films. It can be seen that the increase in percentage of Er dopant shows

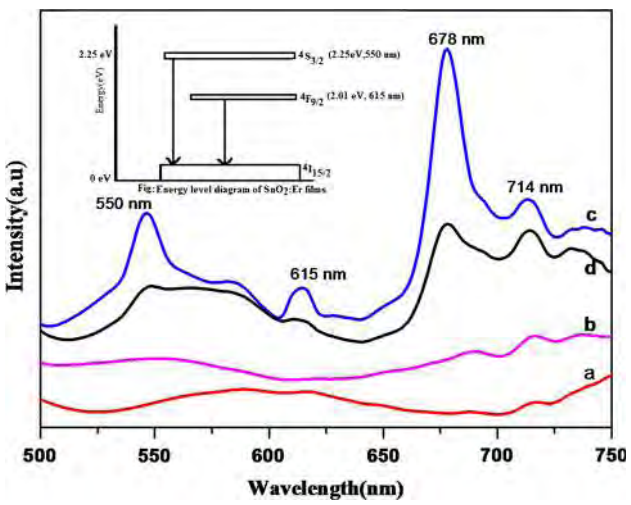

Fig. 9 PL spectra of (*a*) 1 mol% (*b*) 2 mol% (*c*) 3 mol% (*d*) 5 mol% Er in SnO_2:Er films (*inset* energy level diagram of SnO_2:Er films)

mild shift towards shorter wavelength region. The decrease in transmittance of SnO_2:Er films with the increase in dopant concentration may be attributed to the increase in surface roughness. The grain boundaries in polycrystalline films can cause increase in scattering leading to decreased transparency. A nanocrystalline material contains a high concentration of grain boundaries compared to the case of a bulk material. These properties are of considerable importance for electrical transport, optical, and mechanical properties [20–23].

The fundamental absorption, which corresponds to electron excitation from the valence band to the conduction band, can be used to determine the nature and value of the optical band gap. The excitation of electron from valence band to conduction band by absorption of photon energy can occur in two ways usually either in direct or indirect transitions. The optical band gap of semi-conductor materials can be deduced from transmission measurements using Tauc's relation [3].

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^{1/2}$$

where hν is the photon energy, α the absorption coefficient corresponding to frequency ν, Eg is the optical band gap, A is a constant. The Eg values of SnO_2:Er films were obtained by extrapolating the linear portion of $(\alpha h\nu)^2$ versus hν plots to intercept the photon energy axis (inset—Fig. 8). The plots of $(\alpha h\nu)^2$ as a function of energy (hν) for SnO_2:Er films tend asymptotically towards a linear section, which shows that the investigated films have a direct optical band gap. The calculated Eg values are given in Table 1. The values lie in the range 4.00–4.18 eV for the SnO_2:Er films prepared with different doping concentrations. (Table 1: band gap and thickness of SnO_2:Er films for various Er doping concentrations). *The thickness of the SnO_2 films increased with the increase in Erbium doping concentration. Similar studies of change in thickness were reported for fluorine doped SnO_2 films* [24]. The Eg for the undoped SnO_2 film is 4.00 eV and it is increased to 4.18 eV for 5 mol% of the SnO_2:Er films. This slight shift in band gap is due to size effect. In the quantum confinement range, the band gap of the particles increases, resulting in the shift of the absorption edge to lower wavelength as the particle size decrease. Such SnO_2:Er films with wide and direct band gap are applicable in blue and ultraviolet (UV) optical devices, such as light-emitting diodes and laser diodes.

3.6 Photoluminescence property

Rare earth oxides and its compounds have been investigated most frequently because of their unique luminescence properties due to their stability and emission quantum yields. If rare-earth ions can be doped into

semiconductor nanoparticles, then band gap excitation may result in efficient energy transfer and hence intense luminescence could be observed. This is particularly true if through quantum confinement, the band gap state is resonant with an excited state of the rare-earth ion, therefore, semiconductor nanoparticles doped with rare-earth ions are of considerable interest. SnO_2 is an ideal host material to dope Er^{3+} ions. In addition, SnO_2 has advantages of large exciton binding energy, which may influence Er^{3+} ion related emission.

Figure 9 shows the PL spectra of SnO_2:Er films annealed in air at 500 °C for various erbium doping concentration. The excitation wavelength used in this study is 290 nm. There are several emission peaks in the SnO_2:Er films that correspond to the erbium transitions. In this study, the emission peaks of Er in SnO_2:Er films were obtained at 550 (2.25 eV), 615 (2.01 eV), 678 (1.82 eV) and 714 nm (1.73 eV). For 1 mol% Er in SnO_2:Er film, low intense peak at 714 nm and a broad peak at 615 nm were visible. When the doping concentration increased to 2 mol% Er in SnO_2:Er film, the intensity of the peak at 714 nm increased and broad peak at 550 and a small peak at 678 nm were also visible. For 3 mol% Er doping, the intensity of the peaks increased and for 5 mol% Er doping, intensity of the peaks decreased.

When excited, the SnO_2 host absorbs the energy and transfers its energy to Er^{3+} ions, which thus emit photons at various wavelengths. The displayed emission bands of the Er^{3+} ion demonstrate the existence of the energy transfer from the host to the active ion. The increase in the ion concentration promotes the energy transfer process, increasing the emission of the erbium ions. The incorporation of Er^{3+} creates the oxygen vacancies because the charge of the Er and Sn ion has to be compensated in the lattice in the form of oxygen vacancy. The presence of oxygen vacancy is evident from the XPS results. At the same time, the oxygen vacancy might act as the sensitiser for the energy transfer to the Er^{3+} ion [25]. The Er^{3+} ion has a $4f_{11}$ electron configuration. Since the f–f absorption transitions in Er^{3+} ions are parity forbidden, and SnO_2 is a direct-band-gap semiconductor, the number of carriers excited through f–f transitions in Er^{3+} ions is much less than those excited through band-gap excitation of SnO_2 [26]. Thus, the Er^{3+} emission comes mainly from radiative recombination of the large amount of trapped carriers excited from SnO_2 host [27].

The 550 nm green emission bands in SnO_2:Er films correspond to the energy level (Fig. 9) of Er for $^4S_{3/2}$–$^4I_{15/2}$ optical transitions, and the 615 nm red emission bands correspond to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ optical transitions respectively. The emissions in SnO_2:Er films are due to the same transitions from the two levels $^4S_{3/2}$ and $^4F_{9/2}$ to the ground level $^4I_{15/2}$. The green emission ($^4S_{3/2}$–$^4I_{15/2}$), being observed due to Er^{3+} concentration might have originated from the excited state absorption mechanism. For a low Er^{3+} concentration (1–3 mol%), energy transfer rarely occurs between excited ions. The $^4F_{9/2}$ level can only be populated from the $^4S_{3/2}$ level through multiphonon relaxation [28]. The increase in the red luminescence with increased Er^{3+} concentration must, therefore, result from an energy transfer between excited ions.

The orange emission observed at 678 nm might be due to the involvement of interstitial oxygen or due to recombinations from the conduction band and shallow donor levels to the energy levels near the top of the valence band [29]. A broad peak observed at 714 nm for the films may be due to other crystal defects which are formed during the growth of samples.

We can observe that the emission intensity of the SnO_2:Er film increases as the doping concentration of Er changes from 1 to 3 mol%. When the Er doping concentration exceeds 3 mol%, the PL intensity diminishes. The high Er concentration will decrease the luminescence efficiency by energy transfer processes due to ion–ion interactions. This observation confirms the entry of erbium into the lattice of SnO_2 which was also evident from the XRD spectra which showed low crystallisation. This behavior may be also related with decrease of particle size with increasing of Er concentration. The quenching mechanism is thought to be a cross-relaxation process between two closely placed Er^{3+} ions [30]. The short distance between ions results in enhanced luminescence quenching probability. Accordingly, the emission intensity degrades while the Er concentration exceeds. Hence, at higher Er doping concentration, the luminescence efficiency will be low due to the lower degree of crystallization and higher defect density. This agrees with the XRD results. The broadening of the luminescence peaks observed in the PL spectra is due to the introduction of oxygen vacancies for charge compensation. This is evident from XPS spectra of O 1S where the intensity of oxygen peak increases (1–3 mol%) and decreases for 5 mol% Er. When the Er^{3+} concentration increases, the coordination around the Er^{3+} active ions can change causing short-range disorder in the lattice [31–33]. The defects or vacancies would greatly enhanced energy transfer from the band edge to the defect states responsible for the visible emission. Hence, the improvements in visible emissions are attributed to the enhanced defects and vacancies caused by Er^{3+} dopants.

4 Conclusion

SnO_2:Er thin films for different erbium doping concentrations (0–5 mol%) were prepared by dip coating technique. The structural studies show that as the Er concentration

increased, the crystallinity of the films decreased. The optical transmittance for the films were in nearly 80 % and posses a wide band gap finding wide applications in LED. SEM micrographs shows that the particle size decreased with increase in dopant concentration. XPS spectra shows the presence of Er 4d, Sn 3d, C 1S and O 1S states. The SnO_2:Er thin film with 3 mol% of Er dopants has the strongest PL intensity, while the PL intensity decreased for the SnO_2:Er thin film containing 5 mol% Er. The relative luminescence intensity decreased with increasing Er^{3+} concentration is mainly attributed to structural defects, oxygen vacancies and surface states. All the results presented in this work indicate that SnO_2:Er obtained by the sol–gel method is a promising host in the development of rare earth-doped transparent conducting oxides for laser and amplifier applications.

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Effect of Mn doping on the structural and optical properties of ZrO_2 thin films prepared by sol–gel method

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ABSTRACT

Homogeneous and transparent Mn doped ZrO_2 thin films were prepared by sol–gel dip coating method. The films were annealed in air atmosphere at 500 °C. The X-ray diffraction pattern of the undoped ZrO_2 thin film revealed a mixed phase of tetragonal and monoclinic ZrO_2 with preferred orientations along T(111) and M(−111). Grazing Incidence X-ray Diffraction of Mn doped ZrO_2 thin films reveals the introduction of Mn interstitial in ZrO_2 which stabilize the mixed phase of ZrO_2 into tetragonal phase. Atomic force microscope image shows the addition of catalyst (Mn) which stops isotropic agglomeration of particles, instead of anisotropic agglomeration that occurred resulting in growth of particles in certain direction. Average transmittances of >70% (in UV–vis region) were observed for all samples. The optical band gap decreased from 5.72 to 4.52 eV with increase in Mn doping concentration. The reduced band gap is due to the introduction of impurity levels in the band gap, by incorporation of the metal ions into the ZrO_2 lattice. The d-electron of Mn (t_{2g} level) can easily overlap with the ZrO_2's valence band (VB) because t_{2g} of Mn is very close to VB of ZrO_2. This overlap caused a wide VB and consequently decreases the band gap of ZrO_2. The photoluminescence (PL) spectrum of undoped zirconia thin film exhibits an intense near band edge emission peak at 392.5 nm (3.15 eV) and weak emission peaks at 304 (4.07 eV), 604 nm (2.05 eV) and 766 nm (1.61 eV). Additional PL peaks were observed for Mn doped ZrO_2 located at around 420, 447 (blue), 483 (blue) and 529 (green) nm respectively. These peaks were due to the redox properties of various valence state of Mn in ZrO_2. The prepared Mn doped ZrO_2 thin films can be applied in optical devices.

1. Introduction

Zirconia (ZrO_2) is widely used as an essential material in the optical fields including broadband interference filters and active electro-optical devices, due to its excellent optical properties, such as high refractive index, large optical band gap, low optical loss and high transparency in the visible and near infrared region [1,2]. It has wide band gap and short wavelength photoluminescence (PL) emission property [3]. Zirconia can be used as diluted magnetic semiconductor (DMS) material [4] with suitable magnetic material dopant such as Mn. DMS are a class of materials, in which magnetic dopants replace native cations in ordinary semiconductors [5]. The replaced magnetic ion couple with extended electrons in the semiconductor band, and this coupling results in various interesting properties like magneto-optical and magneto-electrical effects [4]. DMS are very interesting materials subjected to their promising applications to spintronics (spin + electronics). Compared with the traditional charge-based semiconductor technology, the semiconductor–spintronics paradigm is advantageous in using both the charge and spin of electrons at the same time, which has been considered to be a solution to the current silicon-based semiconductor's dilemma [6]. The spintronics-based device has been considered to be more powerful, endurable, non-susceptible to radiation damage, and energy efficient than semiconductor-based one [7,8]. Also the ternary nature of the DMS provides a possibility of tuning band parameters by varying the composition of the material [9]. The band structures of ZrO_2 are highly dependent on chemical microstructures, particularly the crystal phases, crystallite sizes and nature of defects [10–12]. Theoretically, the valence band of ZrO_2 is formed mainly by O 2p states with some admixing of Zr 4d states, and the conduction band is constructed primarily of Zr 4d states admixed with some O 2p states. ZrO_2 is an active, photon absorber and photon catalytic among wide band gap (E_g) metal oxides. It has two direct band to band transitions at 5.2 and 5.79 eV [1]. Lattice defects usually introduce extrinsic energy levels between bands and which reduce band gap [13]. It has been observed that doping with 3d metals reduce the E_g of semiconductors by forming inter band-gap localized levels [14]. The dopant atoms are ionized and, for the case of n-doping, the associated electrons occupy the bottom of the conduction band, in the form of an electron gas or conduction electrons. In principle, the optical band gap can be larger or smaller than the one of the undoped host crystal. A widening occurs, since the lowest states in the conduction band are blocked; the well-known Moss–Burstein effect. In our previous studies, we found that Al doped in ZrO_2 a blueshift was observed in the absorption edge [2]. García and Azorin et al. [15,16] observed a decrease in the band gap of metal-doped ZrO_2 which was due to the incorporation of metal ions in the ZrO_2 lattice produce localized energy levels in the energy gap. Therefore,

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it would be worthy to investigate the doping effect on the optical properties of Mn doped ZrO_2.

In our previous studies [1], we observed that a phase transition from tetragonal to monoclinic in ZrO_2 when it was annealed at 500 °C. Jerome Chevalier et al. [17] reported that during phase transition the large stress is induced in the films which would destroy the material thoroughly. A traditional solution to the problem is the introduction of trivalent or divalent cations such as Y^{3+}, Sc^{3+}, Sm^{3+}, and Ca^{2+}, which stabilize the high-temperature phases to room temperature. Recently, the study showed that, ZrO_2 can be stabilized to room temperature by the introduction of Mn cations [6]. In monoclinic ZrO_2, Zr is coordinated with seven O atoms, while the coordination number is changed into six by the introduction of Mn interstitial. In conclusion, the Mn interstitial can stabilize the m-ZrO_2 into tetragonal phase.

The size of ionic Mn is small when compared to ionic Zr. By introducing extrinsic dopant Mn, the defect environment is changed, whether the Mn atom substitutes the zirconia atom or it occupies the interstitial site. Redox properties vary with the valence state of Mn, which caused the change in oxygen vacancy concentration. Changes in defect environment are, therefore, vital in achieving viable applications of ZrO_2. The dopant Mn ions (3d5 configuration) participate actively in order to create very efficient luminescence centers in ZrO_2. This system has several points of interest, especially oxygen ions in the zirconia structure have high mobility and its redox properties vary with the valence state of Mn. The emission can be situated in blue, green and yellow-orange or red regions depending on the host lattice and co-activator ions [18,19]. Thus Mn doped ZrO_2 luminescent materials have wide applications in electroluminescent flat panel displays, color plasma display panels, fluorescent lamps, cathode ray tubes, etc.

The chemical states of dopants, which influence the optical properties and microstructures of the metal-doped ZrO_2, may be changed during the preparation process. Pure and doped ZrO_2 films have been prepared by various techniques such as chemical vapor deposition (CVD), spray pyrolysis, reactive RF sputtering, and sol–gel technique [20].

The sol–gel process is one of the most practical solution–deposition methods of preparing oxide thin films [21]. The basis of the technique is to coat a substrate with a precursor solution containing the requisite metal components in the required proportion, because of solvent evaporation and/or chemical reactions, transforms to a gel layer. The organic components of the gel are then eliminated by various heat treatments, to form the desired crystalline thin film. The main advantage of the sol–gel process is, it has the ability to form inorganic structures at relatively low temperature. Moreover, incorporation of dopant is easy by this technique.

In the present study, Mn-doped ZrO_2 thin films with 0–20% molar concentrations were prepared by sol–gel method. The aim of this investigation is to find, the influence of Mn^{2+}, Mn^{3+} and Mn^{4+} incorporation and annealing on the structure, optical and luminescence properties of ZrO_2 thin films.

2. Experimental procedure

In this study, inorganic precursor route was chosen for the fabrication of nanocrystalline transparent zirconia thin films. Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) (Zigma-Aldrich 99.5%) was used for the preparation of the precursor solution [22]. The mixture of 2-butanol and ethanol (in the ratio 1:1) was used as the solvent. A homogeneous solution of zirconium oxychloride octahydrate (2 wt.%) was prepared by mixing 1 mol of zirconium oxychloride octahydrate in 1/3 of the total volume of mixed 2-butanol and ethanol. The solution was stirred for 45 min using magnetic stirrer. The water for hydrolysis and nitric acid for oxidation of ratio, water: HNO_3: acetylacetone = 20: 0.4: 3 were then added to the salt–alcohol solution. Manganese as a dopant was added in the form of manganese acetate [$CH_3(COO)_2Mn \cdot 4H_2O$] with three different Mn/Zr ratios: 0, 4, 8, 12, 16 and 20 mol% were added with the rest of 2-butanol and ethanol mixed with the required amount of acetylacetone, then they were added to the solution under vigorous stirring in a controlled manner. The stirring was continued for another 90 min to get a clear transparent sol solution. The precursor solution thus prepared was heated at 60 °C and deposited on clean quartz substrates using a locally-built dip-coating apparatus. The dip coating parameters were optimized as 10 cm/min lifting speed and 90° vertical lifting. The dip coated films were dried at room temperature and prefired at 150 °C. This process of coating and drying was repeated for 9-coatings (9-cycles) to obtain films of appropriate thickness (>170 nm) suitable for X-ray diffraction (XRD) analysis. The doped ZrO_2 films were calcined at temperatures 500 °C for 1 h in air, for crystallization. The dip-coated films were then cooled down to room temperature. Structural and optical characterizations of these annealed films were then performed.

Crystalline phase of the Zirconia thin films was characterized by XRD using the X-ray diffractometer (Model-PW 1710 PHILIPS) that have K-Alpha 1 wavelength of 1.54056 and continuous scan type with scan step size of 0.0668. The surface morphology of the deposited films on the nanometric scale is monitored by AFM (Digital Instruments Nanoscope E, Si_3N_4 100 μ cantilever, 0.58 N m^{-1} force constant) measurements in contact mode. Silicon tip with a radius of curvature 10 nm and cantilevers with a nominal spring constant 0.1 N m^{-1} was used. Optical transmittance was studied using a spectrophotometer (Model-JASCO-V550). Emission spectra were recorded by using a Perkin–Elmer Fluorescence Spectrometer (Model-LS55) with a 40 W Xenon Lamp as the excitation source and 2.5 nm excitation and emission slit width.

3. Result and discussion

3.1. Structural studies

Fig. 1(a)shows the XRD pattern of the undoped ZrO_2 thin film (9-coating) annealed at 500 °C in air. The XRD pattern revealed a mixed phase of tetragonal and monoclinic ZrO_2 with preferred orientations along T(111) and M(−111). The structural analysis of Mn (4 to 16 M%) doped ZrO_2 films was done by Grazing Incidence X-ray Diffraction (GIXRD) Fig. 1(b) to detect the metallic Mn characteristic peaks in addition to the ZrO_2 peaks. The GIXRD pattern revealed only the tetragonal structure of ZrO_2 with preferred orientation along T(111) plane. No metallic Mn characteristic peaks have been detected from the GIXRD. In the Mn–Zr–O system, no ternary compounds or complex manganese zirconium oxides have been reported. The GIXRD pattern also shows that the position of T(111) diffraction peak shifts towards higher angle and changes in lattice constants (c) for the Mn doped films, which indicates the changes in stress in the films. The results also show the presence of stabilized tetragonal ZrO_2 in the Mn doped zirconia film [23]. The introduction of Mn interstitial in ZrO_2 restructures the monoclinic cell into an analogous tetragonal cell [6] and stabilizes the mixed phase of ZrO_2 into tetragonal phase.

The grain size (D) of the nanocrystalline films were calculated from the FWHM of XRD using Scherrer equation [24]

$$\mathbf{D = K\lambda/\beta\cos\theta} \quad (1)$$

where D is the grain size, K = 0.9 a correction factor, β the full width at half maximum (FWHM) of the most intense diffraction peak, λ the wavelength of X-ray and θ, the Bragg angle. Table 1 summarizes the diffraction angle, crystallite size, FWHM, and lattice parameter of undoped and Mn doped Zirconia thin films. The particle sizes were found to increase with increase in Mn doping. This is due to the agglomeration of the grains of DMS materials (here ZrO_2) around the dopant. Generally the addition of a catalyst stops isotropic agglomeration of particles; instead anisotropic agglomeration occurs resulting in growth of particles in certain direction [25]. The change in stress of the films is owing to the change in boundaries between grains [26]. These results agree with our AFM images in Fig. 2(a–d).

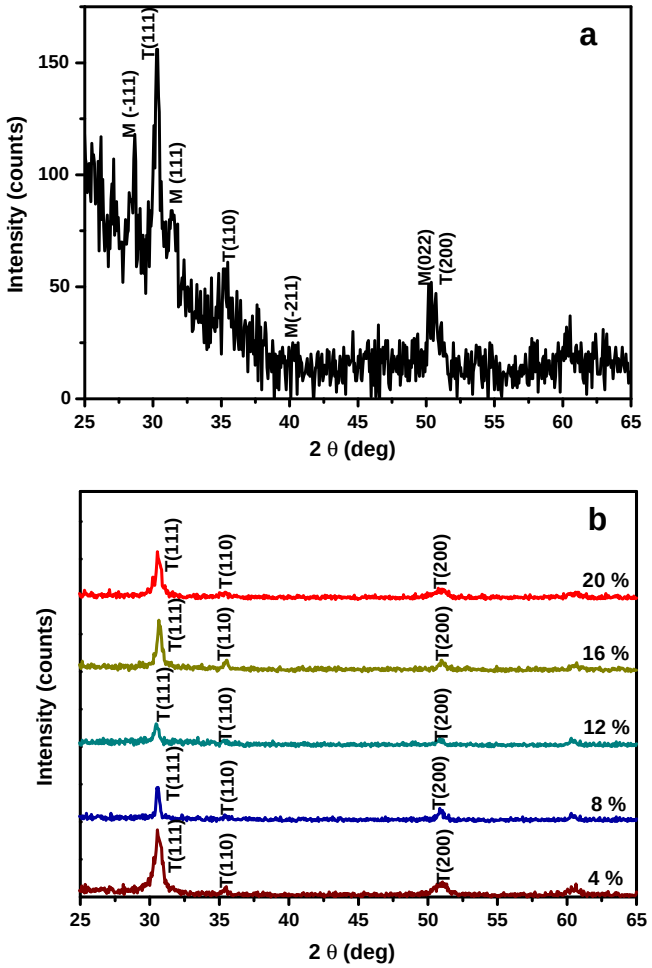

Fig. 1. (a) XRD pattern of undoped ZrO_2 thin films annealed at 500 °C. (b) GIXRD pattern of 4%, 8%, 12%, 16% and 20% Mn doped ZrO_2 thin films annealed at 500 °C.

The lattice parameter of the Mn doped ZrO_2 thin films was found to be less than that of the pure ZrO_2 thin film (Table 1). This may due to the smaller size of ionic Mn (Mn^{4+}, Mn^{3+} and Mn^{2+} ions have ionic radii of 0.53, 0.58 and 0.66 Å respectively), as compared to ionic Zr (ionic radius 0.80 Å for Zr^{4+}). Thus Mn ions can be easily replaced by the Zr atoms at the lattice. Similar results were also observed by Lijavardi et al. in Mn doped ZrO_2 [23]. They reported that, there was a decrease in lattice parameters for Mn^{3+} and Mn^{4+} states. Lijavardi et al. doped Mn with different chemical states into ZrO_2 to understand the changes in microstructures. The stabilization of tetragonal phase and decrease in c-parameters are the proof of the incorporation of Mn ions inside the ZrO_2 crystal lattice.

3.2. Surface morphology studies

Fig. 2 shows the 2-dimentional AFM images of the Mn doped ZrO_2 films annealed at 500 °C. The scan size is 1 μm × 1 μm. The surfaces of all the films are crack free. The characterization of the film surfaces were evaluated by average roughness parameter (R_a) arithmetic average of the absolute distances of the surface points from the mean plane, root mean square (RMS) roughness the standard deviation of the surface from mean plane, within the sampling area and skewness (S_{ka}) which measures the lack of symmetry of the surface profile about its mean plane. It can be seen that grains grown around the particle like a ring formation in the case 4% Mn doped thin films (Fig. 2a). When the Mn dopant increased to 8%, the particles started to coalesce and incomplete nucleation step with irregular growth rate of the grains began. The overall surface yielded a non-uniform and spongy morphology. The fine-microstructure of the grains increased, when the Mn dopants increased to 12%. The grains were nearly spherical in shape. The addition of a catalyst stops isotropic agglomeration of particles, instead, anisotropic agglomeration occurred resulting in growth of particles in certain direction [25]. When the concentration of Mn increased to 16%, the grains were clearly seen. The film consists of grains with non-uniform grain size. The grains were arranged closely, and clear boundaries between neighboring grains were observed.

Table 2 shows the average roughness, RMS and surface skewness of Mn doped ZrO_2 thin films annealed at 500 °C. The RMS value of the surface roughness was calculated from the AFM data. The RMS values increased with the increasing dopant concentration (from 4 to 16 mol%) from 6.5 to 14.2 nm. The higher value of RMS in Mn doped film is attributed to island coalescence [27]. This leads to larger grain size (Table 1). Also the increase in roughness may be due to the different kinetics of the dopant atoms and the host atoms on the film surface and increasing grain size of the films. Hence, we conclude that, as crystalline size increase, the surface roughness also increases, which is in good agreement with the earlier reported results [28,29]. The rough surface enhances light scattering, hence, the transmittance of the films decreases. This agrees with the results obtained from the transmittance spectra (Fig. 3). The higher value of S_{ka} for the film is attributed to more asymmetric surface [1]. It can be seen that the S_{ka} increased with increase in Mn contents. From these results, the increase in S_{ka} of Mn doped ZrO_2 films with increase in Mn results more asymmetric surface. Due to this effect, the interference fringes of the transmittance spectrum (Fig. 3) were deteriorated [30].

3.3. Optical studies

Fig. 3 depicts the optical transmission spectra and direct band gap of undoped and Mn doped ZrO_2 thin films annealed at 500 °C. The undoped films have an average transmittance of 80% in the visible range with defined interference fringes. This exhibited that the film is more homogeneous [1]. By doping Mn in the ZrO_2 films, the average transmittance of the films decreased and the absorption region of the transmittance spectra shift towards higher wavelength region.

Kreibig and Genzel [31] reported that when metals are doped in thin films they can change the medium and the interference conditions of the films. The thickness and refractive index of the films were calculated from Swanepoel's method [32] and is given in Table 3. With the increase in Mn doping concentration, the refractive index increased which in turn reduced the transmittance and thickness of the films. Ruan et al. and Sasanka Deka et al. [33,6] reported an absorption at 420 nm

Table 1
Crystalline phase, diffraction angle, FWHM, crystallite size, and lattice parameter of undoped and Mn doped ZrO_2 thin films.

Thin film samples	Crystalline phase	Diffraction angle 2θ (°)	FWHM 2θ (radian)	Crystallite size (nm)	Lattice Parameter (c) Å
Undoped	T(111)	30.29	0.013	10.3	5.19
	M(−111)	28.64	0.011	12.2	
Mn 4%	T(111)	30.54	0.0102	14.06	5.03
Mn 8%	T(111)	30.52	0.0083	17.24	5.06
Mn 12%	T(111)	30.44	0.0062	22.84	5.07
Mn 16%	T(111)	30.65	0.0059	25.71	5.09
Mn 20%	T(111)	30.58	0.006	25.89	5.09

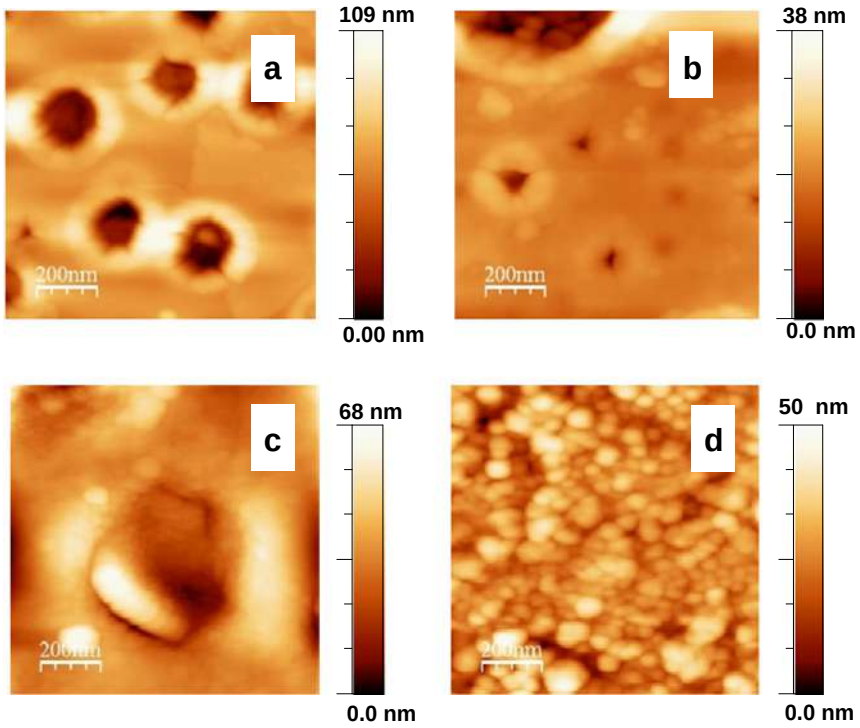

Fig. 2. AFM (1 μm × 1 μm) image of (a) 4% (b) 8% (c) 12% and (d) 16% Mn doped ZrO_2 thin film annealed at 500 °C.

(2.94 eV) in the optical spectra of Mn doped ZnO. This was due to the spin forbidden $A_1^6(S) \rightarrow T_2^4(G)$ transition of Mn^{2+} in a tetrahedral environment [34]. The similar results were observed in this Mn doped ZrO_2 thin films. In conclusion, the absorption in the visible region 400 to 500 nm for the Mn doped ZrO_2, was due to the presence of Mn.

Optical spectra are the most often adapted method to experimentally determine the band structures and band gaps of films. An approximate functional dependence of α on the energy of the incident photon hν is given by the expression [35,36].

The band gap (E_g) values were obtained by extrapolating the linear portion of $(\alpha h\upsilon)^2$ vs hυ plots to intercept the photon energy axis shown in the inset of Fig. 3. From the figure the optical band gap decreased from 5.72 to 4.52 eV with increase in Mn doping concentration, shown in Table 3. The observed decrease in the energy gap, may be due to the combined effect of the quantum confinement effect manifested by the increase in the ZrO_2 crystalline size with the presence of defects such as oxygen vacancies and changes in the carrier concentration. Due to these changes there was a change in electronic levels between the valance and conduction band of ZrO_2.

The addition of Mn interstitial not only provides magnetic moment to ZrO_2 but also free carriers which would shift the E_F to higher energy [6]. The reduced band gap is due to the impurity levels that are introduced into the band gap by the incorporation of the metal ions into the ZrO_2 lattice [37]. The change in the lattice parameter (c) (Table 1) is due to the incorporation of the metal ions into the ZrO_2 lattice. The band gap being directly proportional to inter atomic separation, although it is also possible that the additional states are being introduced by the dopant presence [38]. Theoretically, the valence band of ZrO_2 is mainly composed of occupied O 2p states and the conduction band is the unoccupied de-generated Zr 4d states (lower band Zr 4d x^2–y^2 and z^2 and the higher band Zr 4d xy, yz and zx) [39]. The undoped ZrO_2 thin films have a direct band edged at 5.72 eV. The obtained band gap energy in the investigated tetragonal ZrO_2 film indicated a direct transition, from O 2p to lower lying Zr 4d x^2–$y^2$and z^2 states [1]. The decrease in band gap in the Mn doped metal oxides [34] is due to strong sp–d interactions of Mn with the host matrix. The d orbitals of the magnetic atoms would split into higher double-degenerated e_g orbitals and lower triple-degenerated t_{2g}. Mn-t_{2g} orbitals hybridize with neighbor O 2p [6]. The d-electron of Mn (t_{2g} level) can easily overlap with the ZrO_2's valence band (VB) because t_{2g} of Mn is very close to VB of ZrO_2. This overlap causes a wide VB and consequently decreases the E_g of ZrO_2. The above results show that the band gap in the Mn-doped ZrO_2 decreased with increasing dopant concentration. This concentration effect on the band gap is attributed to the formation of impurity bands arising from an overlap of the electron wave function at impurity levels [40]. At these points, it should be noticed that the band gap of magneto optical materials such as ZrO_2 can be easily tuned by simply changing the concentration of Mn doping in ZrO_2 thin films.

3.4. Photoluminescence studies

Fig. 4 shows the photoluminescence (PL) spectra of the undoped and Mn doped ZrO_2 thin films annealed in air at 500 °C. The PL spectrum of

Table 2
Average roughness (nm), root mean square roughness (nm) and surface skewness of Mn doped ZrO_2 thin films.

Thin film samples	Average roughness (R_a) (nm)	Root mean square (RMS) roughness (nm)	Surface skewness (S_{ka})
Mn 4%	5.3	6.5	1.1
Mn 8%	7.1	10.7	1.9
Mn 12%	9.4	12.91	2.6
Mn 16%	13.5	14.2	2.9

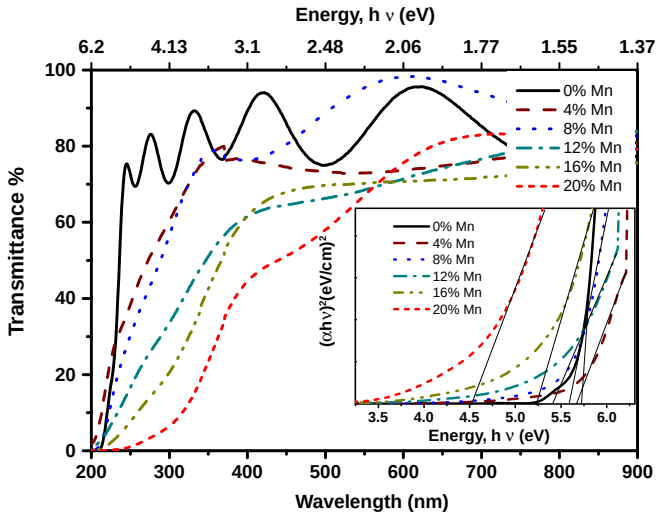

Fig. 3. Transmittance spectra and direct band gaps of undoped, 4%, 8%, 12%, 16%, and 20% Mn-doped ZrO_2 thin films annealed at 500 °C.

undoped zirconia thin film (Fig. 4a) exhibits an intense near band edge emission peak at 392.5 nm (3.15 eV) and weak emission peaks at 304 (4.07 eV), 604 nm (2.05 eV) and 766 nm (1.61 eV). The energy gap of tetragonal ZrO_2 phase is greater than 5.5 eV. Monitoring the 390 nm emission band [41] has revealed that the excitation at 243 nm (5.11 eV) produced a large intensity. The excitation band at 243 nm corresponds to energy near the energy gap of ZrO_2 tetragonal phase and has been assigned to grain boundary defect states, that are an inherent aspect of the nanocrystallinity [21].

The intense zirconia emission peak at 392 nm in the ZrO_2 thin film can be due to the ionized oxygen vacancies (F and F⁻ centers) from the conduction band. Generally UV emission can arise as a result of the radiative recombination of a photo generated hole with an electron occupying the oxygen vacancy [3].

Usman Ilyas et al. [42] reported that in their Mn doped ZnO thin films, the lower ionic size of Mn^{4+}, and Mn^{3+} ions (have ionic radii of 0.53, and 0.58 Å) than the ionic radius of Zn^{2+} (0.60 Å) Mn^{4+}, and Mn^{3+} can substitute in Zn^{2+} lattice of ZnO. The similar result was obtained in the present study such as shift in XRD peak, red shift in transmittance and PL spectra. This may be due to the smaller size of Mn ion (Mn^{4+}, Mn^{3+} and Mn^{2+} ions have ionic radii of 0.53, 0.58 and 0.66 Å respectively), as compared to Zr ion (ionic radius 0.80 Å for Zr^{4+}). From these observations, it is concluded that various states of Mn were substituted in Zr^{4+} lattice.

From Fig. 4(b–e) when the Mn dopant increased, the UV luminescent intensity was suppressed and red shifted. In our earlier reported studies [1], we observed that the decrease in PL intensity with increasing grain size. It can also be due to the decrease in oxygen vacancy with increasing grain size. When Mn was doped in the ZrO_2 film, the incorporation of cation Mn^{4+} ions is more favorable than other cations such as Mn^{3+} and Mn^{2+} ions. It is due to the increasing order of the ionic radii of Mn^{4+}, Mn^{3+} and Mn^{2+} ions of ionic radii 0.53, 0.58 and 0.66 Å. Ling Gao et al. [43] reported that according to the defect reaction

Table 3
Thickness, refractive index and energy band gap of undoped and Mn doped ZrO_2 thin films.

Thin film Samples	Thickness (nm)	Refractive index	Energy band gap (eV)
Undoped	270	2.11	5.72
Mn 4%	212	2.13	5.69
Mn 8%	200	2.17	5.59
Mn 12%	190	2.18	5.44
Mn 16%	185	2.20	5.14
Mn20%	177	2.22	4.42

the increase of Mn concentration in ZrO_2 films increases the oxidation of Mn^{2+} to Mn^{3+} and Mn^{4+}. Doping with cations (Mn^{4+} ions) with a valence similar to Zr^{4+} can suppress the oxygen vacancies in the crystal lattice due to the charge balance. Hence the UV emission intensity decreased.

An additional emission peaks in the range of 350–550 nm have been observed in the prepared Mn doped ZrO_2 thin films. The PL peaks were located around 392(UV), 420, 447 (blue), 483(blue) and 529(green) nm respectively. These peaks were due to the redox properties of various valence state of Mn in ZrO_2.

The blue emission in the wavelength range of 440–500 nm arised from the singly ionized associated oxygen vacancy defects (AOD + centers) [44]. From the observations, we conclude that the AOD^+ centers formed by the substitution of Mn^{2+} along with Mn^{4+}. At the temperature of 500 °C, the oxidation is low when compared to the high temperature. It is noted that, the associated oxygen vacancies have been created due to Mn^{2+} doping, and it is more dominant than that of temperature effect. So, the blue emission increases with the increase of the Mn doping. The green emission 529 nm is due to the 3d orbital electrons in the Mn $^{2+}_{Zr}$ ion relax radiatively from the $^4T_1(^4G)$ excited state to the $^6A_1(^6S)$ ground state [45]. At these points, it should be noticed that this type of luminescent materials can be applied in electroluminescent flat panel displays, color plasma display panels, fluorescent lamps, and cathode ray tubes. With Mn doping in ZrO_2 film, the emission peak at 304 (4.07 eV) has been suppressed. In our previous studies [2,3], when the ZrO_2 thin films doped with Al and annealed at high temperature, the intensity of this (4.07 eV) peak increased, which is related to the trapped positive charge in the metal dioxide. In Mn doping in ZrO_2 film, due to the redox properties of various valence states of Mn in ZrO_2, the amount of trapped positive charges changed.

4. Conclusion

Homogeneous and transparent undoped and Mn doped ZrO_2 thin films were prepared by sol–gel dip coating method. The XRD pattern of the undoped ZrO_2 thin film revealed a mixed phase of tetragonal and monoclinic ZrO_2 with preferred orientations along T(111) and M(−111). In monoclinic ZrO_2, Zr is coordinated with seven O atoms, while the coordination number was changed into six by the introduction of Mn interstitial, which can stabilize the m-ZrO_2 into tetragonal phase. The RMS values were increased with the increasing dopant concentration (from 4 to 16 mol%) from 6.59 to 14.23 nm, it may be due to the different kinetics of the dopant atoms and the host atoms on the film surface and also increasing grain size of the films. An average transmittance of >70% (in UV–vis region) was observed for all samples. The optical band gap decreased from 5.72 to 4.52 eV with increase in Mn doping concentration. The reduced band gap is due to the impurity levels that are introduced into the band gap by the incorporation of the Mn ions into the ZrO_2 lattice. The PL peaks were observed for Mn doped ZrO_2 located at 420, 447 (blue), 483 (blue) and 529 (green) nm, due to the redox properties of various valence states of Mn in ZrO_2. Doping with cations (Mn^{4+} ions) with a valence similar to Zr^{4+} can suppress the oxygen vacancies in the crystal lattice due to the charge balance. This resulted in the decrease of intensity in UV–emission with increasing Mn doping. Thus Mn doped ZrO_2 materials can find wide applications in optoelectronic devices, electroluminescent flat panel displays, color plasma display panels, fluorescent lamps, cathode ray tubes, etc.

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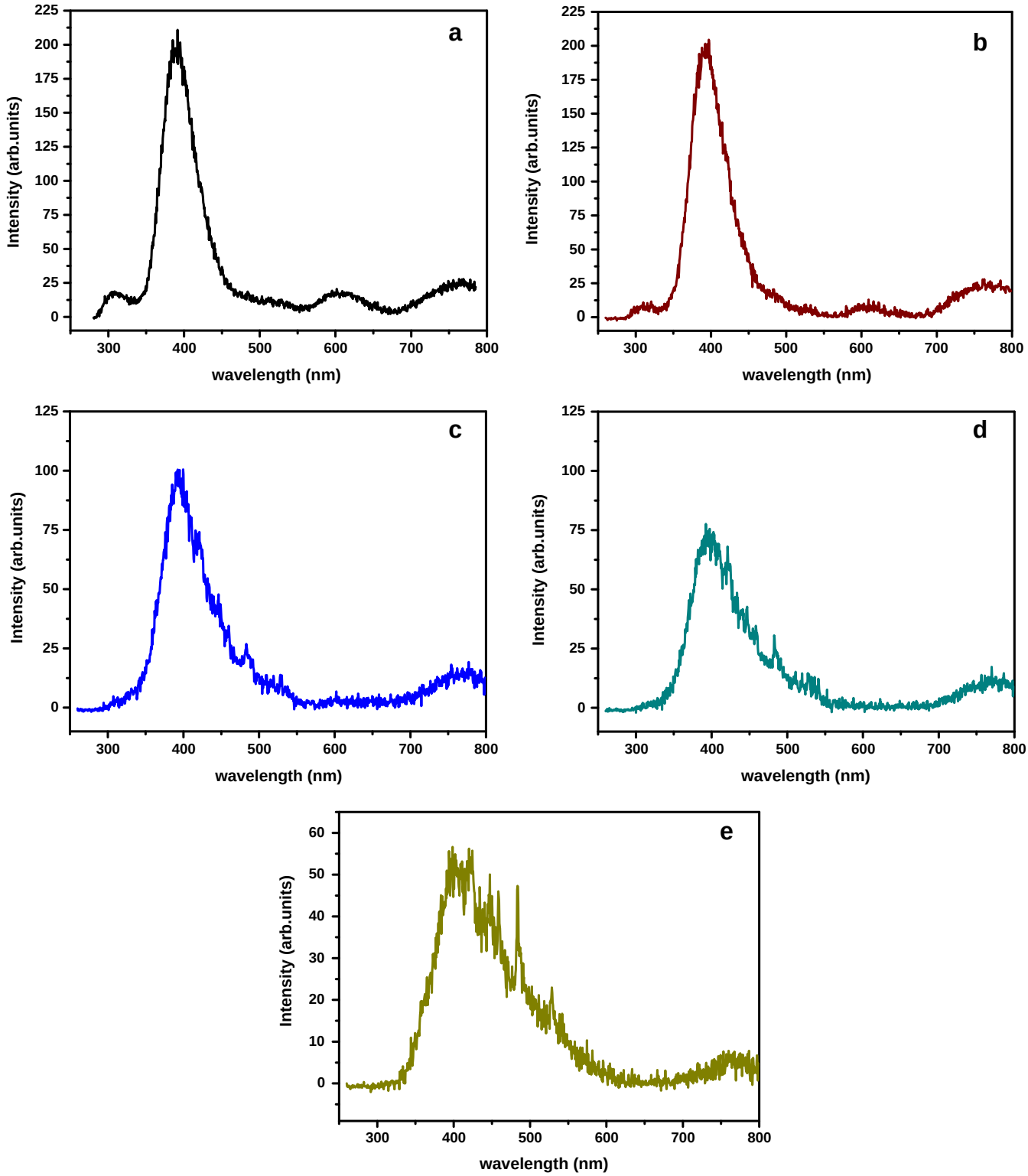

Fig. 4. Photoluminescence of (a) undoped (b) 4 (c) 8 (d) 12 and (e) 16% Mn doped ZrO_2 thin films.

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Anticancer potential of *Bidens biternata* (Lour.) Merr. & Sheriff – An Ethno Medicinal Plant of Wayanadu District of Kerala

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ABSTRACT

***Bidens biternata* (Lour.) Merr. & Sheriff, belongs to the family Asteraceae, is an erect annual herb, up to 1 m height, a wide spread weed of cultivated areas. This plant is common, particularly in Western Ghats regions of Kerala state. It is used as a leafy vegetable by Paniya, Chetti, Kani and Kattunaayika tribes of Waynadu Districts in Kerala and also to cure hepatitis, cold, cough, dysentery, asthma, inflammation etc. The aim of this work is to evaluate anticancer potential of leaves of *B. Biternata* by using cell lines like Dalton's lymphoma Ascites cells (DLA) and Ehrlich Ascites Carcinoma cells (EAC). The result of the present analysis revealed that the ethno medicinal plant *B. biternata*, possess high anticancer effect against the cancer cell lines.**

Keywords *Bidens biternata, DLA, EAC and anticancer potential.*

Cancer is a general term for uncontrolled growth of abnormal cells medically known as neoplasm characterized by autonomous growth of tissues and loss of differentiation. Tumor mass may metastasis and spread to other tissues and organs (Khanum and Khan, 2007). Cancer is one of the leading causes for mortality worldwide and the inadequacy of conventional chemotherapy to reduce mortality indicated that new approaches are critically needed. It is estimated that 7.6 million people died of cancer in 2007 worldwide and it is projected to increase to 11.5 million deaths by 2030 (www.inmu.utoyama.ac.jp/en). The low efficacy of current chemotherapy accompanied with severe adverse reactions has been driving an increasing number of patients towards alternative medicines. In the United States, half of all patients with cancer have tried complementary and alternative medicine (McCann, 1997).

Therefore, there is an urgent need to develop new anticancer agents with minimum side effects. From the earliest times, herbs have been prized for their pain-relieving and healing abilities and today we still rely largely on the curative properties of plants. According to World Health Organization (WHO), 80% of the people living in rural areas depend on medicinal herbs as primary healthcare system (Sakarkar and Deshmukh, 2011). The synthetic anticancer remedies are beyond the reach of common people because of cost factor.

Herbal medicines have a vital role in the prevention of cancer and medicinal herbs are commonly available and comparatively economical (Sakarkar and Deshmukh, 2011). Out of the 92 anticancer drugs approved between 1983 and 1994 for commercial use approximately 62% are directly related to natural origin. Plant derived natural products such as flavonoids, terpenoids, alkaloids, saponins, tannins, glycosides (Arasan *et al.*, 2010) etc. has received considerable attention in recent years due to their diverse pharmacological properties including antioxidant and cancer chemo-preventive effects (Roja and Heble, 1994). Free-radical damage may lead to cancer and some natural products rich in antioxidants interact with these radicals and may prevent the damage caused by them (Muneerudeen *et al.*, 2013).

B. biternata is an annual herb used as green leafy vegetable and eaten by tribes. *Bidens* grows in moist, shady and cool environment with an annual rainfall of 2,786 mm in laterite soil. The chemical constituent in *B. biternata* includes sodium, potassium, carbon, phosphorous, magnesium, manganese, copper, iron, aluminium, different proteolytic enzymes, cyanogenic glycosides and alkaloids (Pradeesh *et al.*, 2012). The leaves of *B. Biternata* have been used in traditional medicine to treat hepatitis, inflammation, diarrhea, asthma etc. by tribes like Paniya, Chetti and

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ISOLATION AND CHARACTERISATION OF QUERCETIN FROM *BIDENS BITERNATA* (LOUR.) MERR. AND SHERIFF – AN ETHNO MEDICINAL PLANT OF KERALA

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Abstract: *Bidens biternata (Lour.) Merr. and Sheriff, belongs to the family Asteraceae, is an erect annual herb, up to 1 m height, a wide spread weed of cultivated areas. This plant is common, particularly in Western Ghats regions of Kerala state. It is used as a leafy vegetable by Paniya, Chetti, Kani and Kattunaayika tribes of Waynadu Districts in Kerala and also to cure hepatitis, cold, cough, dysentery, asthma etc. Phytochemical constituents are responsible for medicinal activity of ethno medicinal plant B. biternata. Column chromatography and Thin Layer Chromatography (TLC) were used for separation of compounds followed by UV, IR, mass and NMR spectroscopic analysis, for the characterization of phytochemical from methanolic leaf extract of B. biternata. From the analysis of various spectra, it was found that the compound isolated was 3, 3', 4', 5, 7-pentahydroxy flavone (Quercetin).*

Keywords: *Bidens biternata,* Western Ghats, Paniya, Chetti, Kani, Kattunaayika UV, IR, quercetin.

INTRODUCTION

Many conventional leafy greens were analyzed for phytochemicals and nutrient content. *Spinacia oleracea* (Chenopodiaceae) and *Basella alba* (Basellaceae) are the green leafy vegetables reported to have high amount of moisture, ash, crude fiber, protein, carbohydrate, iron, calcium and phytochemicals like alkaloids, tannins, flavonoids, saponins, glycosides and phenols (Chaturvedi *et al.*, 2013). *Clerodendron volubile* (Verbenaceae) is a green leafy vegetable with high amount of protein, minerals, vitamins and low amount of anti-nutritional factors like phenols and tannic acids consumed by the Urhobo and Itsekiri tribes of Nigeria (Erukainure, *et al.*, 2011). *Taraxacum officinale* (Asteraceae) used as a ethno medicine by the tribes of Kashmir region of India also reported to have phytochemicals like alkaloids, flavonoids, steroids, saponins, tannins and terpenoids (Amin *et al.*, 2013).

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IN VITRO ANTICANCER ACTIVITY OF A TRAILING HERB- *BOERHAAVIA DIFFUSA L.* IN DLA AND EAC CELL LINES

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Abstract: Boerhaavia diffusa L., belongs to the Family Nyctaginaceae, is a long trailing herb, up to 1.2 m height, a wide spread weed of cultivated areas and road sides. This plant is common in all Districts of Kerala. It is commonly used as a leafy vegetable by rural and ethnic people in the State and also used to cure hepatitis, fever, cold, cough, dysentery, asthma, and inflammation. The aim of this work is to evaluate anticancer activity of the leaves of B. diffusa by using cell lines like Dalton's lymphoma Ascites cells (DLA) and Ehrlich Ascites Carcinoma cells (EAC). The result of the present analysis revealed that the ethno medicinal plant B. diffusa, possess high anticancer effect against the cancer cell lines.

Key words: *Boerhaavia diffusa*, trailing herb, DLA, EAC, anticancer activity

INTRODUCTION

Cancer is one of the greatest human killers worldwide, and is spreading promptly. The study of Ayurvedic classics has revealed that the symptomatology of the disease entity "*Arbuda*"can be correlated to that of the tumor or cancer (Gaidhani *et al.*, 2013). The most out-standing symptom is that of a swelling which continuously goes on increasing in size but never reaches to the stage of suppuration until and unless complicated by super imposed infection. This swelling is circular, immovable, slightly painful, slowly growing and broad based (Gaidhani *et al.*, 2013). According to *Ayurvedic* literature three humors, *Vata* (air), *Pitta* (fire) and *Kapha*(water), mutually coordinate to perform the normal function of the body. In benign tumor (*Vataja, Pittaja*or *Kaphaja*) one or two of the three humors/systems are out of control and therefore not too harmful. Malignant tumors are very harmful; because all the three major humors/systems lose mutual coordination and therefore a failure of regulation is exhibited which results into a deadly morbid condition (Gaidhani *et al.*, 2013). In medical science the methods available to treat a cancer patient mainly includes surgery, chemotherapy and radiotherapy. As these known methods are

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PRELIMINARY PHYTOCHEMICAL SCREENING AND ANTIMICROBIAL ACTIVITY OF *BIDENS BITERNATA* (LOUR.) MERR. & SHERIFF - OF SOUTHERN WESTERN GHATS

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Abstract: ***Bidens biternata*** **(Lour.) Merr. & Sheriff, belongs to the family Asteraceae, is an erect annual herb, up to 1 m height, a wide spread weed of cultivated areas. This plant is common, particularly in Western Ghats regions of Kerala state. It is used as a leafy vegetable by Paniya, Chetti, Kani and Kattunaayika tribes of Waynadu Districts in Kerala and also to cure hepatitis, cold, cough, dysentery, asthma etc. Phytochemical constituents are responsible for medicinal activity of ethno medicinal plant *B. biternata*. Hence in the present study preliminary phytochemical screening and antimicrobial activity of *B. biternata* a medicinal plant was carried out. Qualitative phytochemical analysis of these plants confirm the presence of various secondary metabolites like reducing sugar, glycosides, flavonoids, alkaloids, tannins, steroids, terpenoids, coumarins and saponins. Antimicrobial activity of the crude methanolic plant extract was evaluated by disc-diffusion method and revealed a low antimicrobial property.**

Key words: *Bidens biternata, glycosides, flavonoids, alkaloids and saponins.*

I INTRODUCTION

Medicinal plants are the richest bio-resources of folk medicines and traditional systems of medicine and food supplements, nutraceuticals, pharmaceutical industries and chemical entities for synthetic drugs (Ncube *et al.*, 2008). Modern medicine has evolved from folk medicine and traditional system only after through chemical and pharmaceutical screening (Boopathi and Sivakumar, 2011). India is the birth place of renewed system of indigenous medicine such as Siddha, Ayurvedha and Unani. Traditional systems of medicines are prepared from a single plant or combinations of number of plants. The efficacy depends on the use of proper plant part and its biological potency which in turn depends upon the presence of required quantity and nature of secondary metabolite in a raw drug (Vinoth *et al.*, 2011). There is growing awareness in correlating the phytochemical constituents of a medicinal plant with its pharmacological activity. Turger and Usta (Turker and Usta, 2008), screening active compounds from plants has lead to the invention of new medicinal drugs which have efficient protection and treatment roles against various diseases, including cancer (Sheeja and Kuttan, 2007) and Alzhemir's diseases (Mukherjee *et al.*, 2007). Phytochemicals are responsible for medicinal activity of plants (Savithramma *et al.*, 2011). These are non-nutritive chemicals that have protected human from various diseases. Phytochemicals are basically divided into two groups that are primary and secondary metabolites based on the function in plant metabolism. Primary metabolites are comprise common carbohydrates, amino acids, proteins and chlorophylls while secondary metabolites consist of glycosides, alkaloids, saponins, terpenoids, steroids, flavonoids, tannins and so on (Kumar *et al.*, 2009). Phytochemical constituents are the basic source for the establishment of several pharmaceutical industries. The constituents are playing a significant role in the identification of crude drugs (Savithramma *et al.*, 2011). Though the plant and its extracts have been extensively used in the tribal medicine, information from organized search of published literature does not provide evidences for the secondary metabolites and its antimicrobial potentiality of *B biternata*. So the present study aimed to analyse the preliminary phytochemicals and antimicrobial activity of crude methanolic extracts of *B. biternata*.

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IN VITRO ANTICANCER ACTIVITY OF *BIDENS BITERNATA* (LOUR.) MERR. & SHERIFF – AN ETHNO MEDICINAL PLANT OF KERALA

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Abstract: ***Bidens biternata*** **(Lour.) Merr. & Sheriff, belongs to the family Asteraceae, is an erect annual herb, up to 1 m height, a wide spread weed of cultivated areas. This plant is common, particularly in Western Ghats regions of Kerala state. It is used as a leafy vegetable by Paniya, Chetti, Kani and Kattunaayika tribes of Waynadu Districts in Kerala and also to cure hepatitis, cold, cough, dysentery, asthma etc. Phytochemical constituents are responsible for medicinal activity of ethno medicinal plant *B. biternata*. In the present study, crude methanol extract and isolated bioactive compound of *B. biternata* leaves was analyzed for its *in vitro* anticancer activity. The anticancer activity was evaluated by using different cell lines like L929, H9C2 and A375. In the MTT assay of crude methanol extract, the percentage of viability of the normal cell line L929 were found to be 64.2%, 53.2% and 49.1% when crude sample was applied in a concentration of 100 µg ml^{-1}, 500 µg ml^{-1} and 1000 µg ml^{-1}respectively. In quercetin the percentage of cell viability of L929 were found to be 51.04%, 47.28% and 36.27%. The percentage of cell viability of H9C2 cell line were found to be 90.86%, 64.39% and 40.26% and for isolated compound quercetin, 86.17%, 58.42% and 28.15% for sample concentration 100 µg ml^{-1}, 500 µg ml^{-1} and 1000 µg ml^{-1}respectively. In the MTT assay of crude methanol extract, the percentage of viability of the A375 cell line were found to be 94.17%, 70.14% and 44.58% and isolated compound quercetin, 92.14%, 68.34% and 38.26%. The results revealed that the isolated compound quercetin (3, 3', 4', 5, 7-pentahydroxy flavones) of *B. biternata* possessed high anticancer activity so could be used as an effective therapeutic agent against cancer disorders.**

Keywords: *Bidens biternata, L929, H9C2, A375, MTT assay.*

I INTRODUCTION

Plant drugs have a long history in both traditional and modern societies as herbal remedies or crude drugs. A large number of new drugs derived from plant secondary metabolites have been applied in the treatment and/or prevention of cancer (Parkin *et al.*, 2001). Herbal medicines in the treatment of cancer as complementary and alternative therapy are increasingly accepted with growing scientific evidences of biochemical and clinical traits. Some of the anticancer drugs discovered from herbal medicine have been used in clinical setting as conventional anticancer drugs (Parkin *et al.*, 2001). Recently, research continuously focuses on clues from traditional knowledge of herbal medicines to develop new anticancer drugs as single pure compounds. On the other hand, standardized extracts or fractions with anticancer effects or with adjuvant therapy in cancer treatment coming from single or mixed herbs are also accepted in the forms of dietary supplements and botanical drug products (Yibin *et al.*, 2010). Significant progress has been made in cancer chemotherapy, a considerable portion of which can be attributed to plant-derived drugs (Conforti *et al.*, 2008). Drug discovery from plants still provides important new drug leads, many of which are approved or undergo trials for clinical uses against cancer, malaria, Alzheimer disease, HIV/AIDS, pulmonary pathologies and other diseases (Conforti *et al.*, 2008). The synthetic anticancer remedies are still beyond the reach of common man because of cost factor. Herbal medicines have a vital role in the prevention and treatment of cancer since medicinal herbs are commonly available and comparatively economical (Sundaram *et al.*, 2011).

The potential of using the natural products as anticancer drugs was recognized in 1950's by U.S Natural

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29TH,30TH SEPTEMBER & 1ST OCTOBER 2015

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This is to Certify that Sri/~~Smt~~/~~Dr~~... Akhil. V, Assistant Professor of Commerce, N.S.S College, Pandalam has participated in the three day National Seminar on Sustainable Tourism And Emerging Trends, Challenges and Issues in HRM Organised by the Post Graduate Department of Commerce, NSS College Pandalam held on 29th, 30th September & 1st October 2015. He/~~She served as a resource person~~/has presented a paper titled 'Management of Stress - A Crucial Step'.

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THE BEHAVIORAL PATTERN OF RURAL CONSUMERS TOWARDS THE PURCHASE OF CONSUMER DURABLES IN KERALA

*Preetha. S. Pillai ** B.Gopakumar

ABSTRACT

The Indian rural market is bigger and vast in size with its larger consumer base, its offers the great opportunities or the marketer and stay in tune with the rural marketing offerings. It is relatively easy to measure what rural consumers buy, where they buy from and how much they bumers and how these factors play an important role in the rural consumers buying, decision making process. The factors such as family size, product packaging, age, culture and advertising have an effect on consumers decision making process, where as price is associated to product. Rural consumers are fundamentally different from their urban counter parts. The lower level of literacy and limited exposure to product and services are well-known, but there are also differences in consumption patterns with a diuy. Understanding why they buy is the most difficult in rural India and what patterns induce them to buy. This study tries to find out the factors responsible for different buying behavior of the rural consrect impact on income levels and income flows and a high level of interdependency affecting the dynamics of rural consumer behavior. All contribute to make rural consumer behavior dissimilar from the urban consumer.

Key words: Attribute, buying behavior, culture, decision making, rural market.

INTRODUCTION

Consumer behavior is an inter disciplinary subject that explains and predicts how consumers buy it. It is based on the concepts and theories about people, which have been developed by scientists in diverse disciplines such as psychology, sociology and social psychology, culture anthropology, economics and so on. It embodies all the activities of the buyers, previous buyers and potential buyers from pre-purchased to post-purchased and consumption to discontinuance. It extends from the awareness of wants through the search and evaluation of possible means of satisfying it, and the art of purchase itself, to the evaluation of the purchased item in use, which directly impact up on the probability of repurchase.

Marketing of consumer products in rural areas is a topic of great interest to marketing scholars and practitioners in India now. The major reason for this interest are the growing rural market for consumer's product primarily due to interest in to studies in the rural market. Several factors contribute to the growth of the rural market, the most important of them being the increase in agricultural activities. So the emergence of a cash economy in rural area, where from agricultural products developed, market linkage and commercialization emerged as particular areas for consumer products of urban region. Another reason for the growth of rural market is the massive outlays on rural development. Therefore the rura development programme brought ar additional purchasing power in the hands o farmers and other worker in rural area

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** *Associate Professor , NSS College, Pandalam, Kerala*

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A STUDY ON PROBLEMS OF HOUSING LOAN BORROWERS OF HDFC&LIC HFL IN PATHANAMTHITTA DISIRICT

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ABSTRACTT

Housing is one of the basic needs of mankind and a requirement to the civilized life. It places a significant role in the economic, social and psychological development of individual. There has been tremendous growth in the demand for housing due to population growth, expansion of industrial and commercial activities and the consequent migration of people in large scale in to urban areas.Along with this the aspiration of individual and families are also increasing to ensure better living conditions and standards. Consequently the requirements of housing finance and financing for infrastructure increased significantly. Home is a dream of a person that shows the quantity of efforts scarifies, luxuries and above all gathering funds little by little to afford ones dream. Many banks are providing home loans. But at the same time it has become more competitive especially during the post liberation era due to the entry of new institutions in to the industry, offering variety of loan products. Because of intense competition the players in the housing ´finance sector have to become more customer oriented. Housing Finance Sectors provide quality services to their customers and ensure that customers are satisfied with their experience. Now housing loan segment has become more competitive due to the entry of new institutions in to the industry. Hence the study on housing finance assures great significance.

With the emergence of national housing bank in 1987 the organized housing finance industry has been dominated by the specialized housing finance institutions regulated by NHB the role of commercial bank, cooperative bank and agricultural and rural development banks become secondary. But in pursuance of national housing policy and priority sector lending norms of central government ,commercial bank become more dynamic in the housing finance business ,which posed threat to the specialized housing financial institutions and their market share has considerably diluted. Lowering of interest rate ,entry of many new players, thin spreads, reduced credit off take to industrial sector, indifferent product differentiation etc..have made competition in housing finance industry very stiff. Further the borrowers are confronted with many problems as they are not fully aware of the different aspects of housing

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A STUDY ON THE DOMESTIC AND FOREIGN TOURISTS' VISITS IN KERALA OVER THE YEARS

*C.R Ambily, **B. Gopakumar

Abstract

Tourism industry is one of the few industries in which Kerala has a lot of potential for development. Its importance has grown considerably over the years. Kerala has been branded as one of the most wanted tourism destinations. A great deal of this is due to the proactive marketing and the promotional measures taken during the last ten years. There are three main helping factors for the tourism products in Kerala. They are the attractions of a destination, the facilities at the destination and the accessibility to the destination. This paper aims at discussing the major tourists' sites of Kerala and also to have a look at the tourists' visits, both foreign and domestic, in Kerala during the last few years.

Key words:- Product, Tourism Products, Proactive Marketing, Global Super Brand, Tourists Attractions.

Tourism becomes important for the economic, social, cultural and educational development of a nation. The tourism industry, while being one of the largest in the world, is also one of the fastest growing industries. Tourism plays an important role in the creation of economic and non-economic benefits to a nation. This facilitates a competitive mentality among the nations with destinations to sell their tourism potentials to the people all over the world.

The state of Kerala is at the tip of India. Edged by a thread of unbroken beach line, the green paddy fields and a unique network of rivers and lagoons are all the special features of Kerala. The tourism industry is one of the few industries in which Kerala has a lot of potential for development. Its importance has grown considerably over

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Empowerment of Women with Micro-Credit

Dr. B. Gopakumar & Dr. N. Jayasree

Introduction

A number of schemes have been introduced to reduce the poverty by the Government ever since the beginning of planning in India. Contrary to the expectations, poor have failed to get the full benefits of such schemes. People's active participation in the planning process at the grass root levels is essential to tackle many problems. Ensuring access to reasonably priced financial services to the poor and the needy should be the basic principle of "Institutional credit delivery".

In India, carious models and innovations have been experimented by various agencies in pursuit of augmenting their outreach to the poor. Micro credit is one such endeavor to reach out to the poor at their doorsteps at reasonable terms with the desired output. A salient revolution is taking place in rural areas, where the poorest of rural women are provided with 'collateral free' micro credit for economically viable projects that help in their empowerment. The micro credit

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A STUDY ON JOB SATISFACTION AMONG EMPLOYEES IN ALIND INDUSTRIES, MANNAR

*Preetha S. Pillai, **B. Gopakumar

Abstract

The success of a company basically depends up on its ability to attain goals and objectives. Among the five M's namely man, machine ,materials money and method, human resources are the most important in an organization. No firm can reach its ultimate aim of profit maximum and wealth maximum without satisfying its manpower. It is true that man can never be fully satisfied in his life, as employees spent much time in their work. They will be satisfied in life only, if the job is satisfactory. Job satisfaction is the most important and frequently studied attitude. Job satisfaction means good or positive, attitude or feeling attitudes towards one'sjob. It is the general attitude of employees towards their jobs. When the attitude of an employee towards his or her job is positive, there exists job satisfaction. Job satisfaction is a general attitude towards one's job, the difference between the amount of reward workers receive and the amount they believe they should receive. Employee is a back bone of every organization, without employee no work can be done. So employee's satisfaction is very important. Employees will be more satisfied if they get what they expected, job satisfaction relates to inner feelings of workers.

Key words:- job satisfaction, job security reward, manpower and inner feelings.

Job satisfaction is the collection of tasks and responsibilities regularly assigned to one person, while job is a group of positions, which involves essentially the same duties, responsibility, skill and knowledge. Job satisfaction has always been on important issue ,satisfied employees tent to be more productive, creative, committed to their jobs. Job satisfaction refers to an employee's general attitude towards his job. Every individual has some needs to be fulfilled. Any job which fulfills these needs provides satisfaction. An organization is nothing without human

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OCCUPATIONAL STRESS AMONG TEACHERS OF HIGHER SECONDARY SCHOOL IN PATHANAMTHITTA DISTRICT

*Preetha S. Pillai, **B.Gopakumar, ***Suvarnalakshmi.V

Abstract

The present study aims to explore the occupational stress level experienced by teachers in government and aided higher secondary schools living in different cultural, sociological and economic conditions. 25 aided higher secondary school teachers and 25 government higher secondary school teachers participated in the study. From the study it is understood that aided higher secondary school teachers have more occupational stress level than government higher secondary school teachers. Authorities are advised for conducting the teacher training and assessment programmes with the aim that personal and social impacts and working environments may have an effect of occupational stress on teachers.

Key words:- Teacher Occupational Stress, Role of Stress, Role Ambiguity.

Stress at work place is a relatively new phenomenon in the modern life style. The nature of work has gone through drastic changes over the last century and it is still changing as the wind sweeps by. It has touched almost all professions. Kids at the kindergartens, children at the schools, students at the colleges and universities and everyone in the academic field experience stress every day. All office-goers experience stress of one kind or another. Entrepreneurs and labourers experience a different kind of stress. Homemakers also experience stress while managing their home affairs.

Thus the reasons for stress differ from person to person. But all the same, everyone experiences stress. The stress one experiences should not necessarily be treated as harmful. An optimum amount of stress can always act as an energiser or motivator and propel one to apply more effort to complete their tasks. But a higher level of stress can be a serious threat to the temperament of the individual, which in turn can cause psychological and social problems.

From an individual's point of view, stress is the human body's physical, mental, and chemical reaction to circumstances that frightens, confuses, endangers or irritates him. If it is taken positively, stress is a friend that can strengthen the individual for future encounters, but if taken negatively, it can have adverse effects on both the physical and psychological factors. Stress affects not only the individual but also the individual's surroundings. It also adversely affects the individual's family, work and society.

Occupational stress is any force that pushes a psychological or physical factor behind its range of stability, producing a strain within the individual's knowledge that stress is likely to occur and will constitute a threat to the individual. A threat can cause a strain because of what it signifies to the person. As occupational stress begins to take its toll on the body and the mind of an individual, a variety of symptoms can result. Work in organisations not only provide individuals with life-sustaining income but also exerts its own pressures on them. This can ultimately have negative consequences, both for achieving the goals of the organisation and meeting the needs of the individuals working in them. Thus the work environment that causes social and psychological stress which has harmful effects on the well being of the employees in general, and occupational stress in particular is universal, and frequently disables human involvement arising at work, has a detrimental effect on the behaviour of the individuals which ultimately result in personal and [illegible] inefficiency. Occupational worker to change (disrupt/enhance) his or her psychological or physiological condition so that the person's mind or body is forced to deviate from its normal way of functioning.

Objective of the Study

This study is carried out to analyse the occupational stress among the teachers of higher secondary schools in Pathanamthitta district. The major objectives of the study are:

1. To find out the factors influencing occupational stress among the higher secondary school teachers.
2. To measure the level of occupational stress among the higher secondary teachers of government and aided schools.
3. To study the personal and academic characteristics among higher secondary school teachers of government and aided schools.

Scope of Study

The study is limited to identifying the occupational stress level of higher secondary teachers in government and aided schools only.

Methodology

The present study is based on both primary and secondary data. Primary data has been collected by conducting a survey among a sample of 50 higher secondary teachers comprising of principals and higher secondary school teachers of government and aided schools. Secondary data have been collected from books, journals, newspapers, periodicals, internet

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Socio Economic profile and its changes of Women Micro Entrepreneurs in Kollam District.

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Abstract

The development of small scale industries has been one of the most significant and characteristics features of industrial development in India. The micro enterprises where established for the purpose manufacturing a wide verity of goods in different product lines. Women Entrepreneurs are those who are organize or operate and control an enterprise including small and cottage industries with not less than 80% of the total workers are women and whose holdings in the enterprise is at least 51 %. Micro enterprise is any income generating activity owned operated and managed by a group of at least five and not more than fifteen members. This study is aims to identify "the socio economic profile and its changes of women micro entrepreneurs in kollam district". For the collection of data both secondary and primary sources were used. Interview schedule was administrated for collecting primary data. Even though there was a tremendous changes in the profile of women micro entrepreneurs after joining or starting a business unit.

Key words: Women entrepreneurs, Micro enterprises.

Introduction

Entrepreneurship has been considered as the backbone of economic development. The level of economic growth of a region mainly depends upon the level of entrepreneurial activities of that region. Recently women participation in business increases. The increasing presence of women in the business fields as entrepreneurs or business owners has changed the demographic characteristics of entrepreneurs. Women owned business are playing a more active role in society and in economy, inspiring academics to focus on this interesting phenomenon. Emergence of women entrepreneurs and starting their own enterprises will leads to the key element of economic development of our nation. District Industrial Centers are actively supported the women micro entrepreneurs' mainly providing micro finance and various types of loans. In every DIC Centers a special officer was appointed for look after women industries.

Review of Literature

From the survey of literature it is found that a few attempts have been made to examine the different aspects of women micro enterprises. There for it is relevant to give a brief of these studies. Wayna Nafzinger in his study, "Class, caste and entrepreneurship of Vishakhapattanam in Andhra Pradesh" came in to the conclusion that a highly disproportionate number of entrepreneurs where from high caste and families in the highly socio economic status. Chetana Kalbagh in her study titled "Women and Development: Women in Enterprise and Profession" has discussed the socio economic status and various self employment problems of women entrepreneurs in India. Thus no attempt has been made to examine the socio economic changes of women micro entrepreneurs and its change, this study is made an attempt to overcoming these difficulties.

Innovative Approaches and challenges in Rural Credit

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Chief Editor

THE SCHEMES AND THE CHALLENGES FACED BY THE WOMEN ENTREPRENEURS IN MSMEs: AN OVERVIEW

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ABSTRACT

India has always been a land of entrepreneurs and also occupied a strategic position in the Indian economy, as a developing nation. India and the other developing nations of the world have been focused attention on the development of women entrepreneurship .Women entrepreneurs make sufficiently great contributions to their economies .A s a country like India Women entrepreneurs have to face various challenges .MSME plays a significant role in the development of women entrepreneurs. So this paper focus the problems and challenges faced by the women entrpreneurs and also the government schemes available for the development of existing women entrepreneurs in MSMEs.

Keywords: MSME, SME, Women Entrepreneurs, strategic position, challenges

INTRODUCTION

Entrepreneurship is considered as one of the most important factors contributing to the economic development of the society. Entrepreneurs such as men and women are considered as instrumental in initiating and sustaining socio-economic development of country. The emergence of women entrepreneurs contribution is lesser than the men contribution to the national economy in India .To increase the women contribution government to motivate number of women entrepreneurs in small and medium enterprises.

Women entrepreneurship in India represents a group of women who are explaining new avenues of economic participation .The entry of the women in organized busness is a fairly recent phenomenon .The government of India has defined women entrepreneurs based on women participation in equity and employed of a business. India has around 8 million women who have started and are running their own businesses and the Ministry of MSME believes that the women in India can play a vital role in the growth of the Indian economy

From the year of early 1990s including India the developing countries of the world have been focused attention on the development of women entrepreneurship .However women make nearly 50% of the total

ROLE AND CHALLENGES OF GREEN BANKING IN INDIA

M.Kavithi Krishna
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Abstract

An attempt is made to understand the concept of Green banking ,its issues, challenges and to find out whether the selected Indian banks are using Eco-Friendly Technology and Green methods to bring down the carbon footprint or not. Climate is most complicated issue the world is facing. The world has seen much focus on economic progress, the side effects of this, has resulted in climate change, environmental damage. The banks can play an important role between economic growth and environmental protection. The banking of this kind is termed as "Green Banking". Green Bank is like a normal bank, which considers all the social and environmental factors with an aim to protect the environment and conserve natural resources. It means combining technology and changing client habits in banking business. Green banking practices will be useful not only for environment but also lead to cost reductions in banking activities. To reduce the external carbon emissions, bank should finance green technology and pollution reducing projects.

Keywords: *Green Banking, Solar powered ATM's, Green home loan scheme, carbon footprint, Green Loan and Indian Bank Initiatives.*

Introduction

Industrialization around the globe has triggered the pursuit of ever increasing needs and demands of the population and it has become symbolic of prosperity and development of an economy. But on the other hand it has resulted in the exploitation of the natural environment which in turn has disturbed the ecological balance. The disturbance in ecological balance has adversely impacted the human and its surrounding environment. the recent industrial disasters and natural disaster occur in the last three decades were directly or indirectly linked with the uneven industrialization. This intern has raised an important issue of environmental protection among environmentalists, government and organization from all over the world. Environmentalism is a broad philosophy and social movement regarding concerns for environmental conservation and improvement of the state of the environment. Environmentalism and environment concerns are often represented by the color 'green'. Global warming also called as "Green House Effect" is a global issue that calls for a global response. The warming effect of certain man-made gas emission such as carbon dioxide, methane, nitrous oxideanedhydro fluro carbon is found responsible for distortion in climate changes. The rapid change in climate will probably be too great to allow many eco systems to suitably adapt, since the changes have direct impact on bio diversity, agriculture, forestry, dry land, water resource and human health. however, there is general lack of adequate awareness on the above issues and there is urgent need to promote certain urgent measures for sustainable development and corporate social responsibility. There are many differences compared with normal banking, Green Banks give more weight to environmental factors, their aim is to provide good environmental and social business practice, they check all the factors before lending a loan. whether the project is environmental friendly and has any implications in the future, you will awarded a loan only when you follow all the environmental safety standards.

Defining green banking is relatively easy. Green banking means promoting environmental friendly practices and reducing carbon footprint from our banking activities.

This comes in many forms

1. Using online banking instead of branch banking.
2. Paying bills online instead of mailing them.
3. Opening up accounts online banks, instead of large multi branch banks.

Certificate

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has participated in the three day *National Workshop* on

Data Analysis in Business Research

sponsored by *ICSSR* and co-sponsored by *Mahatma Gandhi University* on *26-28 March 2018*.

He has presented a paper titled

QWL AND ORGANISATIONAL COMMITMENT – A STUDY WITH REFERENCE TO UNAIDED SCHOOL TEACHERS OF ALAPPUZHA DISTRICT

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Dr. Mathew P Joseph

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Assistant Professor, Dept. of Commerce, N.S.S. College, Pandalam

participated/presented a paper entitled FACTORS INFLUENCING QUALITY OF WORK : AN ANALYSIS ON WOMEN EMPLOYEES OF TEXTILE SHOWROOMS IN PATHANAMTHITTA DISTRICT in the International seminar on Women entrepreneurship corridors to economic empowerment and national development organised by Women's cell unit of N.S.S. Training College, Pandalam on 22&23 June 2017.

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Authored by

Sunil Chandran [illegible]

From

NSS College, Pandalam

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RETAILERS' PERCEPTION TOWARDS CASHLESS TRADING

S.Lt.Dr.S.Priya & Sreevidhya S

INDRODUCTION

A cashless society describes an economic state whereby financial transactions are not conducted with money in the form of physical banknotes or coins. But rather through the transfer of digital information (usually an electronic representation of money) between the transacting parties. The government is working at various levels to reduce the dependence on cash. Cash is like a water, a basic necessity without which survival is a challenge. Nevertheless , cash use doesn't seem to be waning all that much, with around 85% of global payments still made using cash. One of the main reasons is that there is nothing to truly compete with the flexibility of notes and coins. In a courageous move to combat black money and counterfeit currency, Sri.Narendra Modi's government scrapped currency notes of INR 500 and INR 1000 denominations which is seen as an unprecedented measure, through a giant leap towards curbing corruption and forged currency. Even the RBI has also recently unveiled a document — "Payments and Settlement Systems in India: Vision 2018" — setting out a plan to encourage electronic payments and to enable India to move towards a cashless society or economy in the medium and long term.

After demonetization cashless payment methods have become a necessity for both rural and urban populations. Be it a farmer, teacher, soldier or even a CEO of a big brand, every citizen of the country needs to know about the available methods to make cashless transactions. With the current cash crunch in the country, the Indian government is aggressively promoting digital modes of banking. The government even waived off the transaction charges on a few payments methods.

Retail trading means an industry that sells primarily to individual. Retailing in India is one of the pillars of its economy and accounts for about 10 percent of its GDP. The Indian retail market is estimated to be US$ 600 billion and one of the top five retail markets in the world by economic value. India is one of the fastest growing retail markets in the world, with 1.2 billion people

OBJECTIVES OF THE STUDY

1. To analyze the attitude of retail traders towards cashless trading.
2. To find out the difficulties faced by the retail traders in cashless trading.

RESEARCH METHODOLOGY

Primary data is collected through sample survey. It was very useful in getting reliable information for this study.

The secondary data regarding cash less trading is collected from various books , journals, reports, newspaper& web site ,etc

TOOLS OF DATA COLLECTION

Pre -tested questionnaire are used for data collection of the study.

SAMPLE DESIGN

There were a lot of retail stores which uses cashless trading system. From this a sample of 50 retailers were conveniently selected.

NEED AND SIGNIFICANCE OF THE STUDY

The Indian retail industry has emerged as one of the most dynamic and fast-paced industries due to the entry of several new players. It accounts for over 10 per cent of the country's Gross Domestic Product (GDP) and around 8 per cent of the employment. India is the world's fifth-largest global destination in the retail space. India is in the midst of a cash management crisis. But this challenge is an opportunity as well. Even though many

A STUDY ON THE EFFECTIVENESS OF RISK MITIGATION MECHANISMS OPERATED IN SELF HELP GROUPS IN ALAPPUZHA DISTRICT IN KERALA

*Sreevidhya S

Abstract

As far as rural poor in India are concerned, to make both ends meet is not an easy task to them. Even though Govt. has taken various measures to overcome poverty, still there are many people especially women who depend on money lenders for meeting their financial needs. Micro finance is implemented by the Govt. as a remedial measure for this situation. The present study titled "A study on the effectiveness of risk mitigation mechanisms operated in self help groups in Alappuzha district in Kerala" addressed the various risk mitigation mechanisms taken by the banks like Grading of SHGs, Frequent visits/monitoring, Capacity Building and Training, Monitoring and Review of SHG Lending, Financial Literacy Campaign, Interest Subsidy, Auditing of accounts and checking of records etc. The participation level of SHG members, positive influence of these mechanisms on the repayment attitude of the members, influence of peer pressure, reduction of loan default rate etc indicates that the risk mitigation mechanisms taken by the banks are proving to be successful in achieving its purposes.

Key words:- Self Help Group, Risk Mitigation, Financial guidance, Grading of SHGs

Indian economy is at present going through a phase of transition from the state of underdevelopment to development. There are various problems which it is facing during this transition phase namely insufficient grow and development of the economy, serious population pressure, massive unemployment and poverty. Every seventh unemployed person in the world is an Indian and every third poor person in the world is also an Indian. The statics speaks about the gravity of the problems of unemployment and poverty which demand an immediate solution.

Our country is predominantly agricultural with 70% of the population earn their livelihood from agricultural

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(8)

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RURAL POSTAL LIFE INSURANCE: INSURING LIVES AND ENSURING PROSPERITY OF RURAL INDIA

S.Sreevidhya
Assistant Professor, Department of Commerce, NSS College, Cherthala

Abstract

The performance of insurance in rural India is not so good as the life insurance is bought lesser by rural people. Majority of the rural population in India is without life insurance cover and these sections are vulnerable to weak social security also. In 1995 Govt. of India extended Postal Life Insurance to extend its coverage to rural people. This paper aims to analyze the various plans offered by RPLI and also investigate into its performance for the last few years.

Keywords: *Rural Postal Life Insurance, rural India etc.*

Introduction

The market share of insurance in rural area is not much good as compared to urban area. Even though the rural market is vibrant and holds tremendous potential for the growth of insurance business, particularly because of strong saving habit of rural people, the performance of insurance in rural India is not satisfactory as life insurance is bought lesser in India by rural population. Rural people are always risk avoiders and therefore insurance cannot apply the similar methodology that they apply to launch products in urban areas. Majority of the rural population in India is without life insurance cover and these sections are also subject to weak social security and pension systems with no old age income security.

The official committee for reforms in the insurance sector (Malhotra Committee) had observed in 1993 that only 22% of the insurance population in this country had been insured, and life insurance funds account for only 10% of the gross household savings. The committee recommended an absolutely smooth course of action to make the scenario better. According to the committee, in the rural area post master enjoys a very trust worthy and friendly relationships with customers and hence this position could be successfully used in popularizing insurance in the nation. The Government accepted the recommendations of Malhotra Committee and allowed Postal Life Insurance to extend its coverage to the rural areas to transact life insurance business with effect from 24.3.1995, mainly because of the vast network of Post Offices in the rural areas and low cost of operations.

Literature Review

1. Mr. B. Muthukrishnan, Doctoral Research Scholar, Department of Management, Pondicherry University, in his research paper titled "An Outlook Of Postal Life Insurance In The Current Era" (Indian Journal of Applied Research, Vol. 3, Issue 5, May 2013, ISSN: 2249-555X) attempts to give an overview on India Post, its various services and insurance schemes, financial performance of PLI, benefits of PLI and best PLI performing circles in India.
2. Dr. Angamuthu Balasubramaniam, Independent Researcher, Coimbatore undertook a study on "Postal Life Insurance: Its Market Growth and Policyholders' Satisfaction" (Samzodhana- Journal of Management Research, Vol. 2, Issue 1, March 2014). This paper is an empirical and analytical study which focuses on the measurement of the growth of PLI over the years and an analysis of the policyholders' satisfaction residing in the Coimbatore and Tiruppur districts of Tamil Nadu state.
3. M. K. Gupta and Nidhi Gupta, Department of Commerce, Pt. J. L. N. Govt. P. G. College, Faridabad, Haryana conducted a study on "An Empirical Study Of Postal Life Insurance

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GST AND ITS IMPACT ON VARIOUS SECTORS

S.Lt.Dr.S.Priya & Sreevidhya S

ABSTRACT

The introduction of Goods and Service Tax (GST) in India is now on the horizon .The current indirect tax structure is major impediment in India's economic growth and competitiveness. Tax barriers in the form of CST, entry tax and restricted input tax credit have fragmented the Indian market. Cascading effects of taxes on cost make indigenous manufacture less attractive. Hence the introduction of GST is considered crucial for economic growth. At the same time it will be favourable to some sectors and unfavourable to other sectors. This paper try to give an overview of proposed GST and analyze the impact of GST on various sectors /industry.

INTRODUCTION

Goods and Services Tax (GST) is the biggest reform in India's indirect tax structure since the economy began to be opened up 25 years ago. It has an impact on every spheres of business activity viz procurement, supply chain, IT logistics, pricing , margin, working capital etc. GST will turn India into one common market, leading to greater ease of doing business and big savings in logistics costs from companies across all sectors. The introduction of Goods and Services Tax (GST) would be a very significant step in the field of indirect tax reforms in India. By amalgamating a large number of Central and State taxes into a single tax, it would mitigate cascading or double taxation in a major way .Some companies will gain more as the GST rate will be lower than the current tax rates they pay, others will lose as the rate will be higher than the present effective rate. Since the central and state taxes are likely to be subsumed under GST, it may result in fungibility of tax credits across intra- and inter-state transactions Consequently, different industries may need to conduct a cost-benefit analysis in terms of applicable input and output.

OBJECTIVES

To get an overview of proposed GST

To analyze the impact of GST on various sectors /industry

METHODOLOGY

This paper is purely based on secondary data , and is collected from different websites , books etc

SIGNIFICANCE OF THE STUDY

The introduction of Goods and Service Tax (GST) in India is now on the horizon .The current indirect tax structure is major impediment in India's economic growth and competitiveness. Tax barriers in the form of CST, entry tax and restricted input tax credit have fragmented the Indian market. Cascading effects of taxes on cost make indigenous manufacture less attractive. Hence the introduction of GST is considered crucial for economic growth. At the same time it will be favourable to some sectors and unfavourable to other sectors. In this scenario, an analysis of GST and its impact on various sectors will help to get a clear view on GST

ANALYSIS - GST & IMPACT ON VARIOUS SECTORS

GST is an indirect tax reform which aims to remove tax barriers between states and create a single market. Currently we have VAT system both at the central and state level and we face cascading burden of tax on tax as there are no complete set-offs for tax paid on inputs or on previous purchases. Once the GST comes in to effect all central and state level taxes and levies on all goods and services will be subsumed with in an integrated tax having two component – a Central GST and State GST.

Objectives of GST

1. Ensuring availability of input credit across the value chain
2. Minimising cascading effect of taxation
3. Simplification of tax administration and compliance
4. Harmonisation of tax base, laws, and administration procedures across the country
5. Minimising tax rate slabs to avoid classification issues
6. Prevention of unhealthy competition among states
7. Increasing the tax base and raising compliance

IMPACT OF SHG ON THE ENTREPRENEURIAL TALENT OF RURAL WOMEN

(June 2019)

Sreevidhya. S[1]

Abstract

The economic development of a country is not possible with out bringing women in to the main stream of development activity. India has been endowed with rich resources which need proper utilization by adopting modern technology, for growth and development of the economy. Therefore entrepreneurship is essential for proper use of renewable and non-renewable natural resources and to provide employment to the employed youth. The empowerment of women is crucial for the development of the country. In India where population maintain equal ratio with males and females, the emergence of women entrepreneurs have great relevance of importance otherwise it will be amounting to neglecting 50 percentage of the entrepreneurial talent of the country. Creative entrepreneurs are the back bone of a nation's industrialization of economic development. Therefore women in to the main stream of development are major concern for the Government of India. This study analyzed the role of SHG in promoting the entrepreneurial talent of rural women and leads to a conclusion that the SHG has a positive impact on the entrepreneurial talent of the rural women.

Key words: *SHG, Entrepreneurship, rural women*

Introduction

Traditionally, an Indian woman had four fold status-role sequences. These were her role as a daughter, wife, housewife, and mother. The woman, whose status and role traditionally was well defined and almost fixed in the society, is now experiencing far-reaching changes. Gandhiji's vision is that women must play an equal and important role in national development. However, the movement for raising the socio-economic status of women had involved generally the middle-class educated women in major urban centres while the great mass of rural women are yet to enjoy the rights and privileges as enshrined in the Constitution.

Among Indian states Kerala is having the first place in the case of women population. In 2011 census, sex ratio is about 1084/1000.There is a lot of problems faced by women in Kerala. Hence there are lot of schemes, programmes, and policies were implemented by the Government. SHG's are one of the main programmes implemented in Kerala for the up gradation of status of women. Self Help Groups are becoming one of the important means for the empowerment of poor women in all most all the developing countries, including India. Kerala is no exception as regards the role played by the women's collective known by different names for emancipation and empowerment of women.

Women entrepreneurs may be defined as the women or a group of women who institute, organize and operate a business enterprise. Emergence of SHG system as pe initiatives of National Bank for Agricultural and Rura Development lead to the empowerment of women fron its very beginning. Through SHGs, government is tryin to inculcate and develop the entrepreneurial talent of it members to bring them to the main stream of country' development.3E's empirical model for wome entrepreneurship through SHGs

Emerging Stage

a. Identification of common interest area of SH members.
b. Identification of Indigenous Entrepreneurs.
c. Blending with latest technology.
d. Technical assistance.

Establishment Stages

a. Linkage with bank
b. Micro Entrepreneurship Establishment.
c. Explore the consumers.

Expansion Stage

a. Marketing.
b. Identification of problems.
c. Sort out problems by group dynamics.
d. Embodies new ideas and innovations.

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"Economic resources of the country should be utilised for the well-being of the poor. The change will commence from this point"

Hon. Prime minister of India

INTRODUCTION

Reducing financial untouchability is a need of hour as the development of the unbanked people is necessary for the development of our country. India has a well developed financial system and it is one of the finest financial system in the world. But the fruits of these well developed financial and banking system does not reach in each and every corner of our country. The more a country is financialised the more people is there, who have no access to financial products. People still find it difficult to manage their hard earned money in a proper manner. This means that despite of the various efforts of govt., the motive of complete financial inclusion could not be achieved even now

"Pradhan Mantri Jan-Dhan Yojana (PMJDY)" is a national mission Financial Inclusion encompassing an integrated approach to bring about comprehensive financial inclusion of all the households in the country. The plan envisages universal access to banking facilities with at least one basic banking account for every household, financial literacy, access to credit, insurance and pension facility. In addition, the beneficiaries would get RuPay Debit card having inbuilt accident insurance cover of ₹ 1 lakh. The plan also envisages channeling all Government benefits (from Centre / State / Local Body) to the beneficiaries accounts and pushing the Direct Benefits Transfer (DBT) scheme of the Union Government. This revolutionary financial inclusion programme was announced by the Hon. Prime Minister of India Shri Narendra Modi on his first independence speech on 15th Aug2014 and a large campaign was also launched by him on 28th Aug.2014.

The objective of PMJDY is ensuring access to various financial services like availability of basic savings bank account, access to need based credit, remittances facility, insurance and pension to the excluded sections i.e. weaker sections & low income groups. This deep penetration at affordable cost is possible only with effective use of technology.

④
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How far Pradhan Mantri Jan-Dhan Yojana (PMJDY) has succeeded in reducing financial untouchability?

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A STUDY ON YOUNG CUSTOMERS' PERCEPTION TOWARDS E-BANKING IN RURAL AREA

Sreevidhya. S

INTRODUCTION

Banking industry is the backbone of the financial system of a country. The need to survive in the changing environment has leaded the banking industry to adopt internet as a medium of operating in the market. E-banking has been viewed as an advanced upgrading from previous electronic delivery systems to open many new business opportunities for the banking industry. A survey revealed that at that time there was a planned 2 billion new investment in the new electronic banking technology within the banking industry. Internet banking provides alternatives for faster delivery of banking services to a wider range of customers. Internet banking refers to the use of internet as a remote delivery channel for banking services. It means any user with a personal computer and a browser can get connected to his bank website to performances of the banking functions.

India is prominently an agriculture country and its above 65% of the population lives in the villages. Spread of E-delivery channels in those areas is very less because of difficulty in reaching technology and other infrastructure which supports and helps in carrying the technology to these areas as well as lack of knowledge of the technology and internet operating training. E-banking in remote rural areas of India is encouraging. It will become one of the most convenient ways of delivering financial services in the future. Over the last few years online banks have started to become more and more popular. There are still quite a few people who are not sure an online account is a good idea for them.

LITERATURE REVIEW

Online banking acceptance has gained special attention in academic studies during the past five years as banking journals have devoted special issues on the topic (Mukherjee and Nath, 2003). Two reasons can be established for online banking development and diffusion. First, banks can save costs by offering online banking services. It has been proven that the online banking channel is the cheapest delivery channel for banking products once established (Giglio, 2002). Second, banks can reduce their branch networks and downsize the number of service staff, which opens the way for online banking as many customers feel that branch banking requires too much time and effort. Therefore, time and cost savings and freedom from place have been found to be the main reasons for underlying online banking acceptance (Howcroft, Hamilton and Hewer, 2002).

Convenience has been identified by a number of studies as an important adoption factor (ACNielsen, 2005; Pew, 2003; Ramsay and Smith, 1999; Thornton and White, 2001). A U.S. survey found the main motivator for internet banking to be convenience in terms of 24/7 access and time savings (Pew, 2003). Interestingly, Chung and Paynter (2002) found that many people who did not use internet banking believed they did not need high levels of convenience. Accessibility, which may be related to convenience, has been found important (Ramsay and Smith, 1999). High levels of workplace internet use have also been associated with the uptake of internet banking (Durkin, 2004).

The relevance of internet banking as an innovation has been found significant. Tan and Teo's (2000) survey of (mostly male) internet users employed Ajzen□s (1985) theory of planned behavior and Rogers□ (1985) theory of innovation diffusion and identified the main influences as: perceptions of relative advantage, compatibility, trialability, and risk. All but risk are known constructs in Rogers' (1985) theory of innovations diffusion. Also supporting the importance of trialability, Chung and Paynter (2002) found that lack of prior use of internet banking inhibited consumer adoption. Their survey further found that consumers who did not use the internet channel did not feel a need to do so, suggesting the

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Management

A STUDY ON THE EFFECTIVENESS OF FLCC PROGRAMME LAUNCHED BY FEDERAL BANK

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Abstract

The new economic reforms of government, advances in technology and great market orientation and financial innovation have reshaped the financial landscape. It means the people have so many investment opportunities. Poor people particularly in rural areas are often wary of banks and finds branches intimidating. A profound lack of financial literacy also reinforces the sense of alienation. The rural poor are also unaware about how to deal with credit, how to avoid incurring debts that cannot be repaid. In order to solve these problems RBI has decided to provide financial literacy along with credit counselling. As such RBI has come out with a model scheme on FLCC and advised banks to set up as many FLCC in order to achieve at least one FLCC per block.

In consonance with RBI directives the Federal Bank, the first bank in the state which started FLCC, established a trust namely 'Federal Ashwas Trust'. The main objective of this trust is the establishment and running of 'Federal Aswas Financial Literacy Centers' (FAFLC) for providing financial education to the public. The objective of the scheme is to provide free financial literacy education and credit counselling to people in rural and urban area. Through this FLCC centers across the state, customers are educated on responsible borrowing, proactive and early savings and also offers debt counselling to individuals.

Keywords: Financial Literacy; Credit Counselling; Debt Management.

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1. Introduction

"The Perfect banking partner"- Federal Bank. Yes, the Federal Bank has become the perfect banking partner of the common man not only in its banking activities but also in their social commitment through inculcating financial literacy among the people. Federal bank is the first private bank which took initiative in implementing RBI directives on financial literacy. Till now

POSTAL LIFE INSURANCE- A POLICY WITH LOW PREMIUM AND HIGH BONUS

Sreevidhya S,
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Abstract

Insurance is a subject matter of solicitation. The growth of insurance industry has been spurred by product innovation, vibrant distribution channels coupled with targeted publicity and promotional campaign. India has allowed private companies in insurance sector in 2000, setting a limit on FDI to 26% which was increased to 49% in 2014. All these reforms leads to a confusion among the public regarding selection of particular insurer which offer high return with lowest premium. Postal Life Insurance (PLI) is an insurance policy managed by Department of Posts under the Government of India.. It was started as the welfare measure for the employees of the Post and Telegraph Department. As it started becoming popular it was extended for the rest of the bodies. The major attractive feature of the PLI is the "low premium and high bonus" when compared to other policies. It is the only insurer in the Indian life insurance industry which gives the highest return with lowest premium charged for any product in the market.Low premium and high bonus is the special feature of this insurance policy when compared to other policies. This paper aims to study in detail the various plans of PLI and also its performance.The study is based on secondary data. An investigation to the details of PLI and its performance shows that, it offers much benefit to the policy holders and its growth has an increasing trend with regard to corpus of fund, sum assured etc.

Introduction

"Life is full of risk, future is uncertain, and human wants are unlimited"- all these prompt us to think of a supporting mechanism which reduces risk, nullify the effects of uncertainty and assisting us to fulfill our wants. Insurance is such a mechanism. It is the equitable transfer of the risk of loss from one entity to another in exchange for money .It is the form of the risk management primarily used to hedge against the risk of a contingent, uncertain loss. The transaction involves the insured assuming a guaranteed and relatively small loss in the form of payment to the insurer in exchange for the insurer's promise to indemnify the insured in the case of a financial (personal) loss. The insured receives a contract called the insurance policy, which details the conditions and circumstances under which the insured will be financially compensated.

Postal Life Insurance Policy (PLI) is an insurance policy managed by Department of Posts under the Govt. of India. It was started as the welfare measure for the employees of the Post and Telegraph Department. As it started becoming popular it was extended for the rest of the bodies. The major attractive feature of the PLI is the "low premium and high bonus" when compared to other policies. It is the only insurer in the Indian life insurance industry which gives the highest return with lowest premium charged for any product in the market.

Significance of the Study

Insurance is a subject matter of solicitation. The growth of insurance industry has been spurred by product innovation, vibrant distribution channels coupled with targeted publicity and promotional campaign. India has allowed private companies in insurance sector in 2000, setting a limit on FDI to 26% which was increased to 49% in 2014. All these

Free Idempotent Generated Semigroups Over Biordered Sets

Karthika M G

Department of Mathematics, NSS college, Pandalam

Abstract

The concept of biordered set was introduced by K. S. S. Nambooripad. In this paper we present the description of free idempotent generated semigroup on a given biordered set. we prove that corresponding to every biordered set E, there is an idempotent generated semigroup S whose biordered set of idempotents is isomorphic to E. We also prove that S is a free object in the category of all idempotent generated semigroups whose biordered set of idempotents is isomorphic to E.

1 Preliminaries

In this section we discuss some preliminary definitions and results on Biordered sets

Definition 1.1. *A partial binary operation on a set E is a function from a subset of $E \times E$ to E. The domain of this function is called the domain of the partial binary operation.*

Definition 1.2. *A relation on a set E which is reflexive and transitive is called a quasiorder on E.*

Definition 1.3. *A partial algebra E is a set E together with a partial binary operation on E. The domain of the partial binary operation will be denoted by D_E. Then*

D_E is a relation on E and $(e, f) \in D_E$ if and only if the product exists in the partial algebra E.

When no confusion is likely we shall indicate the product in E by juxtaposition.

On a partial algebra E, we define

$$\omega^r = \{(e, f) \in D_E : fe = e\}$$

$$\omega^l = \{(e, f) \in D_E : ef = e\}$$

$$\mathcal{R} = \omega^r \cap (\omega^r)^{-1}$$

$$\mathcal{L} = \omega^l \cap (\omega^l)^{-1} \text{ and}$$

$$\omega = \omega^r \cap \omega^l.$$

If T is a statement about E, its left- right dual is denoted by T^*. For $e \in E$ we set $\omega^r(e) = \{f \in E : f\omega^r e\}$ and $\omega^l(e) = \{f \in E : f\omega^l e\}$.

Definition 1.4. *Let E be a partial algebra. Then E is a biordered set if the following axioms and their duals hold. In the following e, f etc denote arbitrary elements of E.*

(B1) ω^r and ω^l are quasiorders on E and

$$D_E = (\omega^r \cup \omega^l) \cup (\omega^r \cup \omega^l)^{-1}$$

(B21) $f \in \omega^r(e) \Rightarrow f\mathcal{R}fe\omega e$

(B22) $g\omega^l f, f, g \in \omega^r(e) \Rightarrow ge\omega^l fe$

(B31) $g\omega^r f\omega^r e \Rightarrow gf = (ge)f$

(B32) $g\omega^l f, f, g \in \omega^r(e) \Rightarrow (fg)e = (fe)(ge)$

Let

$$M(e, f) = \{g \in E : g\omega^l e \text{ and } g\omega^r f\}.$$

Then the set

$$S(e,f) = \{h \in M(e,f) : \text{ for all } g \in M(e,f), eg\omega^r eh \text{ and } gf\omega^l hf\}$$

is called the sandwich set of e and f.

(B4) $f, g \in \omega^r(e) \Rightarrow S(f,g)e = S(fe, ge)$.

The biordered set e is said to be regular if

(R) $S(e,f) \neq \Phi$ *for all* $e, f \in E$

The partial binary operation of a biordered set E is called the basic product of E and the relations ω^r and ω^l are called the right and left quasi orders of E respectively. Since D_E is symmetric and since axioms for biordered sets are self dual, the dual of any true proposition is also true.

Remark 1.5. *If E is a biordered set, then $\mathcal{L}$ and $\mathcal{R}$ are equivalence relations on E.*

Definition 1.6. *Let E and E' be biordered sets and $\theta : E \longrightarrow E'$ be a mapping. Then θ is called a bimorphism if it satisfies the following;*

$$(e,f) \in D_E \Rightarrow (e\theta, f\theta) \in D_{E'} \text{ and } (ef)\theta = (e\theta)(f\theta)$$

If θ is a bijection and θ and θ^{-1} are bimorphisms then θ is called an isomorphism of biordred sets.

Definition 1.7. *Let E be a biordered set and F be a subset of E. Then F is called a biordered subset of E if F is a partial subalgebra of E, in the sense that $D_F = D_E \cap (F \times F)$, and F satisfies the biordered set axioms with respect to the restrictions of ω^r and ω^l to F.*

Proposition 1.8. *Let E be a biordered set and $e, f, g \in E$. Then*

$$g\omega^r f\omega^r e \Rightarrow (gf)e = g(fe) = (ge)(fe).$$

Theorem 1.9. *Let S be a semigroup such that $E(S) \neq \Phi$. Then the partial algebra $E(S)$ is a biordered set.*

2 Biordered Sets Come from Semigroups

In this section we prove that corresponding to every biordered set E, there is an idempotent generated semigroup S whose biordered set of idempotents is isomorphic to E. We also prove that S is a free object in the category of all idempotent generated semigroups whose biordered set of idempotents is isomorphic to E.

The references for this section are [?], [?] and [?]. Through out this chapter E denotes a biordered set. Let $\mathcal{L}$ and $\mathcal{R}$ be the equivalance relations on E which are defined in section1. Let L denotes an arbitrary member of $E/\mathcal{L}$ and R denotes an arbitrary member of $E/\mathcal{R}$. Let L_e be the $\mathcal{L}$ - class containing $e \epsilon E$ and R_e be the $\mathcal{R}$- class containing $e \epsilon E$.

Let $X = E/\mathcal{L} \cup \{\infty\}$ and $Y = E/\mathcal{R} \cup \{\infty\}$, where ∞ is a new symbol. Let $\mathcal{T}(X)$ denote the full transformation semigroup on X and $\mathcal{T}^*(Y)$ denote the dual transformation semigroup on Y. For $f, g \in \mathcal{T}^*(Y)$ the product fg is defined by $(a)(fg) = ((a)g)f$ for all $a \in Y$.

Lemma 2.1. *Let $\rho : E \to T(X)$ be the map defined by $e \mapsto \rho_e$, where*

$$\begin{array}{rcll} \rho_e : & L & \mapsto & L_{xe} \quad \text{if } x\omega^r e \text{ for some } x \in L \\ & & \mapsto & \infty \quad \text{otherwise} \\ & \infty & \mapsto & \infty \end{array}$$

and $\lambda : E \to T(Y)$ be the map defined by $e \mapsto \lambda_e$, where

$$\begin{array}{rcll} \lambda_e : & R & \mapsto & R_{ex} \quad \text{if } x\omega^l e \text{ for some } x \in R \\ & & \mapsto & \infty \quad \text{otherwise} \\ & \infty & \mapsto & \infty \end{array}$$

Then $(e, f) \in D_E \Rightarrow \rho_{ef} = \rho_e \rho_f$, where $(a)(\rho_e \rho_f) = ((a)\rho_e)\rho_f$ and $\lambda_{ef} = \lambda_f \lambda_e$, where $(b)(\lambda_f \lambda_e) = ((b)\lambda_f)\lambda_e$.

Proof. Let $x, y \in L$ such that $x\omega^r e$ and $y\omega^r e$. Since $x, y \in L$, $x \mathcal{L} y$. So $x\omega^l y$ and

$y\omega^l x$. Since $x\omega^l y$ and $x, y \in \omega^r(e)$, by (B22), we have $xe\omega^l ye$. Similarly since $y\omega^l x$, we get $ye\omega^l xe$. Hence $xe\mathcal{L}ye$and so $L_{xe} = L_{ye}$. Therefore ρ_e is well defined and so ρ is well-defined. Dually,we get λ_e and λ is well-defined.

Suppose $(e, f) \in D_e$. Then either $e\omega^l f$ or $e\omega^r f$ or $f\omega^l e$ or $f\omega^r e$. Suppose $e\omega^l f$, then $ef = e$. We have to show that $\rho_{ef} = \rho_e = \rho_e\rho_f$. Suppose $L\rho_e \neq \infty$. So $x\omega^r e$ for some $x \in L$ and $L\rho_e = L_{xe}$. Since $x\omega^r e, e\omega^l f$,by $(B21)$ and $(B21)^*$, we have $x\mathcal{R}xe\omega e$ and $e\mathcal{L}fe\omega f$. So by the transitivity of ω^l, we get $xe\omega^l f$. Again by $(B21)^*$ we have $xe\mathcal{L}f(xe)\omega f$. Thus $f(xe) \in L_{xe}$ and $f(xe)\omega^r f$. So

$$\begin{aligned} L\rho_e\rho_f &= L_{xe}\rho_f \\ &= L_{f(xe)f} \\ &= L_{f(xe)} \text{ , since } f(xe)\omega^l f \\ &= L_{xe}, \text{ since } xe\mathcal{L}f(xe) \\ &= L\rho_e \end{aligned}$$

Thus $L\rho_e = L\rho_e\rho_f$, when $L\rho_e \neq \infty$. Suppose $L\rho_e\rho_f \neq \infty$, then $L\rho_e \neq \infty$. Hence $L\rho_e = L\rho_e\rho_f$, when $L\rho_e = \infty$. Thus $\rho_{ef} = \rho_e\rho_f$. Now suppose $e\omega^r f$, then $fe = e$. Suppose $L\rho_{ef} \neq \infty$, so $x\omega^r ef$ for some $x \in L$ and $L\rho_{ef} = L_{x(ef)}$. Since $e\omega^r f$, by(B21), $e\mathcal{R}ef\omega f$. Then by the transitivity of ω^r, we get $x\omega^r e$. Again by $(B21)$, $xe\omega e$. So

$$\begin{aligned} L\rho_e\rho_f &= L_{xe}\rho_f \\ &= L_{(xe)f}, \text{ since } xe\omega^r f \\ &= L_{x(ef)} \text{ , since } x\omega^r e\omega^r f \\ &= L\rho_{ef} \end{aligned}$$

Thus $L\rho_e\rho_f = L\rho_{ef}$, when $L\rho_{ef} \neq \infty$. Suppose $L\rho_e\rho_f \neq \infty$, then $L\rho_e \neq \infty$, so $x\omega^r e$ for some $x \in L$. Since $x\omega^r e$ and $e\mathcal{R}ef$, we get $x\omega^r ef$. Thus $x \in L$ and $x\omega^r ef$, so $L\rho_{ef} \neq \infty$. Hence if $L\rho_{ef} = \infty$, then $L\rho_e\rho_f = \infty$. Therefore $\rho_{ef} = \rho_e\rho_f$, when $e\omega^r f$. Similarly we get $\rho_{ef} = \rho_e\rho_f$ for the other two cases. Thus we have shown $(e, f) = D_E \Rightarrow \rho_{ef} = \rho_e\rho_f$. By the dual argument we also have $(e, f) \in D_E \Rightarrow \lambda_{ef} = \lambda_f\lambda_e$. □

Lemma 2.2. *Let E be a biordered set and $e \in E$. Let ρ and λ be the maps defined in lemma 2.1 Let $\phi : E \to \mathcal{T}(X) \times \mathcal{T}^*(Y)$ be the map defined by*

$$e \mapsto \phi_e = (\rho_e, \lambda_e)$$

Then for $e, f \in E$,

$$\phi_e\phi_f = \phi_e \Rightarrow e\omega^l f \text{ and } \phi_f\phi_e = \phi_e \Rightarrow e\omega^r f.$$

Proof. Suppose $\phi_e\phi_f = \phi_e$, so $\rho_e\rho_f = \rho_e$. Then

$$L_e = L_e\rho_e = \rho_e\rho_f = L_e\rho_f$$

So $x\omega^r f$ for some $x \in L$ and $L_{xf} = L_e$. Now by $(B21)$, $x\omega^r f \Rightarrow x\mathcal{R}xf\omega f$ and $L_{xf} = L_e \Rightarrow e\omega^l xf$. Thus by the transitivity of ω^l, we have, $e\omega^l f$.

If $\phi_f\phi_e = \phi_e$, then $\lambda_e\lambda_f = \lambda_e$ and by the dual argument, we have $e\omega^r f$. □

Theorem 2.3. *Let E be a biordered set and ϕ is defined as above, then $E\phi$ is a biordered subset of $E(\mathcal{T}(X) \times \mathcal{T}^*(Y))$ and $\phi : E \longrightarrow E\phi$ is an isomorphism.*

Proof. Let $e \in E$.

$$\begin{aligned}\phi_e\phi_e &= (\rho_e, \lambda_e)(\rho_e, \lambda_e)\\ &= (\rho_e\rho_e, \lambda_e\lambda_e)\\ &= (\rho_e, \lambda_e) \text{ , by lemma 2.1}\\ &= \phi_e \text{ .}\end{aligned}$$

So $\phi_e \in E(\mathcal{T}(X) \times \mathcal{T}^*(Y))$. We show that $\phi : E \longrightarrow E(\mathcal{T}(X) \times \mathcal{T}^*(Y))$ is an injective bimorphism.

Let $(e, f) \in D_E$. Then either $e\omega^l f$ or $e\omega^r f$ or $f\omega^l e$ or $f\omega^r e$. Suppose $e\omega^l f$, so $ef = e$ and

$$\begin{aligned}\phi_e\phi_f &= (\rho_e, \lambda_e)(\rho_f, \lambda_f)\\ &= (\rho_e\rho_f, \lambda_e\lambda_f)\\ &= (\rho_{ef}, \lambda_{ef}) \text{ , by lemma 2.1}\\ &= (\rho_e, \lambda_e)\\ &= \phi_e \text{ .}\end{aligned}$$

That is $\phi_e\phi_f = \phi_e$ which implies $(\phi_e, \phi_f) \in D_{E(\mathcal{T}(X)\times\mathcal{T}^*(Y))}$. Similarly we get $(\phi_e, \phi_f) \in D_{E(\mathcal{T}(X)\times\mathcal{T}^*(Y))}$ for the other three cases. Also, by lemma 2.1,

$$\begin{aligned}\phi_{ef} &= (\rho_{ef}, \lambda_{ef})\\ &= (\rho_e\rho_f, \lambda_e\lambda_f)\\ &= (\rho_e, \lambda_e)(\rho_f, \lambda_f)\\ &= \phi_e\phi_f.\end{aligned}$$

Thus $(e, f) \in D_E \Rightarrow (\phi_e, \phi_f) \in D_{E(\mathcal{T}(X)\times\mathcal{T}^*(Y))}$ and $\phi_{ef} = \phi_e\phi_f$. Therefore ϕ is a bimorphism. If $\phi_e = \phi_f$, then $\phi_e\phi_f = \phi_e\phi_e = \phi_e$, so by lemma 2.2 $e\omega^l f$. Again $\phi_e\phi_f = \phi_f\phi_f = \phi_f$, so by lemma 2.2, $f\omega^r e$. There fore $e = ef = f$. Hence ϕ is injective.

Now we show that $E\phi$ is a partial subalgebra of $E(\mathcal{T}(X) \times \mathcal{T}^*(Y))$. Let $\phi_e, \phi_f \in E\phi$ and $(\phi_e, \phi_f) \in D_{E(\mathcal{T}(X)\times\mathcal{T}^*(Y))}$. Then either $\phi_e\phi_f = \phi_e$ or $\phi_e\phi_f = \phi_f$ or $\phi_f\phi_e = \phi_e$ or $\phi_f\phi_e = \phi_f$. In the first two cases $\phi_e\phi_f \in E\phi$. If $\phi_f\phi_e = \phi_e$, then by lemma 2.2 $e\omega^r f$. So $(e, f) \in D_E$. Then since ϕ is a bimorphism, we have $\phi_e\phi_f = \phi_{ef} \in E\phi$. Similarly if $\phi_e\phi_f = \phi_f$ then $\phi_e\phi_f \in E\phi$. Thus $E\phi$ is a partial subalgebra.

Let $\phi^{-1} : E\phi \longrightarrow E$ denote the map $\phi_e \mapsto e$. If $(\phi_e, \phi_f) \in D_{E\phi}$ then by lemma 2.2, $(e, f) \in D_E$. Also $(\phi_e\phi_f)\phi^{-1} = (\phi_{ef})\phi^{-1} = ef = (\phi e)\phi^{-1}(\phi_f)\phi^{-1}$, so ϕ^{-1} is a morphism of partial algebras. Thus ϕ is an isomorphism of partial algebras. Hence $E\phi \cong E$ as partial algebras, so $E\phi$ is a biordered set and hence a biordered subset of $E(\mathcal{T}(X) \times \mathcal{T}^*(Y))$. □

Lemma 2.4. [[?], *Lemma 4*] *Let E be a biordered set. If $\alpha \in E(\langle E\phi\rangle)$ and $\phi_x \mathscr{L} \alpha \mathscr{R} \phi_y$ for some $x, y \in E$, then $\alpha \in E\phi$.*

Let E be a biordered set. Let F denote the free semigroup on E and F^1 be the corresponding free monoid. Elements of E will be called letters and that of F^1 will be called words. Through out this chapter e, f, g, x, y and z with or without subscripts or superscripts will denote letters and u, v, w with or without subscripts or superscripts will denote words.

Definition 2.5. *The length of a word u is defined as the number of letters in u and is denoted by $l(u)$.*

Multiplication in F^1 will be denoted by juxtaposition, so if $(f, g) \in D_E$ then the expression fg is a word of length two and $f * g$ is a single letter which is the product in the biordered set E.

Definition 2.6. *Let v and w be words. We say that v is a subword of w, if $w = uvu'$, for some $u, u' \in F^1$.*

Definition 2.7. *The words $w_1, w_2, \ldots w_n$ is said to cover the word w, if there exist subwords $w_1', w_2', \ldots, w_n'$ of $w_1, w_2, \ldots, w_n$ respectively such that $w = w_1' w_2' \cdots w_n'$.*

Define a relation σ on F by

$$\sigma = \{(fg, f * g)/(f, g) \in D_E\}$$

and let $\sigma^\#$ denote the smallest congruence containing σ. Elementary $\sigma-$ transition will be denoted by T with or without subscripts.

If T transforms w into w', then we write $T : w \mapsto w'$. Hence for some u, v, f and g, T is always of the form

$$ufgv \mapsto uf * gv \quad \text{or}$$

$$uf * gv \mapsto ufgv$$

We say that T is of type (1) if $f\omega^r g$ or $f\omega^l g$ and of type (2) if $g\omega^r f$ or $g\omega^l f$.

Lemma 2.8. *If $f_1, f_2, \ldots, f_n, g_1, g_2, \ldots g_m$ are letters such that $\sigma^\#(f_1 f_2 \cdots f_n) = \sigma^\#(g_1 g_2 \cdots g_m)$, then $\phi_{f_1}\phi_{f_2}\cdots\phi_{f_n} = \phi_{g_1}\phi_{g_2}\cdots\phi_{g_m}$.*

Proof. Since $\sigma^{\#}(f_1 f_2 \cdots f_n) = \sigma^{\#}(g_1 g_2 \cdots g_m)$, $(f_1 f_2 \cdots f_n, g_1 g_2 \cdots g_n) \in \sigma^{\#}$. Then either $f_1 f_2 \cdots f_n = g_1 g_2 \cdots g_m$ or there exist a sequence of elementary $\sigma-$ transitions:

$$f_1 f_2 \cdots f_n = z_1 \mapsto z_2 \mapsto \cdots \mapsto z_k = g_1 g_2 \cdots g_m$$

If $f_1 f_2 \cdots f_n = g_1 g_2 \cdots g_m$, then $n = m$ and $f_i = g_i$ for $i = 1, 2, \ldots n$, so $\phi_{f_i} = \phi_{g_i}$ for $i = 1, 2 \ldots, n$. Therefore $\phi_{f_1}\phi_{f_2} \cdots \phi_{f_n} = \phi_{g_1}\phi_{g_2} \cdots \phi_{g_m}$. Hence the result holds in this case. Otherwise, suppose there is a sequence of elementary $\sigma-$ transitions:

$$f_1 f_2 \cdots f_n = z_1 \mapsto z_2 \mapsto \cdots \mapsto z_k = g_1 g_2 \cdots g_m$$

Using mathematical induction on k we show that $z_1\phi = z_k\phi$. Suppose $k = 2$, That is $z_1 \mapsto z_2$. Then there exist u, v in F^1 and $(f, g) \in D_E$ such that $z_1 = ufgv$ and $z_2 = u(f * g)v$. Now

$$\begin{aligned} & z_1 && = ufgv \\ \Rightarrow\ & z_1\phi && = (ufgv)\phi \\ \Rightarrow\ & z_1\phi && = (u\phi)(f\phi)(g\phi)(v\phi) \end{aligned}$$

$$z_2 = u(f * g)v \tag{1}$$

$$\begin{aligned} \Rightarrow\ & z_2\phi && = (u(f * g)v)\phi \\ \Rightarrow\ & z_2\phi && = (u\phi)(f * g)\phi(v\phi) \\ \Rightarrow\ & z_2\phi && = (u\phi)(f\phi)(g\phi)(v\phi) \quad \text{since } \phi \text{ is a bimorphism} \end{aligned}$$

$$z_2\phi = (u\phi)(f\phi)(g\phi)(v\phi) \tag{2}$$

From (1) and (2) we have $z_1\phi = z_2\phi$. Thus the result is true when $k = 2$.

Suppose by induction that the result is true for $k - 1$. That is if $z_1 \mapsto z_2 \mapsto \ldots \mapsto z_{k-1}$, then

$$z_1\phi = z_{k-1}\phi \tag{3}$$

Now if $z_1 \mapsto z_2 \mapsto \ldots \mapsto z_{k-1} \mapsto z_k$, then as in the case $k = 2$,

$$z_{k-1}\phi = z_k\phi \tag{4}$$

From (3) and (4), we get $z_1\phi = z_k\phi$. Therefore by the principle of mathematical induction the result is true for all k. Hence $z_1\phi = z_k\phi$.That is,

$(f_1, f_2, \cdots, f_n)\phi = (g_1, g_2, \cdots g_m)\phi$

$\Rightarrow (f_1\phi)(f_2\phi)\cdots(f_n\phi) = (g_1\phi)\cdots(g_n\phi)$, $\Rightarrow \phi_{f_1}\phi_{f_2}\ldots\phi_{f_n} = \phi_{g_1}\phi_{g_2}\ldots\phi_{g_m}$.

Hence the proof. □

Lemma 2.9. *Suppose $\sigma^{\#}(w)$ is an idempotent in the quotient semigroup $F/\sigma^{\#}$ such that $\sigma^{\#}(w)\mathscr{D}\sigma^{\#}(e)$ for some letter e. Then $\sigma^{\#}(w)$ contains some letter so that $\sigma^{\#}(e) = \sigma^{\#}(f)$ for some $f \in E$.*

Proof. If $\sigma^{\#}(u)$ and $\sigma^{\#}(v)$ are elements in $F/\sigma^{\#}$. Then $\sigma^{\#}(u)\sigma^{\#}(v) = \sigma^{\#}(uv)$. Now for $e \in E, (e, e) \in D_E$, so $\sigma^{\#}(e)\sigma^{\#}(e) = \sigma^{\#}(ee) = \sigma^{\#}(e * e) = \sigma^{\#}(e)$ and $\phi_e\phi_e = \phi_e e = \phi_e$. Thus $\sigma^{\#}(e)$ and ϕ_e are idempotents. Since $\sigma^{\#}(w)$ and $\sigma^{\#}(e)$ are idempotents and $\sigma^{\#}(w)\mathscr{D}\sigma^{\#}(e)$, then, there exist $f_1, f_2, \ldots f_n, g_1, g_2 \ldots, g_m$ in E such that $\sigma^{\#}(f_1 f_2 \cdots f_n)$ is an inverse of $\sigma^{\#}(g_1 g_2 \cdots g_m)$ and

$$\sigma^{\#}(w) = \sigma^{\#}(f_1 f_2 \cdots f_n)\sigma^{\#}(g_1 g_2 \cdots g_m)$$
$$\sigma^{\#}(e) = \sigma^{\#}(g_1 g_2 \cdots g_m)\sigma^{\#}(f_1 f_2 \cdots f_n)$$

Since $\sigma^{\#}(e) = \sigma^{\#}(g_1 g_2 \ldots g_m f_1 f_2 \ldots f_n)$, by lemma **??**,

$\phi_e = \phi_{g_1}\phi_{g_2}\ldots\phi_{g_m}\phi_{f_1}\phi_{f_2}\ldots\phi_{f_n}$ and so $\rho_e = \rho_{g_1}\rho_{g_2}\ldots\rho_{g_m}\rho_{f_1}\rho_{f_2}\ldots\rho_{f_n}$. Since $e \in L_e$ and $e\omega^r e$, $L_e\rho_e \neq \infty$. So $L_e\rho_{g_1}\rho_{g_2}\ldots\rho_{g_m} \neq \infty \Rightarrow L_e\rho_{g_1} \neq \infty$, so $x_1\omega^r g_1$ for some $x_1 \in L_e$ and $L_e\rho_{g_1} = L_{x_1 * g_1}$. Again $L_e\rho_{g_1}\rho_{g_2} \neq \infty \Rightarrow L_{x_1 * g_1}\rho_{g_2} \neq \infty$, so $x_2\omega^r g_2$ for some $x_2 \in L_{x_1 * g_1}$ and $L_{x_1 * g_1}\rho_{g_2} = L_{x_2 * g_2}$ continuing like this, we get $L_{x_{m-1} * g_{m-1}}\rho_{g_m} = L_{x_m * g_m}$ for some $x_m \in L_{x_{m-1} * g_{m-1}}$ and $x_m\omega^r g_m$. Hence there exist $x_1, x_2, \ldots x_m$ in E such that

$$\begin{aligned} x_1\omega^r g_1 \quad &, x_1 \in L_e \\ x_2\omega^r g_2 \quad &, x_2 \in L_{x_1 * y_1} \\ \vdots \quad &\vdots \\ x_m\omega^r g_m \quad &, x_m \in L_{x_{m-1} * g_{m-1}} \end{aligned}$$

Put $S = F/\sigma^{\#}$. Since $\sigma^{\#}(e) = \sigma^{\#}(g_1 g_2 \cdots g_m)\sigma^{\#}(f_1 f_2 \cdots f_m)$ and $\sigma^{\#}(f_1 f_2 \cdots f_m)$ is an inverse of $\sigma^{\#}(g_1 g_2 \cdots g_m)$, we have,

$$\begin{aligned} \sigma^{\#}(e g_1 g_2 \cdots g_m) &= \sigma^{\#}(g_1 g_2 \cdots g_m) \\ &= \sigma^{\#}(g_1 g_2 \cdots g_m)\sigma^{\#}(f_1 f_2 \cdots f_m)\sigma^{\#}(g_1 \cdots g_m) \\ &= \sigma^{\#}(g_1 g_2 \cdots g_m) \end{aligned}$$

$$\sigma^{\#}(e g_1 g_2 \cdots g_m) = \sigma^{\#}(g_1 g_2 \cdots g_m) \tag{5}$$

Since $\sigma^{\#}(w) = \sigma^{\#}(f_1 f_2 \cdots f_m)\sigma^{\#}(g_1 g_2 \cdots g_m)$ and $\sigma^{\#}(g_1 g_2 \cdots g_m) = \sigma^{\#}(g_1 g_2 \cdots g_m)\sigma^{\#}(f_1 f_2 \cdots f_n) = \sigma^{\#}(g_1 g_2 \cdots g_m)\sigma^{\#}(w)$, we get $\sigma^{\#}(g_1 g_2 \cdots g_m)\mathscr{L}_S\sigma^{\#}(w)$. Therefore by (5) we have

$$\sigma^{\#}(e g_1 \cdots g_m)\mathscr{L}_S\sigma^{\#}(w) \tag{6}$$

Now $x_1\omega^r g_1$ and $x_1 \in L_e \Rightarrow x_1 * e = x_1$ and $e * x_1 = e$

$\Rightarrow \sigma^{\#}(x_1 * e) = \sigma^{\#}(x_1)$ and $\sigma^{\#}(e * x_1) = \sigma^{\#}(e)$

$\Rightarrow \sigma^{\#}(x_1 e) = \sigma^{\#}(x_1)$ and $\sigma^{\#}(e x_1) = \sigma^{\#}(e)$, since $(x_1, e) \in D_E$

$\Rightarrow \sigma^{\#}(x_1)\sigma^{\#}(e) = \sigma^{\#}(x_1)$ and $\sigma^{\#}(e)\sigma^{\#}(x_1) = \sigma^{\#}(e)$

$\Rightarrow \sigma^{\#}(x_1)\mathscr{L}_S\sigma^{\#}(e)$

$\Rightarrow \sigma^{\#}(x_1)\sigma^{\#}(g_1)\mathscr{L}_S\sigma^{\#}(e)\sigma^{\#}(g_1)$, since $\mathscr{L}_S$ is a right congruence.

$\Rightarrow \sigma^{\#}(x_1 g_1)\mathscr{L}_s\sigma^{\#}(e g_1)$ which implies

$$\sigma^{\#}(x_1 * g_1)\mathscr{L}_s\sigma^{\#}(e g_1) \tag{7}$$

Similarly, $x\omega^r g_2$ and $x_2 \in L_{x_1 * g_1}$ implies

$$\sigma^{\#}(x_2)\mathscr{L}_s\sigma^{\#}(x_1 * g_1) \tag{8}$$

From (7) and (8), we have $\sigma^{\#}(x_2)\mathscr{L}_s\sigma^{\#}(eg_1)$

$\Rightarrow \sigma^{\#}(x_2)\sigma^{\#}(g_2)\mathscr{L}_s\sigma^{\#}(eg_1)\sigma^{\#}(g_2)$

$\Rightarrow \sigma^{\#}(x_2g_2)\mathscr{L}_s\sigma^{\#}(eg_1g_2)$

$\Rightarrow \sigma^{\#}(x_2 * g_2)\mathscr{L}_s\sigma^{\#}(eg_1g_2)$.

Continuing like this we get

$$\sigma^{\#}(x_m * g_m)\mathscr{L}_s\sigma^{\#}(eg_1g_2\cdots g_m) \tag{9}$$

From (6) and (9), we have $\sigma^{\#}(x_m * g_m)\mathscr{L}_s\sigma^{\#}(w)$. Let $x = x_m * g_m$. Then $x \in E$ and

$$\sigma^{\#}(x)\mathscr{L}_s\sigma^{\#}(w) \tag{10}$$

Let $w = e_1e_2\cdots e_N$. Since $\sigma^{\#}(x)\mathscr{L}_s\sigma^{\#}(w)$, there exist u and v in F^1 such that $\sigma^{\#}(x) = \sigma^{\#}(u)\sigma^{\#}(w)$ and $\sigma^{\#}(w) = \sigma^{\#}(v)\sigma^{\#}(x) \Rightarrow \sigma^{\#}(x) = \sigma^{\#}(uw)$ and $\sigma^{\#}(w) = \sigma^{\#}(vx)$.

Let $u = x_1x_2\cdots x_r$ and $v = y_1y_2\cdots y_s$. Then $\sigma^{\#}(x) = \sigma^{\#}(x_1x_2\cdots x_re_1e_2\cdots e_N)$ and $\sigma^{\#}(e_1e_2\cdots e_N) = \sigma^{\#}(y_1y_2\cdots y_sx)$. By lemma **??**, we get $\phi_x = (\phi_{x_1}\phi_{x_2}\cdots\phi_{x_r})(\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N})$ and $\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N} = (\phi_{y_1}\phi_{y_2}\cdots\phi_{y_s})\phi_x$, so $\phi_x\mathscr{L}_{\langle E\phi\rangle}\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N}$, where $\langle E\phi\rangle$ is the subsemigroup of $\mathcal{T}(X)\times\mathcal{T}^*(Y)$ generated by $E\phi$.

Dually since $R_e\lambda_e \neq \infty$, there exist $y \in E$ such that

$$\sigma^{\#}(y)\mathscr{R}_S\sigma^{\#}(w) \text{ and } \phi_y\mathscr{R}_{\langle E\phi\rangle}\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N} \tag{11}$$

Now we show that $\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N}$ is an idempotent. Since $\sigma^{\#}(w)$ is an idempotent, $\sigma^{\#}(w)\sigma^{\#}(w) = \sigma^{\#}(w)$

$\Rightarrow \sigma^{\#}(e_1e_2\cdots e_N)\sigma^{\#}(e_1e_2\cdots e_N) = \sigma^{\#}(e_1e_2\cdots e_N)$

$\Rightarrow \sigma^{\#}(e_1e_2\cdots e_Ne_1e_2\cdots e_N) = \sigma^{\#}(e_1e_2\cdots e_N)$

$\Rightarrow \phi_{e_1}\phi_{e_2}\cdots\phi_{e_N}\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N} = \phi_{e_1}\phi_{e_2}\cdots\phi_{e_N}$, by lemma **??**.

Therefore $\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N}$ is idempotent. Thus $\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N} \in E(\langle E\phi\rangle)$ and $\phi_x\mathscr{L}_{\langle E\phi\rangle}\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N}\mathscr{R}_{\langle E\phi\rangle}\phi_y$. Then by lemma 2.4, $\phi_{e_1}\phi_{e_2}\cdots\phi_{e_N} \in E\phi$. Therefore there exist an $z \in E$ such that $\phi_z = \phi_{e_1}\phi_{e_2}\cdots\phi_{e_N}$, so $\phi_x\mathscr{L}_{\langle E\phi\rangle}\phi_z\mathscr{R}_{\langle E\phi\rangle}\phi_y$ and hence

$$\phi_x\mathcal{L}\phi_z\mathcal{R}\phi_y$$

Thus, since ϕ^{-1} is a bimorphism, $x\mathcal{L}z\mathcal{R}y$, so that

$$\sigma^{\#}(x)\mathscr{L}_S\sigma^{\#}(z)\mathscr{R}_S\sigma^{\#}(y) \tag{12}$$

From (10), (11) and (12) we have $\sigma^{\#}(w)\mathscr{L}_S\sigma^{\#}(z)\mathscr{R}_S\sigma^{\#}(w)$. Thus $\sigma^{\#}(w)\mathscr{H}\sigma^{\#}(z)$. Since $\sigma^{\#}(w)$ and $\sigma^{\#}(z)$ are idempotents and no $\mathscr{H}$– class in a semigroup can contain more than one idempotent, we have $\sigma^{\#}(w) = \sigma^{\#}(z)$. Thus $z \in \sigma^{\#}(w)$. Hence the proof. □

Theorem 2.10. *The biordered set E is isomorphic to $E(F/\sigma^{\#})$, the biordered set of $F/\sigma^{\#}$.*

Proof. Let $e \in E$. Then $\sigma^{\#}(e) = \sigma^{\#}(ee) = \sigma^{\#}(e)$, so $\sigma^{\#}(e)$ is an idempotent. Define $\eta : E \longrightarrow E(F/\sigma^{\#})$ by $e \mapsto \eta_e = \sigma^{\#}(e)$. We show that η is a biordered set isomorphism on to $E(F/\sigma^{\#})$. For, let $(e, f) \in D_E$. Then either $e\omega^l f$ or $e\omega^r f$ or $f\omega^l e$ or $f\omega^r e$. Suppose $e\omega^l f$, then $e * f = e$, so

$$\eta_e\eta_f = \sigma^{\#}(e)\sigma^{\#}(f) = \sigma^{\#}(ef) = \sigma^{\#}(e * f) = \sigma^{\#}(e) = \eta_e$$

$\Rightarrow (\eta_e, \eta_f) \in D_{E(F/\sigma^{\#})}$. If $e\omega^r f$, then $f * e = e$, so

$$\eta_f\eta_e = \sigma^{\#}(f)\sigma^{\#}(e) = \sigma^{\#}(fe) = \sigma^{\#}(f * e) = \sigma^{\#}(e) = \eta_e$$

$\Rightarrow (\eta_e, \eta_f) \in D_{E(F/\sigma^\#)}$. Similarly we get the same for the other two cases. Also $(e, f) \in D_E \Rightarrow$

$$(e * f)\eta = \sigma^\#(e * f) = \sigma^\#(ef) = \sigma^\#(e)\sigma^\#(f) = \eta_e\eta_f$$

Therefore η is a bimorphism.

Now we prove that η is injective. For, let $e, f \in E$. If $\eta_e = \eta_f$, then $\sigma^\#(e) = \sigma^\#(f)$ implies $\phi_e = \phi_f$ by lemma **??**. Since ϕ is an isomorphism we have $e = f$. Thus η is an injective bimorphism from E to $E(F/\sigma^\#)$.

Now we show that $E\eta = E(F/\sigma^\#)$. For, let $\sigma^\#(w) \in E(F/\sigma^\#)$. We need to find some $e \in E$ such that $\sigma^\#(w) = \sigma^\#(e)$. However since $\sigma^\#(w)$ is an idempotent, by lemma **??**, it is sufficient to find an $e \in E$ such that $\sigma^\#(w)\mathscr{D}\sigma^\#(e)$. Let $w = e_1e_2\cdots e_n$. Since $\sigma^\#(w)$ is an idempotent, $(\sigma^\#(w))^n = \sigma^\#(w) \Rightarrow \sigma^\#(w^n) = \sigma^\#(w) \Rightarrow \sigma^\#((e_1e_2\cdots e_n)^n) = \sigma^\#(e_1e_2\cdots e_n)$. So there is a sequence of words $w_1, w_2, \ldots, w_N$ and transitions $T_k : w_k \mapsto w_{k+1}$ for $k = 1, 2, \ldots, N-1$, where $w_1 = e_1e_2\cdots e_n$ and $w_N = (e_1e_2\cdots e_n)^n$.

The main idea in what follows is to cover w_k, for $k = 1, 2 \ldots, N$, by subwords $w_k^1, w_k^2, \ldots w_k^n$ (defined below), such that $\sigma^\#(w_k^i)$ lies in some $\mathscr{D}$ class of an element of $E\eta$. By an inductive definition we can locate particular subwords by noting positions of letters from 1 upto $l(w_k)$. Define, for $i = 1, 2 \ldots, n$ $\alpha_1^i = \beta_1^i = \gamma_1^i = i$. For each i, make the following definition, inductive in the subscripts:

$$\beta_{k+1}^i = \begin{cases} \beta_k^i & \text{if} \quad T_k : ufgv \mapsto uf * gv \text{ where } l(u) \geq \beta_k^i - 1 \\ & \text{or} \quad T_k : uf * gv \mapsto ufgv \text{ where } l(u) \geq \beta_k^i \\ & \quad \text{or } l(u) = \beta_k^i - 1 \text{ and } T_k \text{ is of type(1)} \\ \beta_k^i - 1 & \text{if} \quad T_k : ufgv \mapsto uf * gv \text{ where } l(u) \leq \beta_k^i - 2 \\ \beta_k^i + 1 & \text{if} \quad T_k : uf * gv \mapsto ufgv \text{ where } l(u) \leq \beta_k^i - 2 \\ & \quad \text{or } l(u) = \beta_k^i - 1 \text{ and } T_k \text{ is of type (2)} \end{cases}$$

$$\alpha^i_{k+1} = \begin{cases} \alpha^i_k & \text{if} \quad T_k : ufgv \mapsto uf * gv \text{ where } l(u) \geq \alpha^i_k - 1 or l(u) = \alpha^i_k - 2, \\ & \quad \alpha^i_k < \beta^i_k \text{ and } T_k \text{ is of type (1)} \\ & \text{or} \quad T_k : uf * gv \mapsto ufgv \text{ where } l(u) \geq \alpha^i_k - 1 \\ \alpha^i_k - 1 & \text{if} \quad T_k : ufgv \mapsto uf * gv \text{ where } l(u) \leq \alpha^i_k - 3 \\ & \quad \text{or } l(u) = \alpha^i_k - 2 \text{ and either } \alpha^i_k = \beta^i_k \text{ or } T_k \text{ is of type (2)} \\ \alpha^i_k + 1 & \text{if} \quad T_k : uf * gv \mapsto ufgv \text{ where } l(u) \leq \alpha^i_k - 2 \end{cases}$$

$$\gamma^i_{k+1} = \begin{cases} \gamma^i_k & \text{if} \quad T_k : ufgv \mapsto uf * gv \text{ where } l(u) \geq \gamma^i_k \\ & \quad \text{or } l(u) = \gamma^i_k - 1 \text{ and either } \gamma^i_k = \beta^i_k \\ & \quad \text{or } T_k \text{ is of type(1)} \\ & \text{or} \quad T_k : uf * gv \mapsto ufgv \text{ where } l(u) \geq \gamma^i_k \\ \gamma^i_k - 1 & \text{if} \quad T_k : ufgv \mapsto uf * gv \text{ where } l(u) \leq \gamma^i_k - 2 \\ & \quad \text{or } l(u) = \gamma^i_k - 1, \beta^i_k < \gamma^i_k \text{ and } T^i_k \text{ is of type (1)} \\ \gamma^i_k + 1 & \text{if} \quad T_k : uf * gv \mapsto ufgv \text{ where } l(u) \leq \gamma^i_k - 1 \end{cases}$$

From the above definitions for $k = 1, \ldots, N$, $\beta^1_k \leq \beta^2_k \leq \ldots \leq \beta^n_k$ and for each $i = 1, \ldots, n$, $\alpha^i_k \leq \beta^i_k \leq \gamma^i_k$. For integers i and j where $i \leq j$, let $[i, j]$ denote all integers from i upto j. Then for each $k = 1$ to N

$$[1, l(w_k)] = \bigcup_{i=1}^{n} [\alpha^i_k, \gamma^i_k]$$

Let e^i_k denote the β^i_k th letter of w_k and w^i_k denote the subword of w_k obtained by deleting all the letters to the left of the α^i_k th letter and to the right of the γ^i_kth letter. Then w_k is covered by the subwords $w^1_k, w^2_k, \ldots, w^n_k$. In particular w_N is covered by $w^1_N, w^2_N, \ldots, w^n_N$.

We now claim that for some i, $e_1 e_2 \cdots e_n$ is a subword of w^i_N. For, suppose this statement is false. Then w^i_N does not cover $e_1 e_2 \cdots e_n$ for all i. Thus w^1_N does not

cover $e_1e_2\cdots e_n$. Make the inductive hypothesis that $w_N^1, w_N^2, \ldots, w_N^i$ do not cover $(e_1e_2\cdots e_n)^i$. Then since w_N^{i+1} does not cover $e_1e_2\cdots e_n$, we have $w_N^1, w_N^2, \ldots, w_N^{i+1}$ do not cover $(e_1e_2\cdots e_n)^{i+1}$. By induction $w_N^1, w_N^2, \ldots, w_N^n$ do not cover $(e_1e_2\cdots e_n)^n = w_N$, contradicting the above paragraph. Hence our claim must be true. Thus for some $i, e_1e_2\cdots e_n$ is a subword of w_N^i.

Now since $\alpha_k^i \leq \beta_k^i \leq \gamma_k^i$, each w_k^i can be written in the form $w_k^i = u_k^i e_k^i v_k^i$ for some words (possibly empty) u_k^i and v_k^i. We prove, for each i and k

$$\sigma^{\#}(e_k^i)\mathscr{R}\sigma^{\#}(e_k^i v_k^i) \tag{13}$$

and

$$\sigma^{\#}(e_k^i)\mathscr{L}\sigma^{\#}(u_k^i e_k^i) \tag{14}$$

We prove (13) by induction on k. For $k = 1$, we have $w_1^i = e_i$ for each i, so (13) holds. Suppose (13) holds for k. We show (13) holds for $k+1$. The only cases for T_k we need consider are the following:

(a) $u'\underbrace{uf e_k^i v}_{w_k^i} v' \mapsto u'\underbrace{uf * e_k^i v}_{w_{k+1}^i} v'$

(b) $u' f \underbrace{e_k^i v}_{w_k^i} v' \mapsto u'\underbrace{f * e_k^i v}_{w_{k+1}^i} v'$

(c) $u'\underbrace{ue_k^i f v}_{w_k^i} v' \mapsto u'\underbrace{ue_k^i * f v}_{w_{k+1}^i} v'$

(d) $u'\underbrace{ue_k^i f}_{w_k^i} v \mapsto u'\underbrace{ue_k^i * f}_{w_{k+1}^i} v$

(e) $u'\underbrace{ue_k^i v f}_{w_k^i} g v' \mapsto \begin{cases} u'\underbrace{ue_k^i v f * g}_{w_{k+1}^i} v' & \text{of type (1)} \\ u'\underbrace{ue_k^i v}_{w_{k+1}^i} f * g v' & \text{of type (2)} \end{cases}$

(f) $u'\underbrace{ue_k^i v}_{w_k^i}v' \mapsto u'\underbrace{ufgv}_{w_{k+1}^i}v'$ where $e_k^i = f * g$.

case (a) Here $v_k^i = v$. Since $l(u'u) = \beta_k^i - 2$, by definition of $\beta_{k+1}^i, \beta_{k+1}^i = \beta_k^i - 1$, so $e_{k+1}^i = f * e_k^i$ and $v_{k+1}^i = v$. Since (13) holds for k, we have $\sigma^{\#}(e_k^i)\mathscr{R}\sigma^{\#}(e_k^i v_k^i) = \sigma^{\#}(e_k^i v)$. Since $\mathscr{R}$ is a left congruence, we have, $\sigma^{\#}(fe_k^i)\mathscr{R}\sigma^{\#}(fe_k^i v)$, yielding $\sigma^{\#}(e_{k+i}^i)\mathscr{R}\sigma^{\#}(e_{k+1}^i v_{k+1}^i)$. Hence (13) holds for $k+1$ in this case.

case (b) Here $v_k^i = v$. Since $l(u') = \beta_k^i - 2$, by definition of $\beta_{k+1}^i, \beta_{k+1}^i = \beta_k^i - 1$, so $e_{k+1}^i = f * e_k^i$ and $v_{k+1}^i = v$. Then as in case(a) (13) holds for $k+1$.

case (c) Here $v_k^i = fv$. Since $l(u'u) = \beta_k^i - 1$, by definition of $\beta_{k+1}^i, \beta_{k+1}^i = \beta_k^i$, so $e_{k+1}^i = e_k^i * f$ and $v_{k+1}^i = v$. Since(13) holds for k, we have

$$\sigma^{\#}(e_k^i)\mathscr{R}\sigma^{\#}(e_k^i fv) \tag{15}$$

$$\Rightarrow \sigma^{\#}(e_k^i)\mathscr{R}\sigma^{\#}(e_k^i f) = \sigma^{\#}(e_k^i * v) = \sigma^{\#}(e_{k+1}^i)$$

$$\Rightarrow \sigma^{\#}(e_k^i)\mathscr{R}\sigma^{\#}(e_{k+1}^i) \tag{16}$$

From (15) and (16) we have $\sigma^{\#}(e_{k+1}^i)\mathscr{R}\sigma^{\#}(e_k^i fv) = \sigma^{\#}(e_k^i * fv) = \sigma^{\#}(e_{k+1}^i v_{k+1}^i)$. Hence (13) holds in this case.

case (d) Since $l(u'u) = \beta_k^i - 1$, by definition of $\beta_{k+1}^i, \beta_{k+1}^i = \beta_k^i$, so $e_{k+1}^i = e_k^i * f$ and $v_{k+1}^i = 1$, the empty word. Then clearly (13) holds for $k+1$.

case (e) (i)

$$u'\underbrace{ue_k^i vf}_{w_k^i}gv' \mapsto u'\underbrace{ue_k^i vf * g}_{w_{k+1}^i}v' \text{ of type (1)}$$

Here $v_k^i = vf$. Since $l(u'ue_k^i v) = \beta_k^i + 2 > \beta_k^i - 2, \beta_{k+1}^i = \beta_k^i$, so $e_{k+1}^i = e_k^i$ and $v_{k+1}^i = vf * g$. Since T_k is of type (1) either $f\omega^l g$ or $f\omega^r g$. In both case, we have $f\mathcal{R}f * g$, so

$\sigma^{\#}(f*g)\mathscr{R}\sigma^{\#}(f)$

$\Rightarrow \sigma^{\#}(e_k^i vf * g)\mathscr{R}\sigma^{\#}(e_k^i vf)$, since $\mathscr{R}$ is a left congruence.

$\Rightarrow \sigma^{\#}(e_{k+1}^i v_{k+1}^i)\mathscr{R}\sigma^{\#}(e_k^i vf)\mathscr{R}\sigma^{\#}(e_k^i) = \sigma^{\#}(e_{k+1}^i)$.

Thus $\sigma^{\#}(e_{k+1}^i v_{k+1}^i)\mathscr{R}\sigma^{\#}(e_{k+1}^i)$ in this case.

(ii)

$$u'\underbrace{ue_k^i vf}_{w_k^i}gv' \mapsto u'\underbrace{ue_k^i v}_{w_{k+1}^i} f*gv' \text{ of type (2)}$$

Here $v_k^i = vf$, $e_{k+1}^i = e_k^i$ and $v_{k+1}^i = v$.

$\sigma^{\#}(e_{k+1}^i v_{k+1}^i) = \sigma^{\#}(e_k^i v)\mathscr{R}\sigma^{\#}(e_k^i) = \sigma^{\#}(e_{k+1}^i)$. Hence (13) holds in this case.

case (f) Here $v_k^i = v$

(i) Suppose T_k is of type (1). Since $l(u'u) = \beta_k^i - 1$, and T_k is type of(1), $\beta_{k+1}^i, \beta_{k+1}^i = \beta_k^i$, $e_{k+1}^i = f$ and $v_{k+1}^i = gv$. Since (13) holds for k,

$\sigma^{\#}(e_k^i)\mathscr{L}\sigma^{\#}(e_k^i)$

$\Rightarrow \sigma^{\#}(e_k^i)\mathscr{R}\sigma^{\#}(e_k^i)$

$\Rightarrow \sigma^{\#}(f*gv)\mathscr{R}\sigma^{\#}(e_k^i)$, since $e_k^i = f*g$

$\Rightarrow \sigma^{\#}(fgv)\mathscr{R}\sigma^{\#}(e_k^i)$

$$\Rightarrow \sigma^{\#}(e_{k+1}^i v_{k+1}^i)\mathscr{R}\sigma^{\#}(e_k^i) \tag{17}$$

Also since T_k is of type (1), we have $f\mathscr{R}f*g$, so

$$\sigma^{\#}(f)\mathscr{R}\sigma^{\#}(f*g) \Rightarrow \sigma^{\#}(e_{k+1}^i)\mathscr{R}\sigma^{\#}(e_k^i) \tag{18}$$

From (17) and (18)we have $\sigma^{\#}(e_{k+1}^i)\mathscr{R}\sigma^{\#}(e_{k+1}^i v_{k+1}^i)$.

(*ii*) Suppose T_k is of type (2). Since $l(uu') = \beta_k^i - 1$ and T_k is of type (2), $\beta_{k+1}^i = \beta_k^i + 1$. So $e_{k+1}^i = g$ and $v_{k+1}^i = v$. Since T_k is type (2), either $g\omega^l f$ or $g\omega^r f$. In both case $g\mathcal{L}f*g$, so $g\mathcal{L}e_k^i$. Therefore

$\sigma^{\#}(e_{k+1}^i v_{k+1}^i) = \sigma^{\#}(gv) = \sigma^{\#}(ge_k^i v)$.

Since $\sigma^{\#}(e_k^i)\mathscr{R}\sigma^{\#}(e_k^i v)$ and $\mathscr{R}$ is a left congruence, $\sigma^{\#}(ge_k^i)\mathscr{R}\sigma^{\#}(ge_k^i v) = \sigma^{\#}(e_{k+1}^i v_{k+1}^i)$. So $\sigma^{\#}(e_{k+1}^i v_{k+1}^i)\mathscr{R}\sigma^{\#}(ge_k^i) = \sigma^{\#}(g) = \sigma^{\#}(e_{k+1}^i)$. Hence $\sigma^{\#}(e_{k+1}^i)\mathscr{R}\sigma^{\#}(e_{k+1}^i v_{k+1}^i)$ in this case.

Thus (13) follows by induction. Similarly we can prove (14). Hence (13) and (14) holds for every i and k. In particular we have,

$$\sigma^{\#}(e_N^i)\mathscr{R}\sigma^{\#}(e_N^i v_N^i) \tag{19}$$

$$\sigma^{\#}(e_N^i)\mathscr{L}\sigma^{\#}(u_N^i e_N^i) \tag{20}$$

Since $\mathscr{R}$ is a left congruence (19) implies

$$\sigma^{\#}(u_N^i e_N^i)\mathscr{R}\sigma^{\#}(u_N^i e_N^i v_N^i) = \sigma^{\#}(w_N^i) \tag{21}$$

(20) and (21) implies

$$\sigma^{\#}(e_N^i)\mathscr{D}\sigma^{\#}(w_N^i) \tag{22}$$

Now w_N^i is a subword of $w_N = (e_1e_2\cdots e_n)^n$. We proved that, for some i, $(e_1e_2\cdots e_n)$ is a subword of w_N^i. Therefore, for some $i, j, k\alpha$ and β we have,

$$w_N^i = e_j e_2\cdots e_n^n(e_1e_2\cdots e_n)^{\alpha}(e_1e_2\cdots e_n)(e_1e_2\cdots e_n)^{\beta}e_1e_2\cdots e_k$$

$$\begin{aligned}\sigma^{\#}(w_N^i) &= \sigma^{\#}(e_je_2\cdots e_n(e_1e_2\cdots e_n)^{\alpha}e_1e_2\cdots e_n(e_1e_2\cdots e_n)^{\beta}e_1e_2\cdots e_k)\\ &= \sigma^{\#}(e_je_2\cdots e_n(e_1e_2\cdots e_n)^{\alpha+\beta+1}e_1e_2\cdots e_k)\\ &= \sigma^{\#}(e_je_2\cdots e_n)(\sigma^{\#}(e_1e_2\cdots e_n))^{\alpha+\beta+1}\sigma^{\#}(e_1e_2\cdots e_k)\\ &= \sigma^{\#}(e_je_2\cdots e_n)\sigma^{\#}(e_1e_2\cdots e_n)\sigma^{\#}(e_1e_2\cdots e_k),\end{aligned}$$

since $\sigma^{\#}(e_1e_2\cdots e_n)$ is idempotent.

Thus

$$\sigma^{\#}(w_N^i) = \sigma^{\#}(e_j\cdots e_ne_1e_2\cdots e_ne_1e_2\cdots e_k)\mathscr{R}\sigma^{\#}(e_j\cdots e_ne_1\cdots e_n)\mathscr{L}\sigma^{\#}(e_1e_2\cdots e_n)$$

That is

$$\sigma^{\#}(w_N^i)\mathscr{D}\sigma^{\#}(e_1e_2\cdots e_n) \tag{23}$$

From (22) and (23) we have $\sigma^{\#}(e_1e_2\cdots e_n)\mathscr{D}\sigma^{\#}(e_N^i)$. Put $e = e_N^i$, we get

$\sigma^{\#}(e_1e_2\cdots e_n)\mathscr{D}\sigma^{\#}(e)$ for some letter e. Hence $\sigma^{\#}(w)\mathscr{D}\sigma^{\#}(e)$. Therefore by lemma **??**, $\sigma^{\#}(w) \in E\eta$. Thus $E\eta = E(F/\sigma^{\#})$ and so η is an injective bimorphism onto $E(F/\sigma^{\#})$. Hence E is isomorphic $E(F/\sigma^{\#})$. □

Remark 2.11. *From the theorem* **??** *we get every biordered set E is isomorphic to the biordered set of some semigroup. That is every biordered set arises as the biordered set of some semigroup.*

3 Free Idempotent Generated Semigroups

Let E be a biordered set. The collection of all idempotent generated semigroups, whose biordered set of idempotents is isomorphic to E forms a category when one restricts morphisms to those that are one to one when restricted to the set of idempotents. We now prove that the semigroup $F/\sigma^{\#}$ is a free object in this category. That is, if T is an idempotent generated semigroup and $\alpha : E \longrightarrow E(T)$ is a biordered set isomorphism then α extends to a homomorphism of $F/\sigma^{\#}$ to T.

Theorem 3.1. *$F/\sigma^{\#}$ is a free object in the category of all idempotent generated semigroups, whose biordered set of idempotents is isomorphic to E.*

Proof. Let $e \in E$. Then $\sigma^{\#}(e)\sigma^{\#}(e) = \sigma^{\#}(ee) = \sigma^{\#}(e)$, so $\sigma^{\#}(e)$ is an idempotent. Thus for every $e \in E, \sigma^{\#}(e)$ is an idempotent in $F/\sigma^{\#}$. Let $\sigma^{\#}(w) \in F/\sigma^{\#}$. Then $w = e_1e_2\cdots e_n$ for $e_1, e_2, \ldots, e_n \in E$. So $\sigma^{\#}(w) = \sigma^{\#}(e_1e_2\cdots e_n) = \sigma^{\#}(e_1)\sigma^{\#}(e_2)\cdots\sigma^{\#}(e_n)$, where each $\sigma^{\#}(e_i)$ is an idempotent. Hence $F/\sigma^{\#}$ is an idempotent generated semigroup. Also by the theorem **??**, $E(F/\sigma^{\#})$ is isomorphic to E. Thus $F/\sigma^{\#}$ is an object in the category.

Let $\eta : E \longrightarrow F/\sigma^{\#}$ be the map defined by $e \mapsto \sigma^{\#}(e)$. From the proof of the theorem **??**, η is a biordered set isomorphism on to $E(F/\sigma^{\#})$. Suppose T is an idempotent generated semigroup such that $E(T)$ is isomorphic to E. Suppose $\alpha : E \longrightarrow T$ be a map which is a biordered set isomorphism on to $E(T)$. We can

define a homomorphism $\hat{\alpha} : F \longrightarrow T$ by

$$(e_1e_2\cdots e_n)\hat{\alpha} = (e_1\alpha)(e_2\alpha)\cdots(e_n\alpha).$$

Let $(a,b) \in \sigma$. Then $a = fg, b = f * g$, for some $(f,g) \in D_E$ and so $a\hat{\alpha} = (fg)\hat{\alpha} = (f\alpha)(g\alpha)$ and $b\hat{\alpha} = (f*g)\hat{\alpha} = (f*g)\alpha = (f\alpha)(g\alpha)$, since α is a bimorphism. Therefore $a\hat{\alpha} = b\hat{\alpha} \Rightarrow (a,b) \in ker\hat{\alpha}$, where $ker\hat{\alpha} = \{(a,b) : a\hat{\alpha} = b\hat{\alpha}\}$. Since $ker\hat{\alpha}$ is a congruence, we have $\sigma^{\#} \subset Ker\hat{\alpha}$. Define $\bar{\alpha} : F/\sigma^{\#} \longrightarrow T$ by, for $w = e_1e_2\cdots e_n$

$$(\sigma^{\#}(w)) = (e_1\alpha)(e_2\alpha)\cdots(e_n\alpha)$$

For $w = \epsilon_1\epsilon_2\cdots\epsilon_n$ and $w' = \epsilon'_1\epsilon'_2\cdots\epsilon'_m$, $(\sigma^{\#}(w)\sigma^{\#}(w'))\bar{\alpha} = (\sigma^{\#}(w)\bar{\alpha})(\sigma^{\#}(w')\bar{\alpha}$ and

$\sigma^{\#}(w) = \sigma^{\#}(w')$

$\Rightarrow (w,w') \in \sigma^{\#}$

$\Rightarrow (w,w') \in ker\hat{\alpha}$

$\Rightarrow w\hat{\alpha} = w'\hat{\alpha}$

$\Rightarrow (e_1e_2\cdots e_n)\hat{\alpha} = (e'_1e'_2\cdots e'_m)\hat{\alpha}$

$\Rightarrow (e_1\alpha)(e_2\alpha)\cdots(e_n\alpha) = (e'_1\alpha)(e'_2\alpha)\cdots(e'_m\alpha)$

$\Rightarrow (\sigma^{\#}(w))\bar{\alpha} = (\sigma^{\#}(w'))\bar{\alpha}$

Hence $\bar{\alpha}$ is a well defined homomorphism.

Let $\sigma^{\#}(w)$ be an idempotent in $F/\sigma^{\#}$. Then since the map $e \mapsto \sigma^{\#}(e)$ is an isomorphism on to $E(F/\sigma^{\#}), \sigma^{\#}(w) = \sigma^{\#}(e)$ for some $e \in E$. So

$$\begin{aligned}(\sigma^{\#}(w)\bar{\alpha})(\sigma^{\#}(w)\bar{\alpha}) &= (\sigma^{\#}(e)\bar{\alpha})(\sigma^{\#}(e)\bar{\alpha})\\ &= (e\alpha)(e\alpha)\\ &= (e*e)\alpha\\ &= e\alpha, \text{ since } \alpha \text{ is a bimorphism}\\ &= \sigma^{\#}(e)\bar{\alpha}\\ &= \sigma^{\#}(w)\bar{\alpha}\end{aligned}$$

There fore $\sigma^{\#}(w)\bar{\alpha}$ is an idempotent. Thus $\bar{\alpha}$ maps $E(F/\sigma^{\#})$ in to $E(T)$. Also, for

two idempotents $\sigma^{\#}(e)$ and $\sigma^{\#}(e')$,

$\sigma^{\#}(e)\bar{\alpha} = \sigma^{\#}(e')\bar{\alpha}$

$\Rightarrow e\alpha = e'\alpha$

$\Rightarrow e = e'$, since α is an isomorphism

$\Rightarrow \sigma^{\#}(\epsilon) = \sigma^{\#}(e')$.

That is α is one-one, when restricted to idempotents. Hence $\bar{\alpha}$ is a morphism in the category.

Also $(e)\eta\bar{\alpha} = (e\eta)\bar{\alpha} = \sigma^{\#}(e)\bar{\alpha} = e\alpha$. Therefore $\eta\bar{\alpha} = \alpha$. Thus there is a morphism $\bar{\alpha} : F/\sigma^{\#} \longrightarrow T$ such that $\eta\bar{\alpha} = \alpha$.

To prove the uniqueness, suppose $\beta : F/\sigma^{\#} \longrightarrow T$ be a morphism such that $\eta\beta = \alpha$. Then

$$\begin{aligned}
(\sigma^{\#}(w)\bar{\alpha})\beta &= (\sigma^{\#}(e_1e_2\cdots e_n)\beta) \\
&= (\sigma^{\#}(e_1)\sigma^{\#}(e_2)\cdots\sigma^{\#}(e_n))\beta \\
&= (\sigma^{\#}(e_1)\beta)(\sigma^{\#}(e_2)\beta)\cdots(\sigma^{\#}(e_n)\beta) \\
&= (e_1\eta\beta)(e_2\eta\beta)\cdots(e_n\eta\beta) \\
&= (e_1\alpha)(e_2\alpha)\cdots(e_n\alpha) \\
&= \sigma^{\#}(w)\bar{\alpha}
\end{aligned}$$

There fore $\beta = \bar{\alpha}$. Thus $\bar{\alpha}$ is unique and hence $F/\sigma^{\#}$ is free on E. □

Corollary 3.2. *Any free object on E in the category of all idempotent generated semigroups, whose biordered set of idempotents is isomorphic E has the presentation:*

$$\langle E : fg = f * g, (f, g) \in D_E \rangle$$

Proof. Let F_1 be any free object on E. Then , $F/\sigma^{\#}$ is a free object on E. Then F_1 is isomorphic to $F/\sigma^{\#}$. Then, since F is the free semigroup on E and $\sigma = \{fg, f * g) : (f, g) \in D_E\}$,

$$F_1 = \langle E : fg = f * g, (f, g) \in D_E \rangle$$

Hence the proof. □

Definition 3.3. *The free idempotent generated semigroup over a biordered set E is defined as a free object in the category of all idempotent generated semigroups, whose biordered set of idempotents is isomorphic E. It is denoted by $IG(E)$*

By the corollory ?? $IG(E)$ is the semigroup defined by the following presentation:

$$IG(E) = \langle E : fg = f * g, (f, g) \in D_E \rangle$$

Example 3.4. *Consider the biordered set $E = \{f, g\}$ with the partial binary operation $f * f = f, g * g = g$ and $D_E = \{(f, f), (g, g)\}$. Then*

$$\begin{aligned} IG(E) &= \langle E : fg = f * g, (f, g) \in D_E \rangle \\ &= \langle f, g : ff = f, gg = g \rangle \end{aligned}$$

Canonical forms of words of $IG(E)$ are of the form;

$$fgfg\cdots f \text{ or } fgfg\cdots g \text{ or } gfgf\cdots g \text{ or } gfgf\cdots f.$$

It is the free product of the singleton semigroups $\{f\}$ and $\{g\}$. $IG(E)$ is an infinite semigroup. We prove that $IG(E)$ is not a regular semigroup. For, suppose $IG(E)$ is regular. Then every element in $IG(E)$ is regular. In particular fg is regular, so there exist an element x in $IG(E)$ such that $fgxfg = fg$. But the length of the reduced word in the LHS is at least four and the length of the word in the RHS is two, which is not possible. There fore $IG(E)$ is not a regular semigroup.

Example 3.5. *Consider the biordered set $E = \{f, g\}$ with the partial binary operation $f * f = f, g * g = g, f * g = g, g * f = f$ and*
$D_E = \{(f, f), (g, g), (f, g), (g, f)\}$. Then

$$\begin{aligned} IG(E) &= \langle E : fg = f * g, (f, g) \in D_E \rangle \\ &= \langle f, g : ff = f, gg = g, fg = g, gf = f \rangle \\ &= \{f, g\} \end{aligned}$$

$IG(E)$ is finite and regular.

Example 3.6. *Let E be a biordered set such that $D_E = E \times E$. Then every word $w = e_1 e_2 \cdots e_n$ in F reduced to a letter $e \in E$. So $F/\sigma^{\#} = \{\sigma(e), e \in E\}$ can be identified with E. Thus $IG(E) = E$.*

Example 3.7. *Consider the biordered set $E = \{a, b, c, d\}$ with the partial binary operation*

$a * a = a, b * b = b, c * c = c, d * d = d$

$a * b = b, b * a = a, c * d = d, d * c = c$

$a * c = a, c * a = c, b * d = b, d * b = d$

and

$D_E = \{(a,a),(b,b),(c,c),(d,d),(a,b)(b,a)(c,d)(d,c)(a,c)(c,a)(b,d)(d,b)\}$

$$\begin{aligned} IG(E) &= \langle E : fg = f * g, (f,g) \in D_E \rangle \\ &= \langle a, b, c, d : aa = a, bb = b, cc = c, dd = d, ab = b, ba = a, dc = c, \\ &\qquad ac = a, ca = c, bd = b, df = d \rangle \end{aligned}$$

Canonical forms of words in $IG(E)$ are of the form;

$$adad \cdots a \text{ or } adad \cdots d \text{ or } dada \cdots d \text{ or } dada \cdots a \text{ or}$$

$$bcbc \cdots b \text{ or } bcbc \cdots c \text{ or } cbcb \cdots c \text{ or } cbcb \cdots b$$

$IG(E)$ is an infinite semigroup. We prove that $IG(E)$ is a regular semigroup. For, let x be an element in $IG(E)$. If $x = adad \cdots ad$ of length n, then by letting $y = cbcb \cdots c$ of length $n-1$ we get $xyx = x$. If $x = adad \cdots a$ of length n, then by letting $y = bcbc \cdots bc$ of length $n-1$ we get $xyx = x$. Similarly for the other canonical forms of x we get an element y such that $xyx = x$. Hence $IG(E)$ is a regular semigroup.

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