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Editorial

The rapid developments in science and technology and the impacts of globalization are posing challenges to the education system in the country. Although the advancement in Science and technology has improved the physical quality of human life and has come to dominate every sphere of human activity, development without virtues has been posing threat to humanity and challenges to its ethical foundations. "Journal of Current Studies", a journal dedicated to promote and publish original articles in the relevant fields and aims to reduce the gap between research and practice, provides a solid forum to discuss developments in science and humanities and literature, and its impact on modern society; contributing to the progress and extent of knowledge in various disciplines. The journal analyses the implications of science policies, evaluates the environmental issues involved in the application of technology without human face and suggest alternatives. It also provides opportunity for academics to interact and evolve sustainable developmental strategies for a better society.

Research and publication of research results is one of the most important areas which are crucial to any institute of higher education. It is thus with great pleasure and gratitude, S.N.M. College, Maliankara is presenting the 5th issue of our Inter disciplinary / multi disciplinary research journal. The journal's scope is to facilitate the researchers, scholars, resource persons, post graduate students in universities / colleges and other centres of research and practitioners to come on a platform and to share their findings of the research with the rest of the world so that informed decisions can be taken to improve businesses and societies as a whole. Twenty regular research papers in various disciplines are included in this volume which represents the volume 5, issue 1, December 2015.

Authors are encouraged to submit complete unpublished and original works, which are not under review in any other journals. Research papers, short communications, review articles, books reviews and professional news items in all areas of Science, Social Science, English language and literature will be published. The journal insists strict guidelines for papers submitted for publication. Therefore, it is highly necessary that in future, research papers are to be submitted sufficiently earlier for the timely publication of the journal. Manuscripts submitted strictly in accordance with the style prescribed shall only be accepted for publication.

Looking forward to the future we can assure that the journal will continue to deliver the best of recent developments in different disciplines and publish good quality findings of high significance and relevance. On this happy occasion I wish to express my sincere appreciation to research & Journal committee for their enthusiastic support and co-operation to this academic venture. I also extend sincere appreciation of the College Management and the Principal, to the valued readers and authors for their continued interest in JCS, and to every member of the editorial board to this scientific endeavour. We further gratefully acknowledge the enthusiasm and support of the college PTA who provided the financial support for the publication of the journal.

We also welcome valuable suggestions and criticisms of the readers for improvement and augmentation in this regard.

With warm regards

Dr. Jeeju P P
Chief Editor

Contents

EFFECT OF ECDYSTEROID RICH PLANT EXTRACTS ON *BOMBYX MORI* L. –A FIELD STUDY

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Abstract

Sericulture is an art and science of rearing silkworms for silk production. India with its wide variety of silk secreting fauna has the unique distinction as the producer of all the five commercially traded natural silk varieties. In insects the moults and metamorphosis are initiated and coordinated by the interplay of juvenile hormone (JH) and moulting hormone (MH). MH extracts from plants are found to reduce and synchronise the maturation process in Bombyx mori L. Bioprospection of the regional flora led to the isolation of large quantities of plant extracts rich in MH. Based on earlier literature, field level experiments were conducted to test the effect of JH and MH on bivoltine double hybrids FC_1XFC_2. MH isolated from the leaves of Diploclisia glaucescens (Blume) Diels and Coscinium fenestratum (Gaertn.) Colebr collected from Wayanad District, Kerala were used in sericulture for the first time. They brought about synchronisation and significant reduction in maturation time of silkworms. This brings about decrease of labour in mounting and in case of shortage of mulberry leaves complete crop loss may be avoided. It was found that concentration range, geographical regime and time of application are very important in the use of MH.

Keywords: Plant extracts- -moulting hormone- sericulture.

Introduction

The process of moulting and metamorphosis, characteristic to larval growth and development in insects, are controlled by are circulating hormones like juvenile hormone (JH) and moulting hormone (MH) (Wigglesworth, 1985). Ecdysteroids (MH) regulate the time and onset of moulting, while JH determines whether it is larval to larval or from larval to pupal (Sehnal, 1989; Riddiford ,1994). When the threshold JH level to retain the larval features diminishes in the haemolymph below the normal level, the larvae prepares to metamorphose into pupa itself (Nair *et al*., 2003). In China, various plant extracts rich in ecdysteroids are used in the last instar stage of *Bombyx mori* L. for fastening and synchronisation of maturation process (Chow and Lu, 1980). Such studies were totally lacking in India till last decade, but since then some serious attempts have been made in this regard and some plants containing ecdysteroids have been identified (Nair *et al*., 2010). Judicious use of plant extracts towards

the end of last instar stage reduces the labour involved in mounting and help sericulture farmers rescue the crop in case of acute leaf shortage. Ecdysteroid rich extracts were isolated from *Diploclisia glaucescens* (Blume) Diels and *Coscinium fenestratum* (Gaertn.) Colebr collected from Wayanad District, Kerala in considerable amounts. The presence of ecdysterone from *Coscinium* is a new report. Phytoecdysteroid rich extracts from these plants were used in sericulture for the first time on bivoltine di hybrids (FC_1 X FC_2) in field conditions. Reduction in mounting and decline in economic parameters due to phyto ecdysteroid use were recorded. Water extracts of *Diploclisia and Coscinium* containing ecdysteroids were found to be equally good as isolated compound. The plant extracts after enriching with ecdysterone were standardised using HPLC-DAD for the first time.

Material and methods

1. Isolation of ecdysterone from *Diploclisia glaucescens* (Blume) Diels.

The *Diploclisia glaucescens* (Blume) Diels specimen was collected from Kalpetta, ($11^0$59'43" North, $76^0$09'43"East), Wayanad district, Kerala in the month of March 2011. The material was identified with the help of floras and a voucher specimen was submitted in the S.N.M.College Herbarium. 100 grams of leaves were put to sequential extraction with solvents of increasing polarity starting from petroleum ether and ecdysterone positive fractions were obtained in ethyl methyl ketone (MEK) and methanol (MeOH) fractions. MEK and MeOH fractions were put to Column Chromatography and pure white crystals of ecdysterone was obtained from ecdysterone positive fractions. The ecdysterone was later characterised by TLC, HPLC, UV spectroscopy, IR spectroscopy and LC-MS and was found to be more than 98 % pure. The isolated sample was comparable with the standard (Sigma).

2. Rearing of silk worms

A farmer named Sasi (General Secretary, Kerala Sericulture Farmers Association) from Kuthanoor panchayath in Palakkad district Kerala, who had a track record of more than twenty years in sericulture was selected for the present study. The present study was conducted in the month of November 2012 in his well maintained field. Bivoltine double hybrids (FC_1 x FC_2) were brought in the second instar stage from Chawki rearing centre, and grown in field conditions. Temperature was maintained at 23±3^{o}C and humidity conditions were adjusted to 75±5 % relative humidity. 12 hours day/ night period was available during the study period. Mulberry leaves of Victory 1 genotype from a periodically watered garden was fed liberally three times a day.

3. Ecdysterone (MH) preparation and application

A stock solution of 10mg ecdysterone in 100 ml water was prepared. Three concentrations 10, 20 and 30 ppm of ecdysterone respectively

were prepared in water from this stock solution. Thirty larvae each were taken out which were similar in size on the sixth day of fifth instar stage just before the onset of spinning and grown in aerated trays of size (2 feet x 1 feet). Each concentration groups were taken in triplicate. Twenty ml of ecdysterone (MH) solution for each concentration were sprayed on to equal quantity by weight (20 g) of fresh V1 mulberry leaves. The sprayed leaves were allowed to dry up for half an hour and after that fed to larvae as last feed. Medium and absolute controls were maintained in parallel to compare the results. The medium control was treated with an equal quantity of solution with out ecdysterone, while the absolute control was given leaves without any treatment.

4. Preparation of water extracts and positive controls.

Two plants *Diploclisia glaucescens* (Blume) Diels (DG) and *Coscinium fenestratum* (Gaertn.) Colebr(CS) which proved to be good sources for ecdysterone from our early study were selected for the study. 10 gram dried leaves each of Diploclisia and *Coscinium* were weighed in a balance. Leaves were powdered separately to medium sized particles in a blender and were refluxed with 100 ml water each in round bottomed flasks for 1 hour. The extracts were collected and filtered separately and were made up to a constant volume (75 ml). 1 ml each of the extract was centrifuged and the supernatant was taken for HPLC. HPLC profile of the extracts was monitored for ecdysterone absorbance (Figure 1). 10 mg of pure ecdysterone isolated from *Diploclisia* in 100ml water was taken as positive control for the experiment. The HPLC profile of the pure ecdysterone solution gave an absorbance of 100 milli absorbance units (mAU) for ecdysterone peak. One ml of both the DG water extract and CS water extract showed an absorbance of 800 mAU for ecdysterone peaks respectively. Fifteen ml of DG water extract was made up to 100ml as stock solution. The same procedure was done for CS water extract also. Both of them were almost similar in concentration with respect to ecdysterone to that of pure ecdysterone stock solution with 100 ppm ecdysterone content. A commercially available 'phytoecdysteroid' preparation by the name '*Chethana*' was also taken as positive control. It was prepared as prescribed by the manufacturer (1:1dilution with water). 1 ml of that was monitored for ecdysteroid content using HPLC which gave an absorbance of 300mAU for the ecdysterone peak.

15 ppm and 30 ppm dilutions were made from both DG and CS extracts stock solutions for application on silkworm larvae. Ecdysterone positive control was diluted to the same level but '*Chethana*' was used as such without any further dilution. Medium control and general control were also kept for comparison.

Results

The result of ecdysteroid rich plant extracts application on the reduction in maturation time has been shown in the Table 1 and Figure 1. About 80

% maturation was achieved by the larvae by the end of 18hours in case of DG and CS plant extracts in both 15 and 30 ppm concentrations. Ecdysterone positive control also showed similar results in both concentrations. But '*Chethana*', the commercial preparation showed only 70 % maturation within this time. The medium control showed no significant difference from the general control and both exhibited only 50% maturation by this time. A similar result was reported by using plant extracts from *Sesuvium portulacastrum* on silkworm hybrids (Nair *et al.,* 2002) and that from plants of Caryophyllaceae family on pure silkworm breeds (Trivedy *et al*., 2003). Nair *et al*., (2005) in their study with phytoecdysteroids has recorded that within 18 h of the treatment, about 81 % of the larvae matured whereas by the same time in the control only 37 % of the larvae matured. Recently, Rufaie *et al*., (2012) during their study reported a 58% maturation within 12 hours after phyto ecdysterone administration as against 27% observed in control. A small (10-12%) increase in hastening of spinning was shown by DG water extract above all the treatments. This may be due to the presence of a plethora of ecdysteroid related compounds reported from the plant which might had exerted positive synergistic effects. Survival rate was not affected by any of these ecdysterone treatments. An above 90 % survival rate was shown by all the treatments. This results agree with what has been reported early by Shivakumar *et al*., (1995; 1996).

Table 1. Tukey HSD Test Result. EC= ecdysteroid rich plant extract, DG= *Diploclisia* water extract, CS= *Coscinium* water extract.

		Cocoon weight	Shell weight
		Mean Difference	
Gen. Control	15 ppm EC	-0.13667	-0.01667
	30 ppm EC	0.014	0.02333
	15 ppm DG	-0.07533	0.00333
	30 ppm DG	-0.136	-0.01333
	15 PPM CS	0.05267	0.00133
	30 PPM CS	0.01333	0.01733
	CHETHANA	0.108	0.02533
	Med.Con.	0.154	0.00733

* *Significant at P=.05 level.*

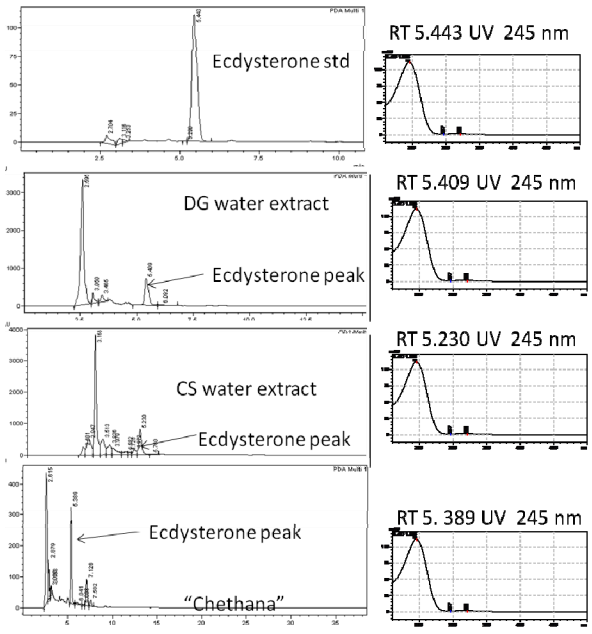

Fig 1. HPLC Profile of Ecdysterone standard and ecdysterone rich water extracts. DG= *Diploclisia glaucescens* (Blume) Diels., CS= *Coscinium fenestratum* (Gaertn.) Colebr., RT= Retention Time.

Table 2. Result of application of Ecdysterone (MH) rich plant extracts on Bivoltine double hybrids (FC_1 x FC_2) at Sasi's farm, Kuthanoor, Palakkad Dist, Kerala

Dosage	Time of application	maturation		Cocoon number (Survival Rate)	Single cocoon wt	Single shell wt	Shell ratio	Filament length	Denier
		Within 18hrs (%)	After18 hrs (%)						
15 ppm EC	On 6th day of last instar when 5% larvae has started spinning	82	18	28.67	1.99	.37	18.59	1085	2.9
30 ppm EC	On 6th day of last instar when 5% larvae has started spinning	84	16	29.33	1.84	.33	17.93	892.5	2.6
15 ppm DG	On 6th day of last instar when 5% larvae has started spinning	94	06	29.33	1.93	.35	18.13	1053.5	2.9
30 ppm DG	On 6th day of last instar when 5% larvae has started spinning	94	06	30	1.99	.37	18.59	852.7	2.8
15 ppm CS	On 6th day of last instar when 5% larvae has started spinning	88	12	30	1.80	.36	20.00	927.6	2.8
30 ppm CS	On 6th day of last instar when 5% larvae has started spinning	85	15	29.67	1.84	.34	18.48	850.3	2.7
Chethana	On 6th day of last instar when 5% larvae has started spinning.	70	30	27.67	1.75	.33	18.86	995.9	2.7
Med control	On 6th day of last instar when 5% larvae has started spinning	53	47	30	1.70	.35	20.59	1127.2	3.2
Gen Control	On 6th day of last instar when 5% larvae has started spinning	53	47	30	1.85	.36	19.46	818	2.7

EC=Ecdysterone, DG=*Diploclisia* leaf water extract, CS=*Coscinium* leaf water extract.

No significant mean difference was observed in the case of cocoon weight with respect to different doses of water extract treatments (Figure 2). This result was in line with the earlier works by Shivakumar *et al*., (1995, 1996). However in the case of shell weight, as recorded by Shivakumar *et al*., (1996) , a slight weight reduction was observed in our study also with respect and 30 ppm concentrations of ecdysterone, CS water extract and 'Chethana' treatments. Chow -Wei-Shan and Lu (1980) has reported that treatment of phytoecdysteroids in the later stages of *Bombyx mori* L. reduced shell weight which coincided with the tendency to curtail the feeding period of the last instar. With 15 ppm concentration level for ecdysterone no significant change of shell weight was observed in any of the treatments. Up to 33 % increase was shown in average filament

length over general control. Results of Tukey HSD test for cocoon and shell weights showed that mean difference for all the seven MH and water extract treatments were not significant (Figure 3).

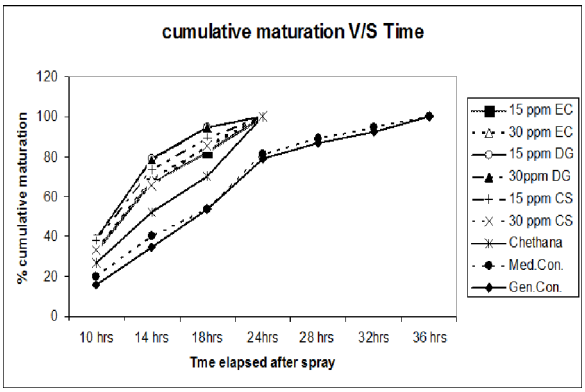

Fig 2. Cumulative maturation of larvae over time after MH Water Extract Spray. EC=Ecdysterone, DG= *Diploclisia* water extract, CS= *Coscinium* water extract.

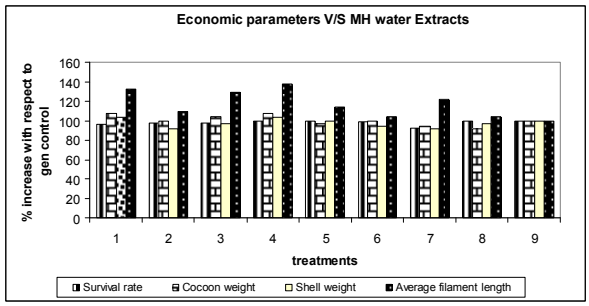

Fig 3. Economic parameter change above General Control due to MH Spray.1=ecdysterone (EC) 15 ppm, 2= EC 30 ppm, 3= *Diploclisia* water extract (DG) 15 ppm, 4= DG 30 ppm, 5= *Coscinium* water extract (CS) 15 ppm, 6= CS 30 ppm, 7="*Chethana*", 8= Medium control, 9= General control.

Discussion

The results of the present study indicates that the problem of non uniform maturation in silkworms could be solved to a large extent by administering ecdysteroid rich plant extract isolated from *Diploclisia glaucescens* (Blume) Diels (DG) and *Coscinium fenestratum* (Gaertn.) Colebr. Water extract of leaves of these plants were equally good in performance with that of the ecdysteroids isolated. The extracts were standardised using HPLC for evaluating the level of ecdysteroids present in them. This technology can be industrially utilised for production of ecdysteroid rich formulation for synchronising maturation and spinning for the benefit of sericulture farmers. Mounting of larvae is a cumbersome process and includes a lot of care and labour. If the cocooning is not synchronised, the larvae which are late in cocooning may damage the already cocooned shells by urinating on it and changing its colour to brown and making it unfit for sale. Phytoecdysteroids induce speedy and synchronised maturation of larvae when applied at appropriate time. The economic parameters were not significantly affected by the ecdysteroid application which otherwise would nullify the effect induced by ecdysteroids. Elevated level of ecdysteroids apparently shifts silk glands to their regression phase and stops protein synthesis. Since the ecdysteroid application is done at the onset of spinning the protein synthesis would have attained its peak by this time and this might be the reason why the economic parameters are not much adversely affected by ecdysteroid spray.

As a concluding note it can be assumed that ecdysteroid rich extracts isolated from the plants can be used to increase the silk production in our country.

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are also grateful to the Chief Wildlife Warden, Kerala Forest Department for permitting us to collect plants from forest areas. We are also grateful to Central Silk Board Officers and members of Kerala Sericulture Farmers Association for providing facilities and guidance during the study.

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AGEING, TEAR AND DIELECTRIC STUDIES OF NATURAL FIBER REINFORCED POLYPROPYLENE COMMINGLED COMPOSITES

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Abstract

Natural fiber reinforced polypropylene composite was fabricated using commingling technique. Banana fiber (extracted via anaerobic process) and coir-sisal yarn were used as reinforcement in PP composite. Ageing, tear and dielectric studies were performed. Solar ageing studies show that treated samples resist the UV radiation to a good extent and the tensile strength decreases as the time of exposure in the solar concentrator increases. Diffusion studies reveal that the treated composites absorb water very rapidly at the initial stage as in the case of untreated composite. The untreated composites show greater water absorption because of the presence of high amount of hemicelluloses and large number of porous tubular structures. Tear properties of the resulting composite reveals that chemical treatments increased the interfacial adhesion between the PP matrix and natural fibers which in turn effectively transfers the stress from the matrix to the natural fibers. This increased efficiency in stress transfer accounts for the increased tear resistance for treated composites compared to untreated ones. Dielectric studies reveal that the dielectric constants and conductivities of treated composites was less than that of the untreated ones due to a reduction in the hydrophilic nature of natural fibers brought about by various chemical treatments.

Keywords: Natural fiber, Poly propylene, Composite, Dielectric

Introduction

The growing concern for the development of environment friendly materials leads to the production of natural fiber based composites. Natural fibres replaced conventional inorganic fibres in every walks of development. The advantages of natural fibres are many, including low-cost, biodegradability, non-abrasiveness, high specific strength etc. The incompatibility between the polymer matrix and the natural fibre reinforcement, lower impact strength, higher moisture absorption etc made them disadvantageous and can be improved by various chemical treatments.

Natural fibres such as coir and banana can be used as reinforcement in polypropylene matrix composites. Coir and banana fibres are easily available in our locality. Coir is very strong as it contains crystalline alpha cellulose and lignin in appreciable level. Also it provides greater employment opportunities for rural people. Coir fibre can be blended with other natural or

synthetic fibres to improve functional properties of the yarn as well as fabric. Central coir research institute has developed a blend of coir and sisal fibres which can be used as the reinforcement in polymer matrix composites [Ravi PK (2007)].

Banana fibres can also be used in composite as reinforcement. The conventional way of banana fibre extraction is through a cumbersome manual process, wherein the pseudo stem sheaths are scarped and the fibre is separated by using a metal scraper. This is a tedious process and an alternate route is by mechanical process that may lead to heavy damage to the fibres. CSIR – NIIST has developed a new technology for banana fibre extraction which is through an anaerobic process. The brilliant white coloured fibres can be used as reinforcement in PP matrix composites.

Composite fabrication can be done in many ways. The conventional methods such as injection moulding, internal mixer etc which causes damage to natural fibres and the consequent reduction of properties can be avoided by adopting an entirely new fabrication technique called 'commingling'. In this method the matrix fibre and the reinforcement fibre are intermingled together at the filament level. The commingled composites were then compression moulded during which the low melting polymer matrix will melt and fills the space between the matrix and the reinforcement. This method is more advantageous than the other conventional methods, as it does not involve high shear forces and it requires fewer quantities of reagents during the processing stages. Also it resulted in a uniform distribution of the matrix and reinforcement, i.e. they can be blended intimately. The cost effectiveness of the technique also makes it advantageous [George G et al. (2013)].

This presentation covers the effect of chemical treatments on the moisture absorption, tear and dielectric properties of natural fiber reinforced polypropylene composites. Also investigate the effect of solar irradiation on tensile properties of these composites.

Materials and Methods

Materials

Polypropylene supplied by Superfil products Ltd., Chennai, India was used as the matrix. The supplied PP was in a monofilament form and is having a diameter of 0.5 m, denier value of 1609 and 25% elongation. Coir–sisal yarn supplied by Coir research institute, Alleppey, India. Banana fibre was supplied by NIIST Trivandrum were used as the reinforcement fibres. The other chemicals used were of analytical grade.

Extraction of Banana Fibre

Banana fibre can be used as an efficient reinforcement in PP matrix composite. An entirely new extraction technique has developed by CSIR-NIIST involves an anaerobic process. Banana pseudo stems and empty bunches are soaked in a tank and for four to six days and the soaked liquor is circulated

through an attached anaerobic reactor. The fibres are separated by enzymes produced in- situ through microbial action in an anaerobic reactor.

Fabrication of Composites

Commingled composite fabrication can be done by using a specially designed winding machine. A metal plate onto which the polypropylene and coir-sisal blended yarn was wound in a particular pattern and the plate was then compression moulded.

Fibre Surface Treatments

Various surface treatments with maleic anhydride grafted PP, $KMnO_4$ and VTMO have to be made in order to improve the compatibility between the polymer matrix and the natural fibre reinforcement.

Result and Discussion

Diffusion and Solar Ageing Studies

- **Effect of chemical treatment on moisture absorption behavior**

Effect of chemical treatments on moisture absorption behavior of both PP/CS and PP/BF composites are shown in Fig. 1 (a) and (b) respectively. In PP/CS composite, the magnitude of water uptake decreased from 48% to 34%, 26% and 25% in $KMnO_4$, MAPP and VTMO treated composite respectively. The chemical treatments improve the interfacial adhesion between the matrix and reinforcement which in turn decrease the number of voids so that the route for solvent passage is somewhat restricted.

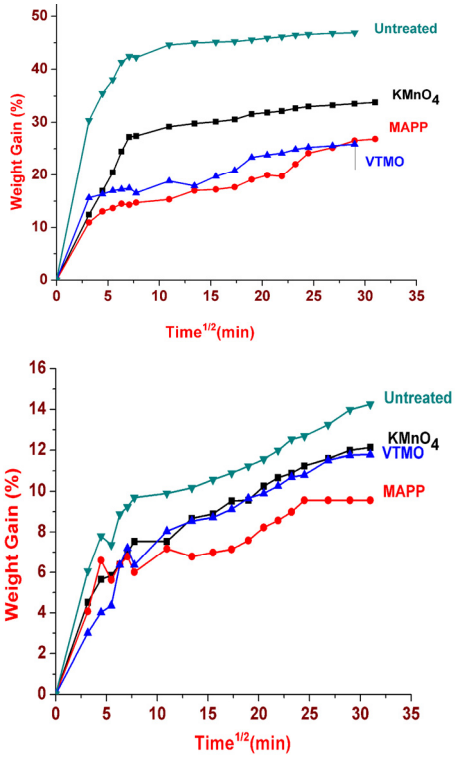

Fig. 1 Effect of chemical treatments on the moisture absorption behavior of (a) PP/CS composite (b) PP/BF composite

- **Effect of solar irradiation on tensile properties**

Effect of solar irradiation on the tensile strength and tensile modulus of PP/CS composite is given in Fig. 2.When the composites are subjected to solar irradiation, their tensile properties decreases to a considerable extent. From figure it is clear that treated composites show higher tensile strength because of the increased interfacial adhesion between the matrix and the reinforcement. The increased bonding will oppose the photo oxidation and crack propagation thereby reduces the tensile properties.

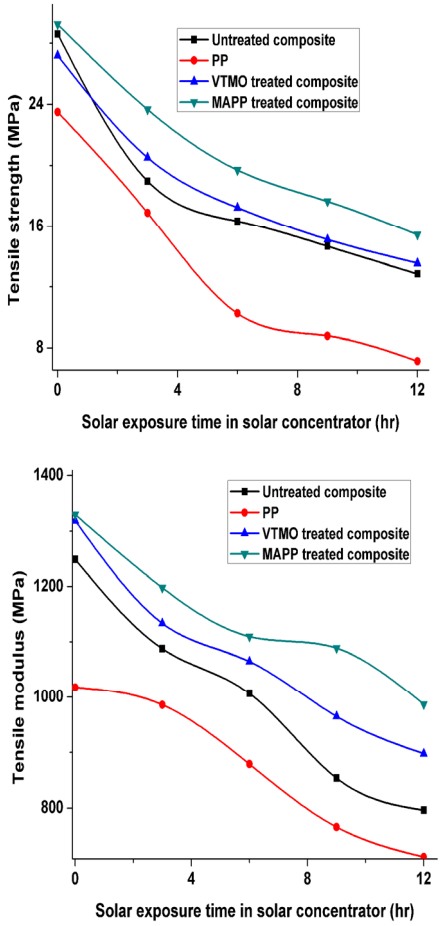

Fig. 2 Effect of solar irradiation on the (a) tensile strength (b) tensile modulus of PP/CS composites

Effect of chemical treatments on tear behavior

Polypropylene and natural fibers were subjected to different chemical treatments in order to increase the interfacial adhesion between the PP matrix and natural fibers. The increased interfacial adhesion between the PP matrix and natural fibers results in composites with increased tear resistance compared to untreated ones. The increased interfacial adhesion effectively transfers the stress from the matrix to the reinforcement and effectively resists the tearing process to certain extent. $KMnO_4$ and MAPP treated samples showed much improved tear resistance compared to other treatments in the case of PP/CS composite and VTMO treatment was found to be good in PP/BF composite. $KMnO_4$ and MAPP treatments effectively remove the cellulosic –OH groups from natural fibers thereby decreasing the hydrophilic tendency of natural fibers and thus increasing the interfacial adhesion with PP matrix. The effect of chemical treatments on the tear resistance of PP/coir-sisal yarn and PP/banana fiber commingled composites is shown in Fig. 3.

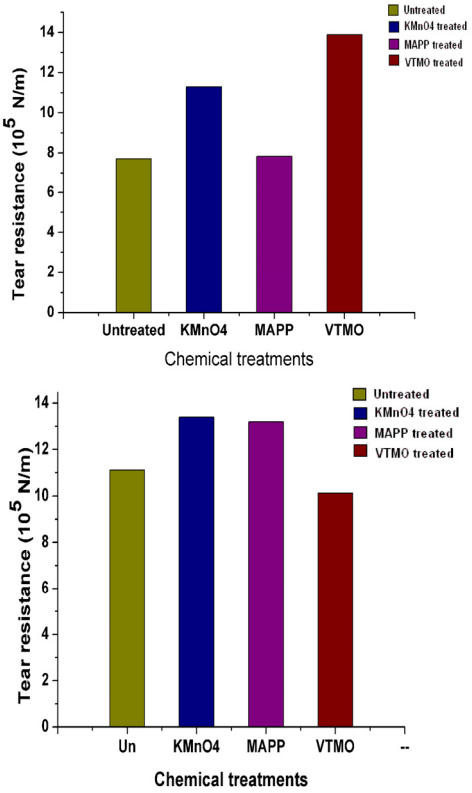

Fig. 3 Effect of chemical treatments on the tear behaviors of (a) PP/CS (b) PP/BF composites

Effect of chemical treatments on dielectric properties

All the treatments reduced the hydrophilic nature of natural fibers thereby making it more compatible with the hydrophobic PP matrix. The effect of chemical treatments on the dielectric

constant of PP/natural fiber commingled composites as a function of logarithm of frequency is shown in Fig. 4.

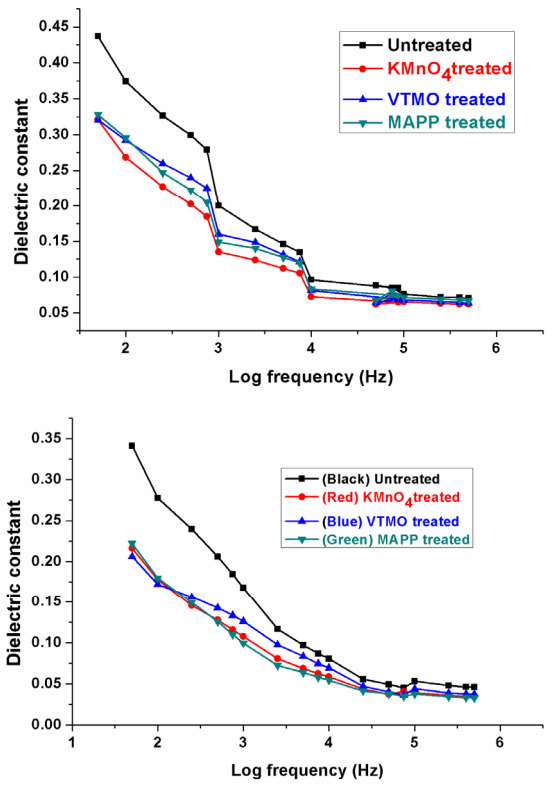

Fig. 4 Effect of chemical treatments on the dielectric properties of (a) PP/CS (b) PP/BF composites

Chemical treatments decrease the hydrophilic nature of natural fiber thereby reducing the number of polar groups and moisture absorption which in turn leads to a decrease in the net orientational polarization. All these factors contribute to a decrease in dielectric constant values with different chemical treatments. Chemical treatments increase the interfacial adhesion between the natural fiber and PP matrix thereby reducing the number of voids and irregularities present in the system. This also contributes effectively to a reduction in the dielectric constant values. VTMO react readily with the natural fiber surface and makes it rougher. This increased roughness increased the surface area leading to an increase in moisture absorption which in turn increases the orientational polarization leading to higher dielectric constant. Hence VTMO treated composites showed a dielectric constant value in between that of $KMnO_4$ and MAPP treated composites.

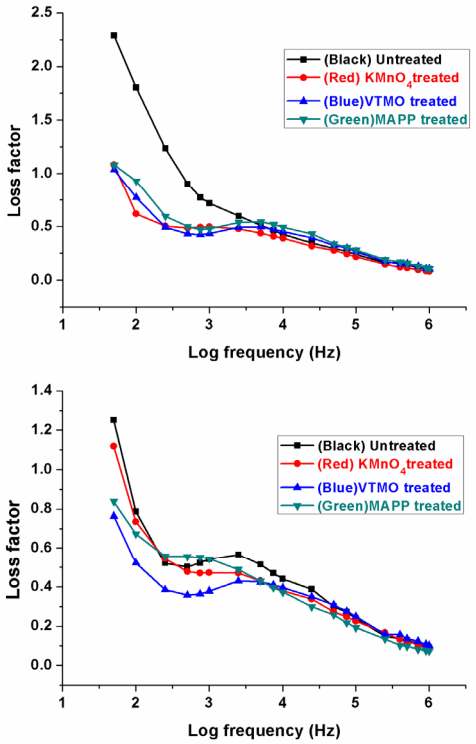

Fig. 5 Effect of chemical treatments on the loss factor of (a) PP/CS (b) PP/BF composites

The same trend is observed in the case of loss factor also. The effect of chemical treatments on the loss factor of PP/natural fiber commingled composites as a function of logarithm of frequency is shown as Figure 5. Different chemical treatments reduce the loss factor of PP/natural fiber commingled composites.

Conclusion

Polypropylene and natural fibers were used to prepare bio-composites using commingling technique. Chemical treatments increases the interfacial adhesion between the matrix and natural fibers causing further reduction in the number of voids and free volume of the composite. Hence the percentage of water intake decreases in chemically treated composites compared to untreated ones. Solar ageing studies reveal that upon solar irradiation the tensile properties of the composites decrease considerably. The tear resistance of the PP/natural fiber commingled composites was studied with respect to various chemical treatments. Chemical treatments increased the interfacial adhesion between the PP matrix and natural fiber which in turn effectively transfers the stress from the matrix to the natural fibers. This increased efficiency in stress transfer accounts for the increased tear resistance for treated composites compared to untreated ones. A chemical treatment increases the dielectric properties considerably. VTMO treated composites showed a dielectric constant value in between that of $KMnO_4$ and MAPP treated composites.

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AGRICULTURAL BIO WASTE FOR ZnO NANOPARTICLES SYNTHESIS - CHARACTERISATION & STUDIES ON THEIR BIOLOGICAL APPLICATION

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Abstract

In this work, Zinc oxide nanoparticles were successfully synthesized by microwave method using the agro waste Pomegranate peel (Punicagranatum L.) extract as reducing agent. The study involved the synthesis of Zinc Oxide nanoparticles using biological and chemical reducing agents. The aim was to compare the yield, nature and biological activity of nanoparticles synthesized by the two methods. UV-Visible Spectroscopy (UV-Vis Spectroscopy) , Scanning Electron Microscopy (SEM) , powder X-ray Diffraction and FTIR spectroscopy were used to confirm the formation of zinc oxide nanoparticles. The synthesized nanoparticles were tested for their antibacterial & antioxidant potential. The preliminary feasibility studies proved that agro wastes can be potentially used as bio templates for zinc oxide nanoparticle synthesis.

Keywords: ZnO NPs, XRD, SEM, FTIR, Pomegranate peel extract

1. Introduction

The "green" route for nanoparticle synthesis is of great interest due to eco-friendliness, economic prospects and wide range of applications in nanomedicine, catalysis, water pollution remediation etc. Plants provide a better platform for nanoparticle synthesis as they are free from toxic chemicals as well as provide natural capping agents. It is a new and emerging area of research in the scientific world, where day by- day developments is noted which ensures a bright future for this field. Another thrust area of interest is the management of waste materials and reutilisation of the waste as a natural resource for nanoparticle synthesis. The disposal of agricultural food waste is a severe environmental issue nowadays.

Investigations were made on waste reutilization & evaluation of the waste materials based Nps for possible value added applications (1-3). The use of agro waste for nanoparticle synthesis serves dual purpose of using this inexpensive, easily available source of active biochemical constituents and also helps in the prevention of pollution which might result due to its improper disposal.

The synthesis of transition metal oxide nano structures through using green ligation agents

obtained from natural resources is one of the thrust areas of interest (4-6). The reason for the increasing interest in the synthesis of metal and metal oxide based nano-particles lies behind their extraordinary abilities to function as catalysts and help in numerous processes of industrial and physical application. ZnO nanostructures are the forefront of research among metal oxides due to their unique properties and wild applications. ZnO nanostructure exhibits high catalytic efficiency, strong adsorption ability and are used more and more frequently in the manufacture of sunscreens, ceramics and rubber processing, wastewater treatment, and as a fungicide (7, 8)

Even though plant mediated biosynthesis can be carried out at ambient conditions, the time required for nano synthesis is much longer than the chemical methods. Microwave assisted biosynthesis is a remedy to this problem (9-11). It has several attractive features such as shorter reaction time, lower energy consumption, and better product yield.

In the present study, agricultural waste Pomegranate peel (Punicagranatum L.) extract were used as reducing agent for zinc oxide nanoparticle synthesis. This plant material has high polyphenol content which is known to form complex with metal ions and reduce it [12, 13]. The preliminary characterization of as-synthesized nanoparticles was done using UV-Vis spectroscopy and SEM, XRD & FTIR spectroscopy. The above synthesised ZnO nanoparticles were evaluated for their anti bacterial & anti oxidant potential.

2. Materials and Methods

All glass wares were washed with double distilled water and dried in oven before use. Pomegranate fruit peels were collected and washed thoroughly with double distilled water, dried and cut in to fine pieces and grind in to fine powder.

2.1 Preparation of Pomegranate peel extract

12g of Pomegranate fruit peel in the powder form was taken in a 250ml beaker and added 200ml double distilled water, and then boiled in water bath for 45 minutes at 75^0C. After cooling, filtered through Whatmann filter paper No.40 and kept in a refrigerator for analysis.

2.2 Preparation of Zinc oxide nanoparticle

(a). Chemical method : 0.1M $Zn(NO_3)_2.6H_2O$ was prepared in 100ml standard flask. 50 ml of the above solution was taken in a beaker & placed in a magnetic stirrer-heater. 2 M NaOH solution was added drop by drop under constant stirring with heating at room temperature till pH change to 12. It was magnetically stirred for 2 hours at room temperature. After completion of reaction, the solution was allowed to settle for overnight and supernatant liquid was discarded. The white precipitate formed was washed thoroughly with double distilled water to remove all the ions and then centrifuged at 3000 rpm for 10 minute. The obtained precipitate was dried in a hot air oven at 80^0C for 6 hrs. During drying, complete

conversion of $Zn(OH)_2$ into ZnO occurs. The above resulting dried precursors was crushed in to powder and stored in air tight container for further analysis. This powder was then calcinated in muffle furnace at 450^0C for 2 hrs.

(b). Microwave method: 0.1M $Zn(NO_3)_2.6H_2O$ was prepared in 100ml standard flask and 75 ml of this solution was taken in a 250ml beaker, added 20ml previously prepared pomegranate peel extract and stirred well. It was then paced in a domestic microwave oven (sharp R-219T (W)) operating at a power of 800W and frequency 2450MHz. The solution was then subjected to micro wave irradiation for 8 minute. The formation of ZnO nanoparticle was monitored by analysing the reaction mixture at 1, 2, 3, 4, 5, 5.30, 6, 6.30, 7minutes of microwave action. After completion of reaction (8 min), a white precipitate of ZnO was obtained and was calcinated for 2hrs at 450^0C. After calcinations, it was subjected to XRD measurements and then analysed by SEM and FT-IR methods

Fig. 1 ZnO NPs after calcination

2.3 Characterisation of synthesised ZnO Nps

a) UV-Vis spectrum of nano zinc oxide particles

UV-Vis spectrum of ZnO NPs was recorded using LAMBDA 650-PERKIN ELMER spectrometer range from 200 nm to 800 nm wavelengths.

b) Powder X – ray diffraction

The crystalline phase of all the sample was identified at room temperature using RigakuMiniflex 600 X-ray diffractometer with CuK_α (λ = 1.5406 A^0) as the radiation source

c) SEM analysis of ZnO NPs

The surface morphology of the prepared samples was evaluated by using JEOL JSM-6390 LV scanning electron microscope with a dynamic light scattering technique. The SEM studies revealed to visualise the shape and surface morphology of synthesised Zinc oxide nanoparticles.

d) FT-IR Spectroscopy

The FT-IR spectral studies were carried out in KBr medium using Thermo Nicolet, Avatar 370 model FT-IR spectrometer in range of 400-4000 cm^{-1} with resolution of 4 cm^{-1}.

2.4 Biological study of green synthesised zinc oxide nanoparticles

(a) Antibacterial assay

The agar well diffusion method was used to screen the antibacterial activity of the green synthesised ZnONPs [14]. The Gram-positive bacteria species *Staphylococcus aureus (S.aureus)* had been used in this study. 24hrs fresh culture was prepared and the standardized inoculum was made and used for the antibacterial assay. Approximately

20ml of molten and cooled media (Nutrient agar) was poured in sterilized petri dishes. The plates were left overnight at room temperature to check for the appearance of contamination. After inoculation and cultivation of target bacteria on top of nutrient agar, wells were placed in selected area on different plates. Agar wells of 5mm diameter were prepared with the help of a sterilized stainless steel cork borer. About 0.05 ml of various concentrations (1, 2, 3 mM) of two different ZnO nanoparticles were added in the wells. The plates containing the bacteria and zinc oxide nanoparticles were incubated at 37°C. The plates were examined for evidence of zones of inhibition which appear as a clear area around the wells. The diameter of such zones of inhibition was measured using a meter ruler and expressed in millimeter.

(b) Antioxidant activity

The antioxidant activity of Zinc oxide nanoparticles were studied by the Ammonium Molybdate method [15].

3. Results and discussions

3.1 UV-VIS spectrum of nano zinc oxide particles

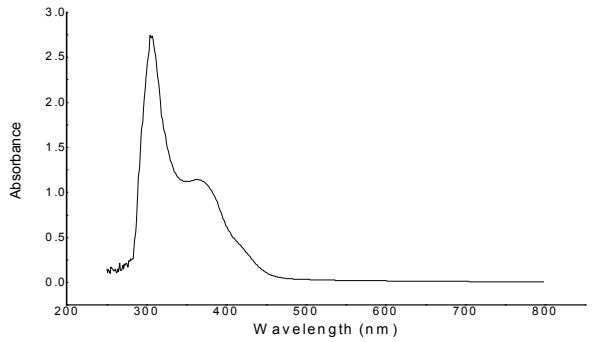


Fig.2. UV-spectrum of ZnO NPs prepared by microwave-method using pomegranate peel extract

The absorption spectrum of ZnO NP prepared by microwave assisted bio-method was shown in above figure (2). Confirmation of the green synthesised ZnO nanoproduct was exhibited by the highly blue shifted absorption maximum occurring around 325 nm. For bulk ZnO the absorption maximum usually around 385 nm approximately.

3.2 XRD patterns of nano zinc oxide

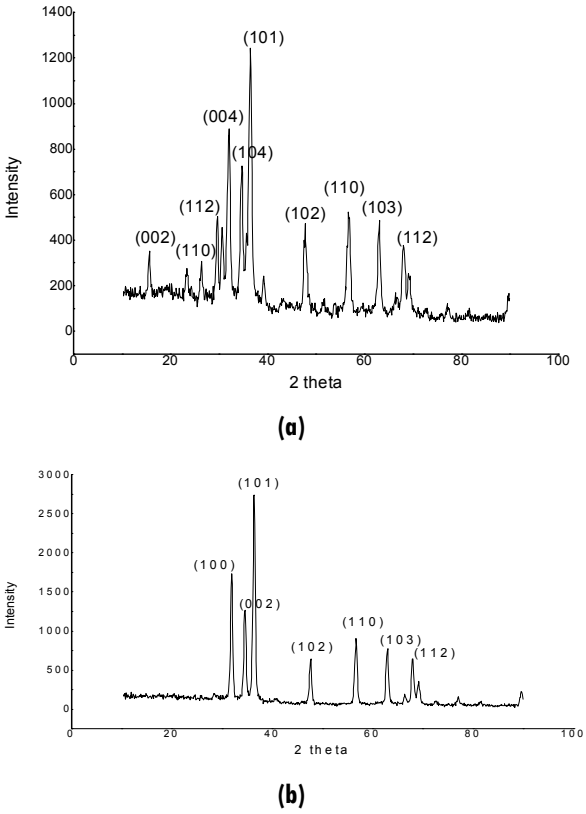


Fig.3 XRD spectra of ZnO NP prepared by (a) by Chemical method (b) by microwave method using pomegranate peel extract

The XRD spectra of the 'as prepared' and 'calcined' ZnO nanoparticle were shown in the above figures(3.a & b). The Calcination at 450^{0}C for 2hrs is essential for the complete removal of water and to obtain higher crystallinity. XRD analysis pattern gives the intensity of peak, its

position and width. The 2 theta values of 31.84^0, 34.61^0, 36.33^0, 47.83^0, 56.73^0, $62.94^0$and 68.08^0 etc. corresponds to the prominent peaks (100) (002) (101) (102) (110) (103) (112) planes respectively and agree well with the JCPDS no.75-0576 and 76-0704, confirming the hexagonal wurtzite structure of the ZnO nanoparticle. The average particle size (D) of synthesized nanoparticle was calculated from the Full Width at Half Maximum (FWHM) of more intense peak corresponding to (101) plane located at 36.33^0 using Debye-Scherrer's formula $D= 0.8\lambda / \beta \cos \theta$ where λ is wave length of X-ray source (CuK_αline 1.541 A^0), β is the FWHM in radians and θ is Bragg's diffraction angle. The calculated the particle size were given in the following table (1).

Table 1. Particle size of synthesised ZnO NPs

Method	FWHM	Particle size (D)
Chemical method	0.6638^0	12.49 nm
MW- assisted green method	0.5085^0	16.27 nm

3.3 Scanning electron microscopy analysis

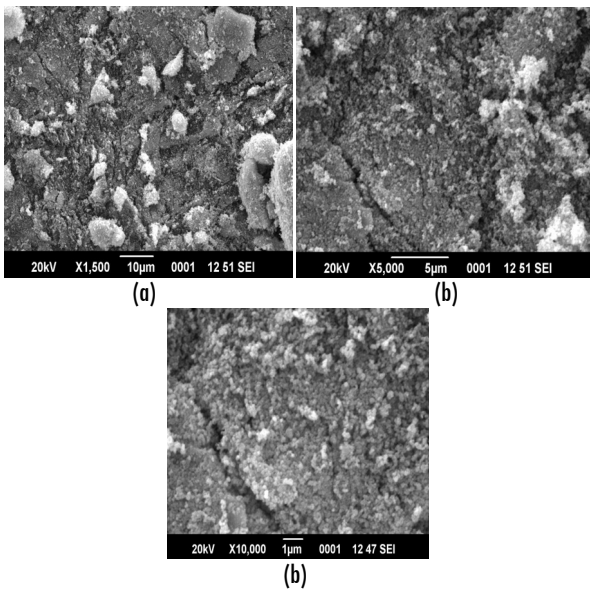


Fig.4. (a), (b) & (c)) SEM images of green synthesised nanoZnO at different magnifications

The SEM analysis was used to determine the shape and surface morphology of nano materials. The fig. 4. (a), (b) & (c)) represents the SEM images of ZnO nanoparticles at different magnifications X1,500 X5,000 X,10,000. The low magnified observation (fig.4.a) showed that in the morphology it give the individual ZnO NPs as well as a number of aggregates. The closer observations (Fig.4. (b) & (c)) showed that surface of the product was smooth and shape of ZnO NPs was approximately spherical.

3.4. FT-IR Spectroscopy

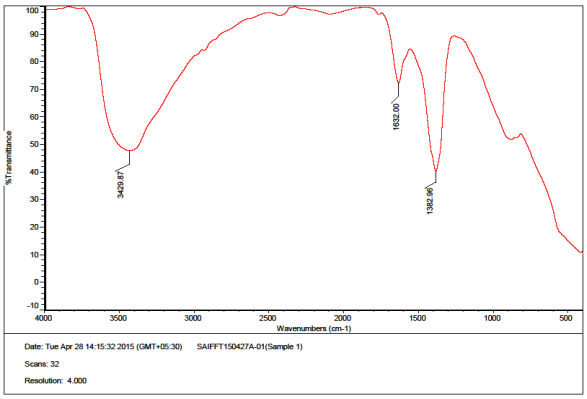


Fig.5 FT-IR spectra of ZnO NPs prepared by microwave method using pomegranate peel extract.

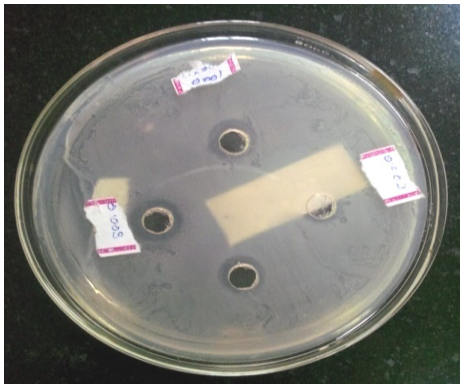
FT-IR studies were carried out in order to ascertain the purity and nature of the metal oxide nanoparticles. In the IR spectrum the bands at the 3427 cm^{-1} is due to the stretching vibrations of O-H groups in water, alcohol and phenols and N-H stretching in amines. The C-N stretch of amides in protein gives the band at 1382 cm^{-1}. The peak at 1632 cm^{-1} is attributed to the C=C stretch in aromatic ring and C=O stretch in poly phenols.

Metal oxides generally give absorption bands in finger print region i.e below 1000 cm^{-1} arising

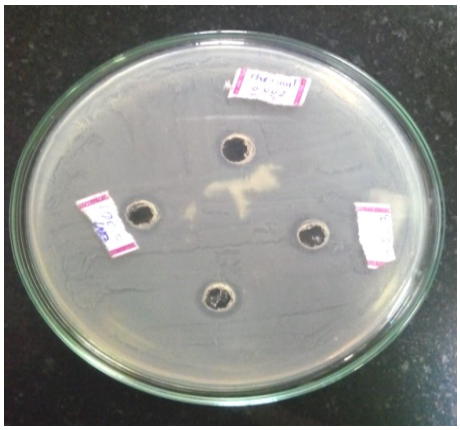
from inter-atomic vibrations. Thus from IR spectrum it can be observed that the peak appearing in the range 400-500cm^{-1} are the characteristic peaks of ZnO molecule. It may concluded that the presence of phenolic group of molecules are responsible for the reduction process and the amines and amide linkage in protein are responsible for the stabilisation of the ZnO nanoparticle.

3.5 Biological study of green synthesised zinc oxide nanoparticles

a) Antibacterial assay



(a) ZnO NPs by microwave method



b) ZnO NPs by chemical method

Fig 6 (a) & (b) Antibacterial activity of ZnO NPs against *S.aureus* at different concentrations

The particular concentrations of ZnO NPs which show the inhibition towards Gram-positive bacteria *S.aureus* were found (3mM & 1mM) respectively for microwave method and chemical method. The maximum Zone Of Inhibition (ZOI) was 7mm for 3mM in the case of microwave assisted pomegranate peel extract method fig.6(a) and 4mm for 1mM in the case of chemical method fig.6 (b). From these results it was found that the green synthesised ZnO NPs show more antibacterial activities than chemically synthesised ZnO NPs.

b) Antioxidant activity

The total antioxidant capacity of the ZnO NPs was determined by Ammonium Molybdate method using vitamin c as standard. An aliquot of 0.2 mL sample ZnO NPs with different concentrations (0.001 g/mL, 0.002 g/mL & 0.003 g/mL) was mixed with 2.0 mL of the reagent (0.6 M sulfuric acid, 28.0 mM sodium phosphate and 4.0 mM ammonium molybdate). Experiments were conducted in triplicate for each sample. The blank solution was made mixing 2.0 mL of the reagent solution with appropriate volume of the same solvent used to dissolve the sample. The tubes were capped and incubated at 95 °C for a period of 90 minutes. The sample and blank were left on the shelf for half an hour to cool down to room temperature. The absorbance of the sample was measured against blank solution at 695 nm. This UV readings were compared with standard readings and determined the corresponding milligram vitamin C equivalent per gram weight (mg vitamin C eq/gwt) .The total antioxidant activity of the samples were expressed as mg vitamin C eq/gwt. shown in the Table 2 .

Table 2. UV readings converted to corresponding milligram vitamin C equivalent per gram weight (mg vit C eq/gwt)

SAMPLE	Concentration	Sl.No	mg vit C equ/gwt
ZnO NPs CHEMICAL METHOD	0.001g/mL	1	30
		2	36
		3	0
	0.002g/mL	1	16
		2	10
		3	17
	0.003g/mL	1	7.333
		2	12.666
		3	12
ZnO NPs Microwave assisted green method	0.001g/mL	1	22
		2	12
		3	14
	0.002g/mL	1	8
		2	0
		3	8
	0.003g/mL	1	9.333
		2	7.333
		3	3.333

The above results were subjected to statistical treatment (ANOVA) & shown in the table no.3. Draw the error bar diagram by using this results (fig.7). The antioxidant potential of synthesised Zinc oxide nanoparticles can be analysed from the diagram.

Descriptive Statistics

Table no. 3 Dependent Variable: Antioxidant activity in vitamin C equivalents

Concentration	Sample	Mean	Std. Deviation	N
0.001g/mL	chemical	33.3333	3.05505	3
	peel	13.0000	1.00000	3
0.002g/mL	chemical	14.3333	3.78594	3
	peel	8.0000	.00000	3
0.003g/mL	chemical	10.6663	2.90589	3
	peel	8.3330	1.00000	3

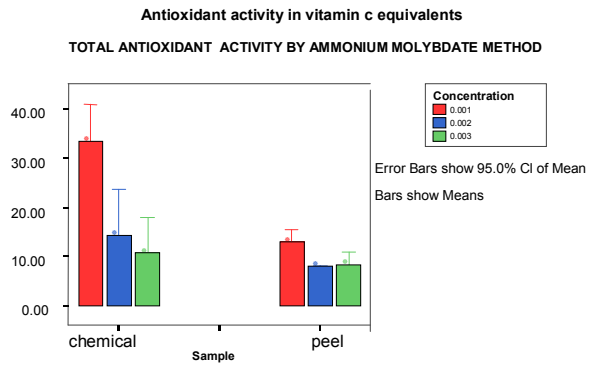


Fig.7. Error bar diagram showing the antioxidant activity of ZnO NPs

As seen from the fig, the chemically synthesised ZnO nanoparticles has better antioxidant activity at very low concentration & when the concentration increases there is a considerable decrease in their antioxidant activity. Similarly green synthesised ZnO NPs showed antioxidant activity at lower concentration 0.001g, but no significant change in antioxidant activity was noticed with increase of concentration

4. Conclusions

In this study, a simple approach was attempted to obtain a green eco-friendly way for the synthesis of zinc oxide nanoparticles using the agricultural waste Pomegranate peel extract. Microwave assisted biomethod is the one of the easier way to obtain fine powder of Zinc oxide nanoparticles within minutes. The yield, nature and biological activity of ZnO nanoparticles synthesized by the microwave assisted green method was compared with the chemical method. The characteristics of the obtained zinc oxide nanoparticles were studied using UV-Vis absorption spectroscopy (UV/Vis), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). The antibacterial activity experiment performed on *S. aureus* clearly demonstrated that the green synthesised ZnO NPs showed more antibacterial activities than chemical ZnO NPs. The antioxidant study of green synthesised Zinc oxide nanoparticle showed a considerable antioxidant effects at low concentration & no significant change was noticed with increase of concentration. Thus ZnO NP

synthesis using Pomegranate peel extract offers a promising route for managing environmental agricultural /food waste.

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SYNTHESIS AND D C ELECTRICAL CONDUCTIVITY STUDIES OF POLYANILINE NANOSTRUCTURES

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Abstract

Polyaniline (PANI) is one of the highly pursued conducting polymers owing to its high electrical conductivity, interesting optical properties and excellent environmental stability. The. Electrical conductivity can be tuned from the insulating to the metallic regime using available cost effective monomer and precursors. Comparably high room temperature D.C electrical conductivity with negligible temperature variation is observed in the pellet samples of acid doped PANI nanostructures.
Keywords: Polyaniline, Nanostructures, Electrical conductivity, Monomer.

Introduction

Electroactive polymers or Conducting polymers have been an area of immense interest over the past 30 years since the first discovery of conducting polyacetylene in 1977 by Shirakawa et al [1]. Extensive research on several conjugated polymers including poly(p-phenylene), polyaniline (PANI), polypyrrole, polythiophene, polyindole, polycarbazole, polyfluorene, poly (p-phenylenevinylene), and their substituted derivatives have led to their applications in rechargeable batteries, microelectronics, sensors, electrochromic displays, and light-emitting and photovoltaic devices. Among the various conjugated polymers, PANI has received special recognition owing to its good stability, easy and cheap synthesis route, high yield of polymerisation, excellent and tunable electrical properties and interesting redox behavior [2–5]. In the past few years, several novel methodologies have been developed for the preparation of nanostructured PANI in the form of dispersions, nanowires, nanofibers, and nanotubules. Conducting polymer nanostructures have become a rapidly growing field of research, because they display new properties related to their nanoscale size and have greatly improved the performance of devices [6-11]. Compared with bulk conducting polymers, conducting polymer nanostructures are expected to display improved performance in technological applications [12], because of the unique properties arising from their nanoscale size.

Though extensive investigations have been reported on the electrical conductivity behaviour of doped PANI both in bulk and thin film forms [5, 13-15] detailed investigations on the nanostructured PANI are scanty. In the present work, we have attempted to synthesize PANI nanostructures via a self-assembly process and have carried out D.C electrical conductivity measurements on nanostructured PANI pellets doped with Camphor Sulphonic acid (CSA). We have observed a maximum conductivity of 10.52 S/cm in doped PANI nanostructures. The morphology of the synthesized PANI nanoparticles has been investigated.

Experimental

Sample preparation

Polyaniline nanoparticles were synthesized by *in situ* doping polymerization of aniline in the presence of CSA as the dopant and using ammonium peroxidisulphate (APS) as an initiator. In this method, the dopant serves both the doping and template functions at the same time. Freshly distilled aniline (1 ml) was dissolved in the dopant acid (CSA) solution in water (0.75 M) and the mixture was stirred well for 2 hours to obtain a uniform suspension. APS (0.5 M) dissolved in water (aniline/APS molar ratio=1.5) was added drop-by-drop to the above solution within 1-2 hours and stirring was continued for another 15 hours. The polymerization was performed at ~5^0C temperature. The precipitate obtained was centrifuged, washed and dried under vacuum for 12 hours.

Characterization

The X-ray diffraction (XRD) pattern of the samples were taken on a fully automated Bruker AXS D8 Advance X-ray diffractometer with X-ray source of Cu (wavelength-1.5406 A^o). Scanning was carried out in the 2θ range from zero to 80^o, at a scan speed of 5^0 per minute.

SEM images of the nanoparticles are obtained with JEOL Model JSM - 6390LV scanning microscope. SEM micrograph is representative of the surface topography and distribution of elemental composition on the surface.

Fourier transform infrared (FTIR) spectrum of the sample was obtained with AVTAR 370 DTGS FT-IR spectrophotometer in the wave number range 500 -4000cm^{-1}.

DC electrical conductivity of the samples in the form of pellets / films was measured using a standard four-probe setup.

Results and discussion

It is easy to form CSA micelles in aqueous solution due to the hydrophilic nature of CSA. It is reasonable to propose that CSA micelles and/or aniline/CSA clusters might act as templates in the formation of the PANI/nanoparticles. In fact, micelles formed by dopant (CSA), aniline/dopant clusters and free aniline all exist together in the reaction system. Obviously, their content in the reaction system should affect the morphology and size of the micelles as templates, resulting in morphology and size variation of the doped PANI. However, it has been found that the templates differed depending on the polymerization method, dopant and synthesis conditions. For instance, it has been proved that CSA micelles act as templates in the formation of the PANI– CSA synthesized by either chemical or electrochemical methods [5].

XRD Analysis

The X-ray Diffraction pattern of PANI is shown in figure 1. CSA doped polyaniline nanostructures show a crystalline, sharp peak at 25^o. Peak at 27^0 is less crystalline and other peaks at 21^o, 15^o and 30^o are amorphous. Accommodating large sized dopant ions demand greater rearrangement of bonds along the polymer backbone, leading to better crystallanity [17].

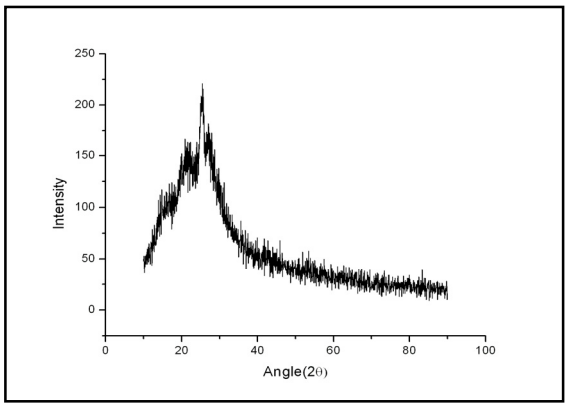

Figure 1: XRD pattern of PANI

The graphite- like diffraction peak at around 25^0[17, 18] is characteristic of the extent of Π conjugation in PANI. In short, the benzenoid and quinonoid units are orderly arranged in acid doped nanostructures.

FT IR Analysis

The FT IR spectrum of CSA doped PANI is shown in figure 2.

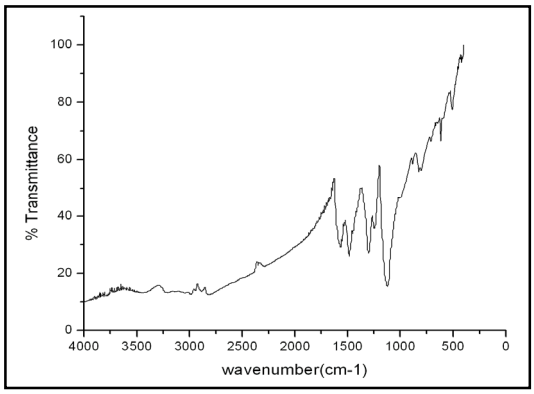

Figure 2: FT IR spectrum of CSA doped PANI

The major peaks are at around 3500 cm^{-1}(NH stretching vibration), 2900 cm^{-1} (CH stretch), 1570 cm^{-1}(C=N stretch of the quinonoid unit of PANI), 1470 cm^{-1} (C=C stretch of the benzenoid unit of PANI) and 1100 cm^{-1}(quinonoid unit vibration of doped PANI) as reported earlier[17, 19, 20].

SEM Analysis

The morphology of the synthesized PANI is investigated using SEM analysis. Figure 3 shows the SEM images of CSA doped PANI nanostructures, the agglomerates of which having granular/spherical morphology with an average size of 200 nm.

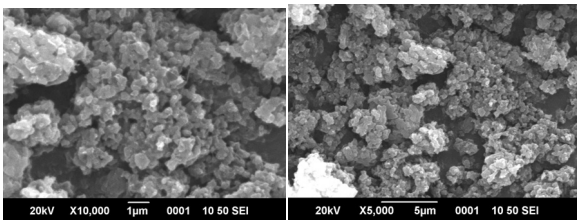

Figure 3: SEM images of PANI

DC Electrical Conductivity Studies

The temperature dependent D.C electrical conductivity plots of PANI nanostructure samples synthesized with various aniline to APS feed ratio are given in figure 4. (S/cm).

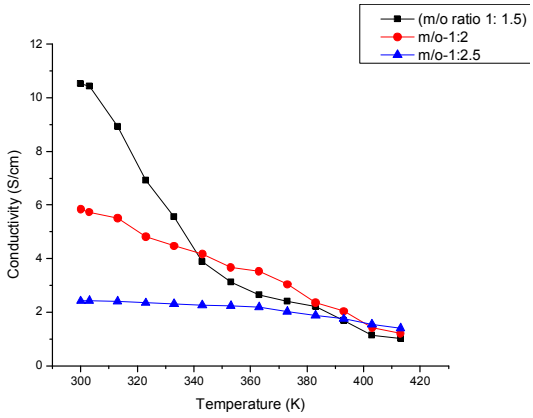

Fig 4: Temperature dependent D.C electrical conductivity plots of PANI nanostructures (synthesized with various aniline to APS feed ratio)

The PANI nanostructures exhibit better D.C electrical conductivity than PANI (microsized) (2S/cm). The better crystallanity of PANI nanostructures implies greater long range order favouring effective charge transfer along the chains. This results in higher electrical conductivity. PANI

nanostructures synthesized with aniline to APS feed ratio 1:1.5 has better room temperature D.C electrical conductivity (10.5 S/cm) than that with aniline to APS feed ratio 1:2 (5.8 S/cm). The conductivity of PANI nano rods is observed to decrease with temperature, unlike the nearly flat temperature dependent behaviour of ordinary PANI. The possible reason may be the greater scattering of the charge carriers at the nanostructure boundaries.

Conclusion

The structural, morphological and electrical properties of polyaniline nanostructure samples are investigated. The polyaniline samples exhibit better crystallanity as compared to micro sized PANI. SEM measurements reveal that they are small in size. All the nano polyaniline samples show better D.C electrical conductivity. The samples exhibit better crystallanity. Obviously the nano polyaniline sample with the lowest APS feed ratio exhibits the highest room temperature D.C electrical conductivity.

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MODIFICATION OF NATURAL RUBBER USING NANO ZINC ALUMINATE

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Abstract

Natural rubber is an important renewable material and agro-product. This paper presents the findings of a study on incorporating zinc aluminate spinel into natural rubber for property improvement. Zinc aluminate was prepared by sol gel method and blended with the natural rubber by two roll milling. The cure characteristics and mechanical properties of such modified vulcanizates were determined and compared with those of unmodified samples. Cure time and scorch time were not affected much on modification. Mechanical properties showed only a marginal improvement.

Keywords: Natural rubber, nano zinc aluminate, spinel, modification

1. Introduction

Natural rubber is an important elastomer with the unique attribute of being a renewable agricultural product. Synthetic rubbers are more uniform in quality and compounds prepared from are more consistent in processing and product properties. Natural rubber crystallizes on stretching giving high tensile strength to the gum vulcanizate; on the other hand gum vulcanizate of synthetic rubbers like styrene butadiene rubber, nitrile rubber etc. are generally weak and requires the incorporation of reinforcing fillers to produce products having high strength.

NR remains the best choice of elastomer for many applications that require low heat build up such as large tires, carcasses of passenger car tires, vibration dampers, springs, engine mountings and bearings. Other products like hoses, conveyer belts, gaskets, seals, rollers, rubberized fabrics, elastic bands, latex foams, adhesives, pharmaceutical and medical products also consume a major part of NR. It is the most widely used naturally occurring elastomer and is a homopolymer of isoprene having a cis 1,4 configuration and available in a variety of types and grades including latex, technically specified grades, sheets, crepes, etc.

It has the highest resilience (except BR) which is responsible for its very low heat build up. It shows very low compression set and stress relaxation, good electrical insulation and good resistance to abrasion, tear and fatigue. As in any unsaturated elastomer, NR vulcanizates are susceptible to attack by atmospheric oxygen and ozone and hence its heat and weather resistance are poor. It is not resistant to petroleum based oils

and fuels as it contains no polar groups, but can be used with a wide range of organic and inorganic chemicals such as non petroleum based automotive break fluids, silicone oils and greases, glycols, alcohols, water and non oxidising aqueous solutions of acids, alkalis and salts.

1.1 Modification by addition of fillers

Fillers are one of the major additives used in natural rubber compounds and have a marked effect on rubber properties. Filler functions to modify the physical and to some extent, the chemical properties of vulcanizate (15) The mechanism of reinforcement of elastomers by fillers has been reviewed by several workers (16).They considered that the effect of filler is to increase the number of chains which share the load of a broken polymer chain. It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. These include particle size, particle shape, particle dispersion, surface area, surface reactivity, structure of the filler and the bonding quality between the filler and the rubber matrix. In rubber industry, fillers in common use are carbon black, china clay, silica and calcium carbonate.

1.2 Zinc Aluminate as filler

One important aluminium spinel is zinc aluminate. Zinc aluminate possesses a unique combination of desirable properties such as high thermal stability,high mechanical resistance, low temperature sinterability, better diffusion and ductility and low surface acidity(17). Due to these properties it was used as high temperature materials, catalysts and optical coatings. It was widely used in many catalytic reactions, such as dehydration and hydrogenation. Zinc aluminate is one of the most important functional oxides with a direct, wide band gap (3.37eV) and large excitation binding energy (60meV), exihibiting many interesting properties including transparent conductivity and piezoelectricity. Zinc aluminate is also a candidate material for optical coating applications and is currently employed in catalysis for applications such as cracking, saturated alcohol dehydration, methanol and other alcohol synthesis and as a catalytic support. The catalytic functionality of sub-micron particles is strongly affected by microstructure with different facets showing differences in catalytic activity.

The aim of this project is to study the effects of nano zinc aluminates on the physicomechanical properties of natural rubber aluminate nano composites.

2. Experimental

2.1 Materials

Zinc nitrate, Aluminium nitrate, propane diol, *Natural rubber* (*ISNR-5*), *Zinc Oxide* (activator) *Stearic acid* (co-activator), *CBS* (accelerator) and *Tetramethyl thiuram disulphide* (*TMTD*) (accelerator) *Sulphur* (crosslinking agent).

2.2 Synthesis of nano zinc aluminate

Zinc nitrate hydrate and aluminium nitrate hydrate taken in 1:2 molar ratio were dissolved in

propylene glycol, by adding propylene glycol in small quantities, to form a saturated solution. The solution was heated at 70°C with constant stirring on a magnetic stirrer for several hours until gel formation had taken place following a chemical reaction. The gel was heated at a temperature of 180°C placed on a heating mantle until combustion had taken place forming slightly rose coloured fine powder. This powder was analysed using X-ray diffractometry and it was found that the phase of zinc aluminate was not yet formed. This powder was calcinated at 600°C and had been analysed using XRD. Zinc aluminate nanocrystallites thus formed were characterized using X-ray diffractometry (XRD) (Rigaku D-max with Cu Kα X-ray source), and Fourier transform infrared spectroscopy (FTIR).

2.3 Compounding and curing

The mixes were prepared on a laboratory size two roll mill (16x33cm) at a friction ratio 1:1.25. The mixing was done according to ASTM D 3184-89(2001). The natural rubber was initially masticated well on the mill. Then the compounding ingredients were added in the following order: activators, accelerators, filler and sulphur. After mixing, the stock was passed six times through tight nip and finally sheeted out. Both gum and filled NR compounds were prepared. The formulations of the mixes are given in Table 2.1 and 2.2.

Table 2.1 NR formulation for varying filler content

Sample	NR (phr)	$ZnAl_2O_4$ (phr)	ZnO (phr)	St.acid (phr)	CBS (phr)	TMTD (phr)	S (phr)
1	100	0	4	2	0.8	0.2	2.5
2	100	1	4	2	0.8	0.2	2.5
3	100	2	4	2	0.8	0.2	2.5
4	100	3	4	2	0.8	0.2	2.5
5	100	4	4	2	0.8	0.2	2.5
6	100	5	4	2	0.8	0.2	2.5

Cure characteristics of the mixes were determined at 150°C and vulcanization to optimum cure time was carried out in an electrically heated hydraulic press at 150°C**.** The moldings were cooled quickly and stored in a cool dark place for 24 hours prior to physical testing.

2.4 Quality evaluation

The following evaluation methods were adopted for the NR vulcanizates.

a) Cure characteristics

Cure characteristics of the mixes were determined at 150°C using Rubber Process Analyser, RPA 2000 supplied by Alpha Technologies, USA as per ASTM Standard, D 2084-01.

b) Tensile properties

The tensile properties were measured using Shimadzu Autograph AG-1 Series' Universal Testing Machine (UTM) with a grip separation of 40mm, using a crosshead speed of 500mm/min as per ASTM D 412-1998 (Method A). All the tests were carried out at 28±2°C. Dumb bell specimens were punched out of the moulded sheet along the mill grain direction using a dumb bell die (C-type). The thickness of the narrow portion was measured using a digital thickness gauge. The sample was held tight by the two grips or jaws of

the UTM, the lower grip being fixed. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

c) Tear strength

This test was carried out as per ASTM D 624-1998 using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on Shimadzu Autograph AG-1 Series' Universal Testing Machine (UTM) with a grip separation of 40mm, using a crosshead speed of 500mm/min. The test temperature was 28±2°C.

d) Hardness

The hardness (Shore A) of the moulded samples was determined using Zwick 3114 Hardness Tester in accordance with ASTM D 2240-1997. The tests were performed on unstressed samples of 30mm diameter and 6mm thickness. The readings were taken after 10 seconds of indentation since firm contact had been established with the specimen.

e) Abrasion loss

The abrasion resistance of the samples was determined using a DIN Abrader (DIN 53516). Samples having a diameter of 6±0.2mm and 12mm thickness were prepared as per ASTM D 3183 and the abrasion loss was measured as per ASTM D 5963-04. The samples were kept on a rotating sample holder and a 10N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The difference in weight is the weight loss on abrasion. The volume loss on abrasion was calculated using the equation

Volume loss on abrasion = weight loss on abrasion/ specific gravity of the sample

Abrasion resistance is the reciprocal of volume loss on abrasion. The density of the sample was measured using Archimedes principle.

3. Results and Discussions

3.1 Structural characterization

X-ray diffractogram of synthesized zinc aluminate calcined at 180°C and 700°C are shown in the figure 3.1 and 3.2 respectively.

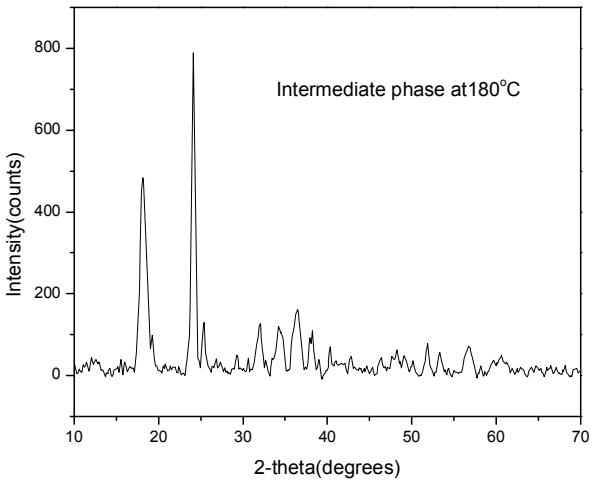

Figure 3.1 XRD of Zinc aluminate calcined at 180°C

Figure 3.1 is the XRD diagram of the intermediate phase formed at 180°C.This compound seems to be a mixture of aluminium hydroxides and zinc hydroxide with a non cubical structure. Figure 3.2 shows the XRD diagrams of

the compound calcined at 700°C. It can be seen that the phase formation is complete at 700°C. All peaks are well defined pointing to the high crystalline nature of the sample. The XRD pattern was compared with JCPDS files (file no. 74-1138) and all the diffraction peaks are in good match with the reported result and the peaks were indexed with the help of these reported patterns. The average particle size was found to be 15 nm.

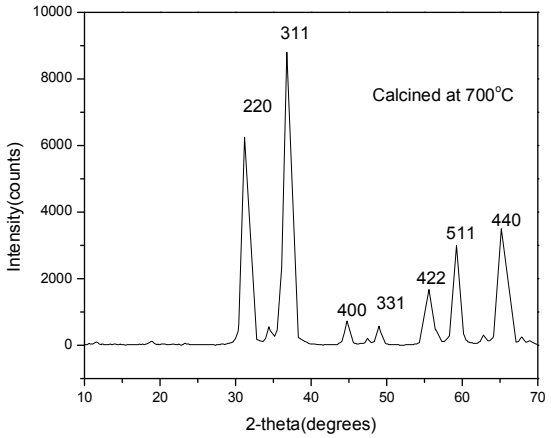

Figure 3.2 XRD of Zinc aluminate calcined at 700°C

Figure 3.1 is the XRD diagram of the intermediate phase formed at 180°C.This compound seems to be a mixture of aluminium hydroxides and zinc hydroxide with a non cubical structure. Figure 3.2 shows the XRD diagrams of the compound calcined at 700°C. It can be seen that the phase formation is complete at 700°C. All peaks are well defined pointing to the high crystalline nature of the sample. The XRD pattern was compared with JCPDS files (file no. 74-1138) and all the diffraction peaks are in good match with the reported result and the peaks were indexed with the help of these reported patterns. The average particle size was found to be 15 nm.

3.2 Nano zinc aluminate as a filler in Natural rubber

3.2.1 Cure characteristics

Cure parameters are given in Table 3.1. Scorch time and cure time remain more or less constant indicated that less interaction of NR with zinc aluminate. Maximum torque throws light shear modulus of the fully vulcanized rubber at the vulcanization temperature. Maximum torque decreases slightly with filler. These values are a reflection on the filler polymer interaction.

Table 3.1 Cure characteristics of NR compound with Zinc aluminate

Filler content (phr)	Scorch time (mm)	Cure time (mm)	Minimum Torque (dNm)	Maximum Torque (dNm)
0	3.32	5.74	0.39	9.17
1	3.15	5.47	0.39	8.74
2	3.23	5.57	0.37	8.75
3	1.04	4.6	0.16	6.97
4	3.51	5.67	0.40	8.86
5	3.25	5.38	0.39	8.86

3.2.2 Mechanical properties

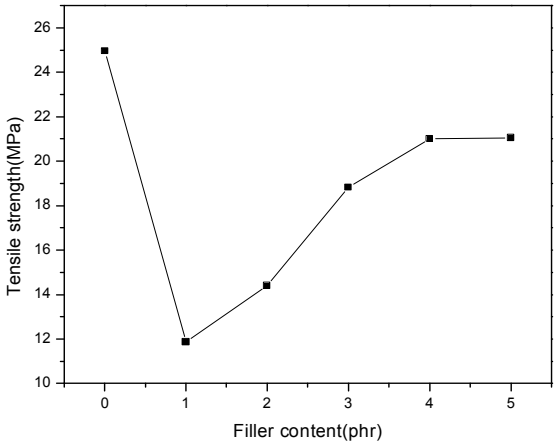

Fig.3.5 Variation of tensile strength with filler content

Fig.3.5 shows the variation of tensile strength on addition of zinc aluminate. Tensile strength drops at 1 phr of filler and then increases with filler loading. The initial drop at lower levels of filler is a

result of dilution effect. At higher levels of filler shows a better reinforcing efficiency resulting from the higher surface area and better interaction with the rubber. As the particle size decreases, the interface area between the filler and the rubber increases which leads to better reinforcement characteristics.

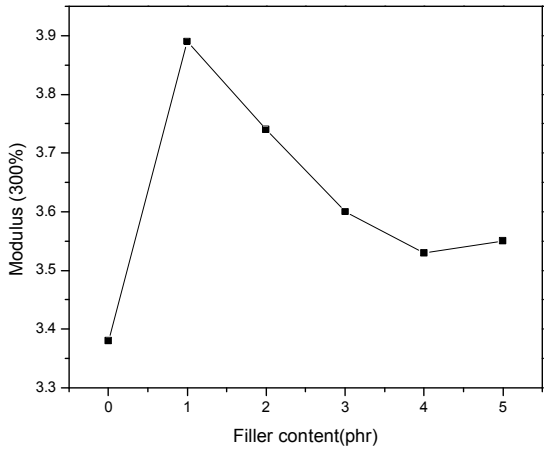

Fig.3.6 Variation of 300% modulus with filler content

Figure 3.6 shows the variation of modulus. Initially there is a stiffening of the rubber chains resulting in an improvement in modulus, the trend reverses on adding higher amounts of filler.

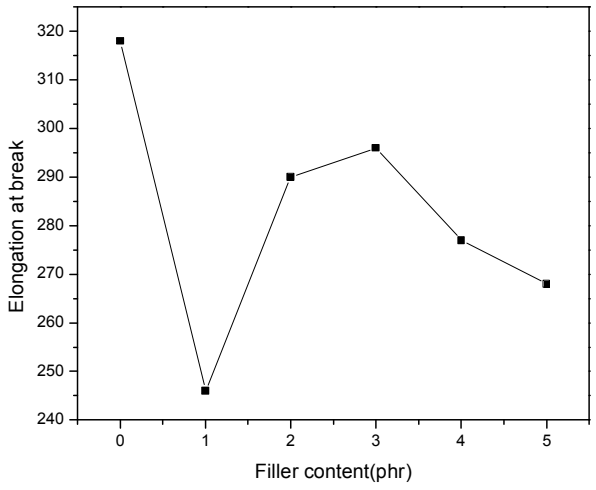

Fig.3.7 Variation of elongation at break with filler

Figure 3.6 shows the variation of modulus. Initially there is a stiffening of the rubber chains resulting in an improvement in modulus, the trend reverses on adding higher amounts of filler.

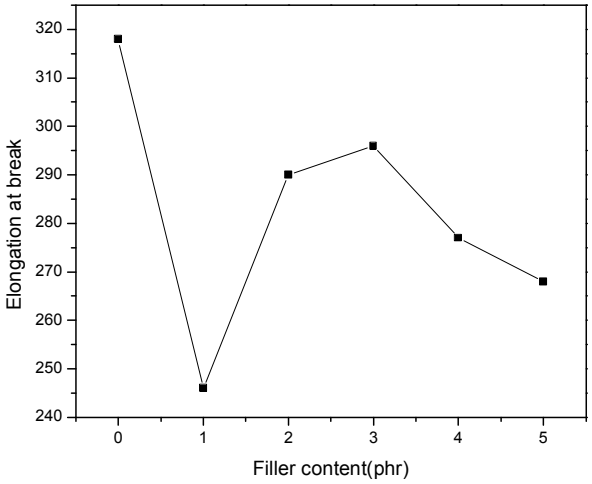

Fig.3.7 Variation of elongation at break with filler

Elongation at break (Fig.3.7) is governed by the extent of crosslinks present at the time of rupture. Increase in elongation at break with filler loading is due to the increase in the stress bearing capacity of the filler-matrix interface.

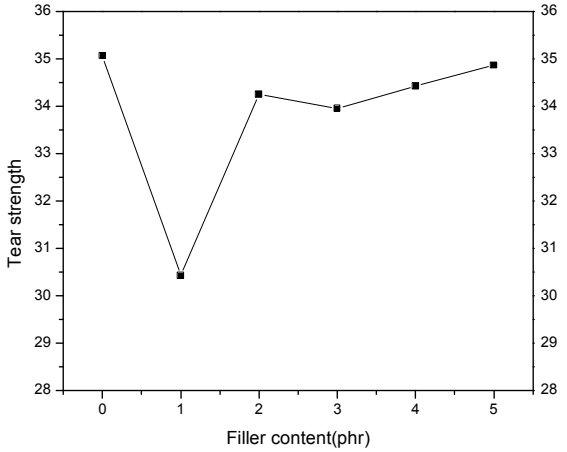

Fig.3.8 Variation of tear strength with filler content

Tear strength (Fig.3.8) drops first as in the case of tensile strength and tends to improve at

higher filler loading. In a matrix containing fillers, the filler interacts with the elastomer chains and create a barrier for the tear path. Filler particles present at the propagation tip arrest the propagating cracks and thus increase the tear strength.

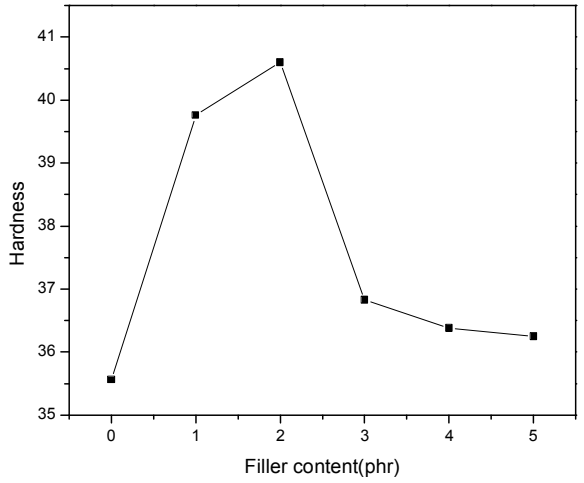

Fig.3.9 Variation of hardness with filler content

Hardness (Fig.3.9) also shows improvement upto 2phr of the filler. After that it decreases. Hardness represents a measure of modulus at low strains.

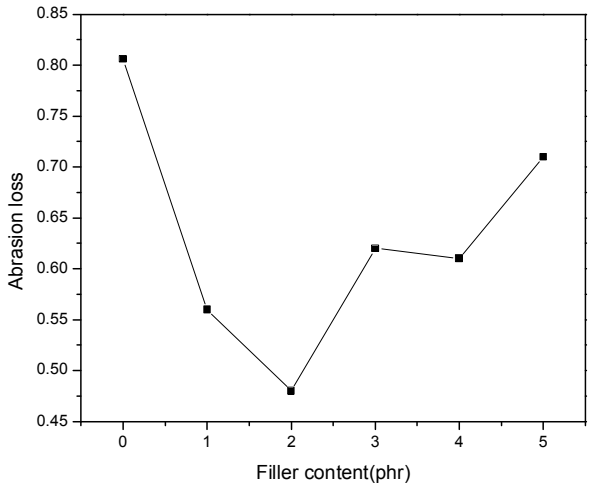

Fig.3.10 Variation of abrasion loss with filler content

Upto 2phr abrasion loss decreases after that it increases (Fig.3.10). It may be due to less interaction at higher loading of filler. Abrasion resistance is more for filled composite than the gum NR.

4. Conclusion

Nano zinc aluminate can be successfully prepared by sol gel method. The particle size was calculated to be 15 nm from the XRD results. NR aluminate composites were prepared by incorporating zinc aluminate at varying proportions into NR matrix. Cure studies indicated that the addition of zinc aluminate was not much affected the scorch time and cure time in the case of NR. The interaction between NR and zinc aluminate was very poor. Filler agglomeration occurred at higher filler loading. Only a marginal improvement in the mechanical properties.

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STRUCTURAL AND OPTICAL CHARACTERIZATION OF POTASSIUM DOPED ZINC OXIDE NANOSHEETS

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Abstract

This paper presents the synthesis of potassium (K) doped zinc oxide nano sheets at room temperature by wet chemical method. The structure and morphology of the crystals prepared for different molar concentrations of K were analysed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Absorption studies reveal that absorption is minimum in the visible region and band gap energy is found to decrease with increase in K concentration.

Keywords: X-ray diffraction, Wet chemical method, scanning electron microscopy.

1. Introduction

ZnO is a II-VI semiconducting material with novel properties and promising applications. It gains great commercial and scientific interest because of the special features like direct band gap (~3.3eV), large exciton binding energy (~60meV), non toxicity and excellent optical and electrical properties. These features make it unique for the fabrication of highly useful optoelectronic devices like blue light emitting diodes [1, 2], field effect transistors[3], ultra violet laser diodes, sensors[4] etc. Several interesting structures of ZnO such as nanotubes[5], nanowires[6], nanorods[7], nanoribbons[8], nanoflowers[9], tetrapodes[10], nanosheets[11] have been reported, in which two dimensional ZnO nanosheets posses some special interesting features like high surface to volume ratio, promising optical and photo catalytic activities, nano meter scale thickness and these features make them ideal components for nanoscale devices used in different fields [12].

2. Experimental

All the chemicals used were of analytical grade. 50 ml of 0.5 M potassium hydroxide [KOH] solution was added drop by drop to 50 ml of 0.1M zinc acetate [Zn $(CH_3COO)_2$] solution using methanol as solvent and stirred for 1 hour at room temperature. Experiment was repeated for different concentration of K (0.5 to 2M)

The chemical reaction involved can be written as:

$$Zn(CH_3COO)_2 + 2KOH \rightarrow Zn(OH)_2 + 2K(CH_3COO).$$

$$HO\text{-}Zn\text{-}OH \rightarrow ZnO + H_2O$$

The K doped ZnO nanopowder extracted from the colloidal solution was characterized by X-ray diffraction using Bruker AXS D8 advance X-ray diffractometer. The morphology and

microstructure of ZnO nanostructures were examined using JEOL JSM 7600F field emission scanning electron microscope. UV-Vis absorption spectra of the samples were analyzed using Shimadzu UV Vis –NIR Spectrophotometer

3. Results and discussions

3.1 Structural Characterization

3.1.1 X-ray Diffraction

Figure 1 shows the XRD pattern of ZnO synthesized at different molar concentrations of K. The diffractogram shows the characteristic reflections from (100), (101) and (002) planes of ZnO, in well agreement with JCPDS file 36-1451 having wurtzite crystal structure. The diffraction peaks get shifted to lower values as the doping concentration is increased which is due to the change in lattice parameter due to doping.

The grain size (D) of the samples were calculated using Debye –Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the wavelength of light used, β is the full width at half maximum (FWHM) and θ is the glancing angle. There is a steady decrease in broadening and hence the FWHM with doping concentration there by increasing the crystallite size from 10nm to 17nm

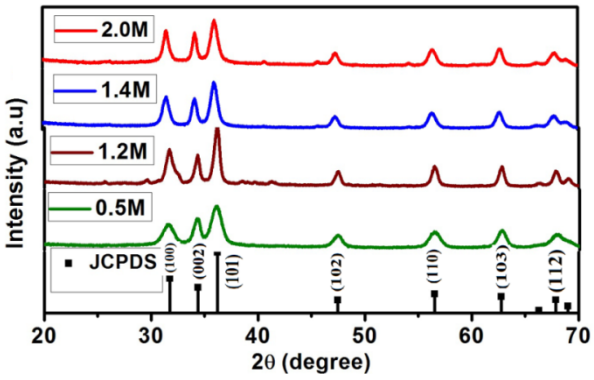

Fig 1

3.1.2 SEM Analysis

SEM images of the different samples are shown in Fig .2. From the images we can see that the synthesized material is formed by the accumulation of 2D nano sheets of ZnO and the individual sheets appear to have a lateral dimension in the micrometer scale. The sheets are mostly joined and do not exhibit hexagonal shapes. At smaller doping concentrations these nano sheets exhibit flower like structure. As doping concentration increases and becomes 1.4M and 2M this flower like appearance is lost and the sheets appear to be scattered. SEM images give an impression that the size of the sheets decreases with increase in doping concentration.

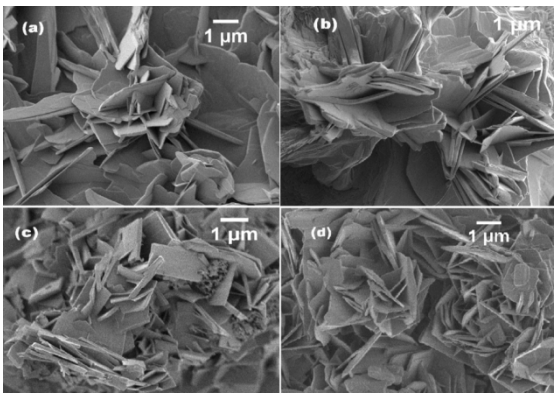

Fig 2

3.2 Optical Characterization

3.2.1 UV-VIS Absorption Spectroscopy

The absorbance spectrum for the doped ZnO is as shown in Fig. 3. All the samples exhibit less absorption in the visible region except the 1.4M sample which shows very good absorption in visible region.

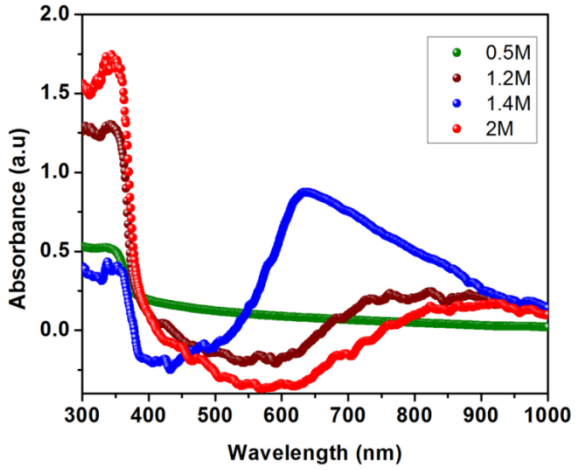

Fig 4

Conclusions

In this work K- doped ZnO nano sheets were prepared by wet chemical method, without any capping agent. XRD pattern showed that the nano structures are composed of hexagonal phase of ZnO. It is found that with doping concentration, crystallite size increases.SEM images reveal the accumulation of nanosheets and the density of sheets increases with K concentration whereas , the size of individual sheet decreases. The high surface area of nanosheet makes it feasible for optoelectronic device applications like dye sensitized solar cells.

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WORK LIFE BALANCE OF WOMEN FACULTIES IN COLLEGES WITH SPECIAL REFERENCE TO TRICHIRAPPALLI CITY

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Abstract

The main objectives of this paper is to study the work life balance of working women in Trichy. This paper analyses the causes of work and life imbalance with respect to female teachers.

Keywords: Work- Life Balance, Women in Teaching Profession, Causes of Imbalance, Stress, Achieving Work Life Balance.

Introduction:

Work-Life balance is a wide concept which includes proper prioritizing between career and ambition on one hand, compared with pleasure, leisure, family and spiritual development on the other. It is an important factor which determines employee satisfaction, loyalty and productivity. Globalization, working couples, nuclear families, and technology are some important factors contributing to work life imbalance. Work-Life Balance of women employees has become an important subject since the time has changed from men earning the family living in today's world where both men and women equally share the responsibility of earning for the betterment of their family life. Hence it is very necessary to know how the women balance very professional and domestic life. In the initial stages, women had to struggle a lot to establish their identity in this competitive world, both in the society as well as in the professional life. But with the advancement in educational and training institutions, things have improved to a great extent. As per Census 2011, the workforce participation rate for females at the national level stands at 25.51 percentage compared with 53.26 percentage for males. In the rural sector, females have a workforce participation rate of 30.02 percentage compared with 53.03 percentage for males. In the urban sector, it is 15.44percentage for females and 53.76percentage for males. The State of Himachal Pradesh had the highest female work participation rate (44.8 percentage) whereas the lowest was reported in case of Delhi (10.6 percentage).

Objectives of the Study

1. The study the perception of female faculty members working in teaching profession with respect to work Life balance.
2. To find out the causes of work life imbalance.
3. To study the Inability to achieve work life balance and the frequency of stress experienced.

4. To find out the ways to achieve work life balance.

Research Methodology

Research Design used by the researcher is descriptive in nature which studies about the characteristics of a particular Individual or a group. The Researcher has selected 25 women faculties by using purposive sampling.

Data Collection

The primary data is collected by direct survey on the women faculties who are affected by imbalance in their work life. This has been done through the questionnaire method. The researcher has collected secondary data from newspapers, books, magazines, journals and websites.

Limitation of the Study

1. The study examines the level of work life balance on the basic of opinions collected from women faculties working colleges in Thiruchirapalli city.
2. As the survey is contacted at the work place of women faculties some the respondents were hesitant to give correct information.

Sample and sampling

Table 1: The Grouping of Respondents on the basis of Age:-

Groups	Respondents
20-30years	11
30-40years	8
40-50years	3
Above50years	3
Total	25

Table 2: The Grouping of Respondents on the basis of Monthly Salary:-

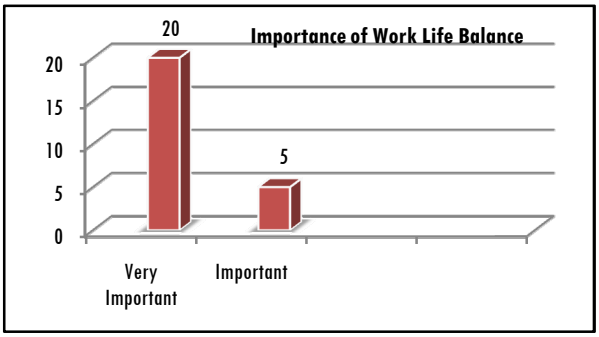
Groups	Respondents
UptoRs.10,000	3
Rs.10,000-20,000	13
Rs.20,000-30,000	3
Rs.30,000-40,000	2
AboveRs.40,000	4
Total	25

Table 3: The Grouping of Respondents on the basis of Family Status

Groups	Respondents
Unmarried	9
Married without any child	7
Married with 1 child	4
Married with 2 or more children	5
Total	25

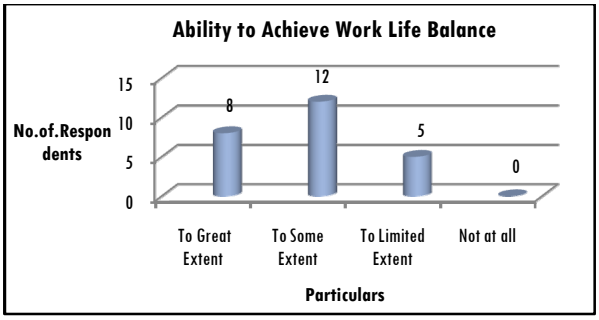
Analysis & Findings:

Chart1: Importance of Work life Balance:



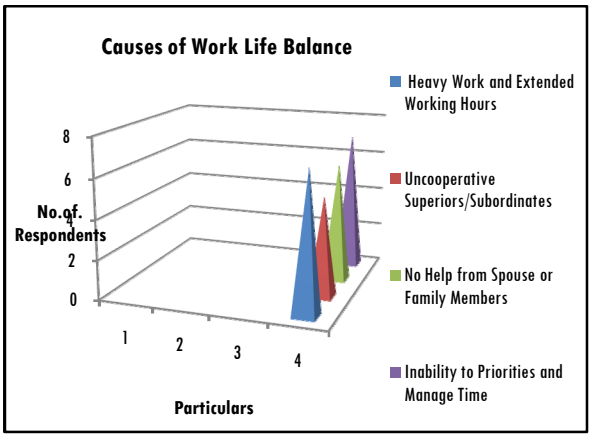
20 respondents felt that it is very important and 5 respondents felt that it is important to achieve work-life balance. There were no respondents who were undecided or who felt that it is not important to balance between work and life. This clearly indicates that there is definitely high amount of importance attached to work-life balance by women from the teaching field. This is a very good significance considering work-life balance important is the first step towards achieving it.

Chart 2: Ability to Achieve Work-Life Balance



8 of the respondents said that they were able to achieve work life balance to great extent, 12 of the respondents said that they were able to achieve work life balance to some extent, where as 5 respondents were said that they go with to a limited extent. Thus, there were some respondents who were not sure whether they are able to achieve work life balance or not.

Chart 3: Causes of Work-Life Imbalance:



7 Respondents accounted heavy and extended working hours work load & extended working hours to be responsible for work life imbalance. This is in contrast with the general conception that teaching profession is suitable for women since the work load and working hours are suitable and convenient. 7 Respondents said that inability to priorities and manage time is the causes for work life imbalance. 6 Respondents said that no help from the spouse or family members.5respondents felt that un cooperative superiors and subordinates.

Chart 4: Inability to achieve work life balance and the frequency of stress experienced

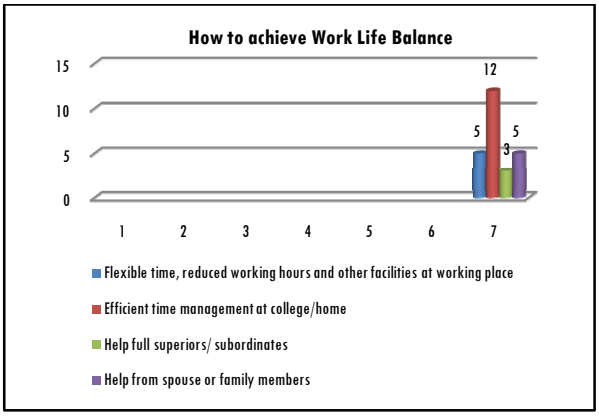
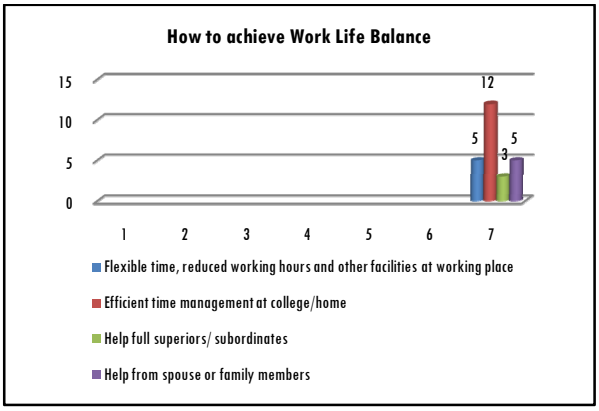


Chart 5: How to achieve work-Life Balance



According to 12 respondents felt that efficient time management (at college/home) is the key to achieving work life balance. While 5 of the respondents said that flexi-time, reduced working hours & other facilities at the work place can help to achieve work life balance, 5 of the respondents said that help from spouse &family members is required.

Conclusion:

Women teachers should try to strike a balance between their professional and family roles. They should not hesitate to take up responsibilities in addition to teaching. It not only improves their status in the organization, but also promotes their self-confidence. They should learn more and more by participating various training programmes, seminars, conferences, workshops and by taking up further courses of study. They have to develop a harmonious relationship among colleagues, with students and the management to reduce their stress.

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LIVELIHOOD PATTERN OF NON LITERATE WOMEN IN TIRUCHIRAPPALLI DISTRICT

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Abstract

The present paper is made an attempt to cull out the ground reality the livelihood pattern of non literate women in the Tiruchirappalli City Corporation in this article the author highlights significance of the research problem by way of using various parameters like to study the occupational style, to find out their savings and expenditure pattern from their income, to identify the sources of their basic amenities and comforts of study area. A person's livelihood refers to their "means of securing the basic necessities -food, water, shelter and clothing- of life". An illiterate person is a burden to society as he consumes national wealth but contributes nothing to nation. Socrates philosophy quotes "Woman once made equal to man becomes his superior". Women build about half of the population of the country, but their situation has been depressing. The poor people are not affording education to their children because of the poverty. In this paper the above mentioned three different definitions are combined and made an empirical verification in the Tiruchirappalli City Corporation in three wards by way of personal interview method with the help of structured and well defined interview schedule.

Keywords: Livelihood; Illiteracy; Women

Introduction

Livelihood is defined as a set of activities, involving securing water, food, fodder, medicine, shelter, clothing and the capacity to acquire above necessities working either individually or as a group by using endowments (both human and material) for meeting the requirements of the self and his/her household on a sustainable basis with dignity. The activities are usually carried out repeatedly. A livelihood is a means of making living. It encompasses people's capabilities, assets, income and activities required to secure the necessities of life. This livelihood endure their life to survive in this environment where have's and have's not (Bourgeoisie's 7 **proletariat**, Karl Marx) which leads to economic inequality, gender inequality, illiteracy in the society and also it fueled to class struggle and restless society. These are all the major ingredients of Poverty and feminine society like India. The army of women non literate is significantly contributing to the national average but it is not exhibited by the policy makeover to

the public. Attention of these parameters in the economy needs attention to literacy especially to women in India.

Illiteracy is compared to darkness. All the great men of the world lay emphasis on literacy. Illiteracy is the lack of literacy. A non literate person is a burden to society as he consumes national wealth but contributes noting to nation. The poor people are not affording education to their children because of the poverty. The poverty stricken people who are unable to earn their living cannot think of sending their kids to schools to receive education.

A part from this superstition and ignorance add to this problem to great extent to those who consider it unnecessary to educate their female children. It's a curse which cannot be removed overnight. Primary education is the basis of all education. The government should make mandatory to send their female children to schools.

Research problem background

Socrates philosophy quotes "Woman once made equal to man becomes his superior". Women build about half of the population of the country, but their situation has been depressing. Since from birth they have been intentionally ignored opportunities of growth in the name of religion and socio-cultural practices. Indian society esteems and salutes the women as Janani on one hand and the other hand they close the eyes to their sisters, mothers and wives. Gender insensitivity makes women's work invisible, unaccounted and therefore, bereft of any values. They were victims of widespread illiteracy, segregation in the dark and dingy rooms in the name of forced child marriage, indeterminable widowhood and opposition to remarriage of widows and divorcees turning many of them to prostitutes, polygamy, female infanticide, violence and complete denial of individuality.

The veiled Indian women, loving in traditional environment could come out with their Charkha-spun threads to deposit them and get the price at the collection centers which they called congress this Charkha became the great source of livelihood of the millions of Indian women, especially the poor and the widows, which popularized the congress, the concept to Marx that "slavery is an economic category also proved to be correct". In rural areas, a significant proportion of non literate people are daily wage lobourers working on construction sites, small scale industries, tiny industries, quarries, farm and field works and other works followed by those employed in shops. The female participation is huge among these areas because of illiteracy and they also force their children to involve in the same ground to get their basic amenities.

Research gaps found

In Tiruchirappalli District the non literate women has participating indirectly to the national income with their discriminating livelihood pattern. The specific objective is to find their livelihood pattern with respect to their region.

Objectives

To evaluate the pattern of livelihood pattern of non literate women in Tiruchirappalli City Corporation is the broad objective of the present study. Base on the this objective to have scientific investigation with empirical validity the researcher split the broad objectives into the specific objectives, they are

- To find out the occupational style in study area
- To study their savings and expenditure pattern from their income
- To identify the sources of their basic amenities and comforts

Methodology

The present study undertaken by the researcher based on the primary data as well as secondary data. To have scientific and meaningful inferences the researcher employed sampling technique to collect primary data from the sample respondents. The study purposely selected Tiruchirappalli City Corporation due to examine the non literate women population in the selected area of the present study. The study area has been identified by the researcher based on the research issues i.e. livelihood pattern of the target population. At Tiruchirappalli City Corporation have 60 corporation wards of which researcher selected three wards i.e. 5 percent of the total wards in the Tiruchirappalli city. Of the three selected wards researcher has given equal weightage to each wards to select samples. The size of the sample consists of 20 from each ward, in total there are 60 samples have been identified. The sample respondents detail consist of personal profile, social profile, economic profile, environmental profile, health profile, infrastructural profile and other related information were collected from the informant.

Limitation

The present study was restricted to three wards. It is due to geographical profile and non availability of authentic records about the non literate women in study area the researcher conducted a micro level study with small size of samples. Besides the researcher restricted variables which are influencing non literate women are occupational style, savings and expenditure pattern from their income, basic amenities and comforts, health condition, to find out the credit habits of non literate women.

Literate Review

Miyuki Iiyama University of Tokyo, Livelihoods Diversification Patterns among Households and their Implications on Poverty and Resource Use: A Case Study from a Kerio River Basin Community, International House of Japan has studied and found livelihood diversification portfolios affect income levels through economic returns attached to components of livelihood activities and does not allow households to move out of the vicious cycle of poverty traps.

R.N. Ali, F. Begum, M.M. Salehin and K.S. Farid, Livelihood pattern of rural women

garment workers at Dhaka city, has found that changing livelihood pattern of women workers who move from rural to urban areas in Dhaka city. 71.1 percent of women workers entered the job to help their family financially and those who work at the garments were exhausting the health of the work force.

A Report on Urban Livelihood profiling study of Jagatpura, Jaipur declared that poor earners at construction site want to switch to new livelihood and intend to set up own shop e.g. vegetable, food, snacks and those who engaged in labourers at construction site, sweeper, rag pickers intend to switch to stitching, embroidery, tailoring etc. The report says that 60 percent of respondent prefer to start up shop.

A significant milestone reached in Census 2011, is that the total number of non literates has come down from 304,146,862 in 2001 to 272,950,015 in 2011, showing a decline of 31,196,847 persons. One of the interesting features of Census 2011 is that out of total of 217,700,941 literates added during the decade, female (110,069,001) out numbers males (107,631,940).

Results and Discussion

The representative sample of Tiruchirappalli District urban poor comprise of mostly low income category. Out of 60 samples 61 percent belong to Low income, 23 percent from middle income, and 16 percent from high income category. An analysis of adult women surveyed in these three wards equally indicates that average age of women in 34 years. Almost 65 percent of women fall in age of 25 to 40 years and alarming to show that 35 percent are totally non literate while 42 percent are just literate. This signifies that almost 77 percent practically non literate. Over 80 percent of have regular occupation on the all the three different zones of wards and rest off them are irregular.

Further examination of these 60 non literate women shows some motivating insights. Almost 16 percent of them are engaged as servant mates, 15 percent of them preparing homemade foods in all the three zones. Table below elaborates on activities taken by women in percent in three different wards of Tiruchirappalli district.

Livelihood Activity of non literate women in percent

North Area Siriangam	In Percent	West Area Jeewa nagar	In Percent	South Area E.Pudur	In Percent
House mate	12	House Mate	20	House Mate	17
Preparing Homemade foods	15	Preparing Homemade foods	20	Preparing Homemade foods	10
Bamboo handy craft	3	Beedi workers	13	Laboures at construction site	20
Hotel barer	2	Hotel barer	5	Hotel barer	1
Day care servants	4	Day care servants	5	Day care servants	9
Vegetable vendor	12	Vegetable vendor	8	Vegetable vendor	8
Sweepers	9	Sweepers	12	Sweepers	12
Agricultural workers	8	Agricultural workers	-	Agricultural workers	8
Stitching	-	Stitching	5	Stitching	4
Shop workers	5	Shop workers	10	Shop workers	8
Flower Vendors	25	Flower Vendors	2	Flower Vendors	3
Bricklin workers	5	Bricklin workers	-	Bricklin workers	-

Source: Primary data

In Srirangam ward non illiterate women has given more concentration on Flower vendors as their occupation than others because the area is place of worship. On the second ward Jeeva nagar livelihood equally depends on houses and preparing of homemade foods. The other part E. Pudur women attention pays to construction field though it's a irregular income of them. As there is hope of construction their allied activity namely bricklin workers are found. There is another common livelihood of them as sweepers either in hospitals or in shops.

Livelihood pattern of families

Basic Amenities and Comforts

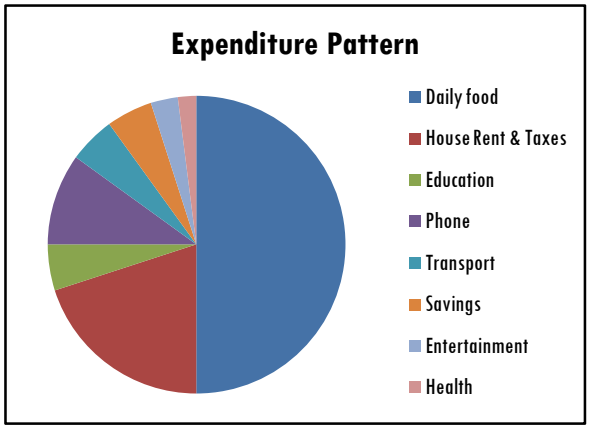
Household Assets	Percent of households who own
Mobile	76
Fan	76
Gas Connection	65
Cooler	20
Gold & Silver	10
Two Wheeler	20

Source: Primary data

The study of household amenities and comforts of these three wards point outs that mobile, fan and TV is owned by two third of the respondents. Analysis of precious metals owned by households indicates that they possess less of gold and silver.

Family Income and Expenditure

The research paper analysed income of their family which depicts almost of them has regular but daily wage structured labourers. Hence over 75 percent of household have monthly income less than or equal to Rupees 5000/-. The researcher further analyzed the expenditure pattern of their families. It has represented through a pie diagram as follows:



As shown in the diagram expenditure pattern depicts that food place half of their income then second most part place rent. There is a key point is that the mobile place a third position and the researcher find that the service sector plays a vital role in their life. Savings has a smaller amount of fraction and finally the health rest a least part in their everyday expenditure.

Findings & Suggestions

The empirical data reviewed that the livelihood pattern of non-literate women which depicts as follows:

- The first observation is obvious and predictable that the diversified pattern of livelihood act as a locked door for them and it is to be opened by the key word of literacy. The government has to implement certain policies to make their livelihood stronger by enacting educational importance.
- The second observation is that non literate women can be given financial supports

according to their livelihood pattern in our region. They should be protected against the private money lenders and awareness to be given.

- Income and Expenditure habits are practically down to earth from the results. Hence it has to be modulated and near future the importance of health responsiveness is to be set.

Conclusion

Non illiterate women are assets of our economy and are mostly involved in informal sector of urban and rural economy. They have diversified and unstructured sources of income due to their irregular and seasonality of livelihood pattern. The common areas of interest for earning are daily wage labourers, small scale business including vending; and household workers. The amount of family income largely depends on ethnic background, working hours, nature and seasonality of works. Among other, there is a significant impact of education and working hour on household income. It is fact that large numbers of non literate women are contributing to informal income to boost the economy. They have poor accessed of modern banking and financial, in many cases, policies discouraged them for providing credit facilities. However the government has to revise policies and working mechanism to persuade for development process.

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AN ASSESSMENT OF THE PROBLEMS & PROSPECTS OF INTERNATIONAL CONTAINER TRANSSHIPMENT TERMINAL (ICTT), KOCHI

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Abstract

Container terminal is a facility where the cargo containers can transhipped. The transhipment may be between container ships and land vehicles like trains or trucks. International Container Transshipment Terminals are major plays in the shipping industry. India is the major commodity exporters in this world. International Container Transhipment Terminal (ICTT) is playing very important role in shipping industries because exports gives major income for the country. ICTT commissioned in 2011 at Vallarpadam, Kochi with the announcement of huge prospects and benefits for the Indian exporters. But, there are some problems for the smooth functioning of the export/import process. The study is mainly tries to find out the major problems. The following are the important objectives of the study, to understand the customs procedural formalities of exports of goods through ICTT, to make a comparative study of performance of ICTT vis-à-vis other major ports in India, to study the influence of Terminal Handling Charge in ICTT on the export business done through ICTT and the same make comparison in respect with other ports in India and finally to know which commodity is exporting through ICTT in large quantity and to understand the different kinds of export incentives and promotion schemes India.

Keywords: ICTT, SEZ, THC, DPW, BOT, SSR

Introduction

International Container Transhipment Terminal (ICTT) locally known as Vallarpadam Terminal is a Container Transhipment. International Container Transhipment Terminal (ICTT) commissioned by Dr. Manmohan Singh, the Prime Minister of India on 11th February, 2011. International Transhipment Terminal is the only transhipment port in India and first Container Terminal operates in a Special Economic Zone (SEZ). This terminal is situated in the state of Kerala. It was on 16th February, 2005 Dubai Port World (DPW) signed an agreement with the Cochin Port Trust construct, develop and operate an International Container Transhipment Terminal – An India Gateway Terminal at Vallarpadam, Cochin. International Container Transhipment Terminal is presently being operated by Dubai Port World (DPW) which will operate it for 30 years after which control of this operation will come back to the Cochin Port Trust. DP World

is a global leader in Container terminal operation and large investments in ports along with the Indian coastlines. DP World has The Ports are the major players in the transport industry. ICTT is the first and only transhipment terminal in India. So there is tremendous potential to come up as the most preferred export destination in India.

Objectives of the Study

(1) To understand the customs procedural formalities of export goods through ICTT and to make a closer study of problems which is happening daily in ICTT.

(2) To make a detailed study of the commodity-wise export performance after ICTT starts and the influence of Terminal Handling Charges (THC) on export business.

(3) To make suggestions for more effective exports of commodities through ICTT.

Previous Study

Joseph .P.S , Researcher along with his Guide Manoj P.K (2015) has studied a commodity-wise exports through ICTT (2011-2014) based on the data from 2011 to 2014 and pointed out that many exporters still prefer other ports like Mangalore, Tuticorin and Chennai. There are many reasons for the poor performance of ICTT because of Higher THC, Strict Customs Procedural formalities, various expenses etc.

Relevance and Significance of the Study

The Main problems in ICTT are that the existing Terminal Handing Charge (THC) is very high at Cochin compared to other major ports in India. (Table 1 and Table II) Even though charges like THC, Labour Charge, and Transportation Charges are very higher at ICTT, the exporters can save transit-time of their exports as more mother vessels now berth at ICTT. Besides, the exporters can save freight charges as there is no need for transhipment of containers at Colombo, Singapore ICTT. Mother Vessels now voyage to direct destinations from ICTT. Similarly export containers can come down to ICTT from International Container Depot (ICD) Coimbatore, Bangalore etc., by using Vallarpadam rail line and four line roads. Most of the Clearing and Forwarding Agent's (C & F) offices, Steamer Agents Offices, the head office of Cochin Customs are even situated on Willington Island. There is 15 kilometres distance between Cochin Port Container Freight Station (CFS) and ICTT. So It is very inconvenient to transact containers to ICTT from Port CFS and for this purpose Ro-Ro Service is arranged for container movements between these two locations. Higher THC and other limitations as above have contributed to poor performance of ICTT in the recent past.

Table 1: Terminal Handling Charges (THC) (Rupees) at Major Ports – Import Containers

Import (Size/Type)	Cochin ICTT	Mangalore NMPT	Tuticorin PSTL	Vizag VCTPL	Chennai CCTL	Goa MPT
20'Dry	7451	5720	4400	4912	4500	8000
40'Dry HC	10555	6800	5700	7118	6500	11500
20' Reefer	14487	13300	4400	12400	10000	13500
40' Reefer	20197	15700	5700	18400	14500	15000
20' Hazardous Cargo	9313	5720	5500	6140	5625	8000
40' Hazardous Cargo	13194	6800	7125	8898	8125	11500

Source: Customer Advisory – DELMAS – (CMA CGM Group) Steamer Agent

Table II: Terminal Handling Charges (THC) (Rupees) at Major Ports – Export Containers

Import (Size/Type)	Cochin ICTT	Mangalore NMPT	Tuticorin PSTL	Vizag VCTPL	Chennai CCTL	Goa MPT
20'Dry	7451	5720	4400	4912	4500	6500
40'Dry HC	10555	6800	5700	7118	6500	8700
20' Reefer	14487	13300	4400	12400	10000	13500
40' Reefer	20197	15700	5700	18400	14500	15000
20' Hazardous Cargo	9313	5720	5500	6140	5625	6500
40' Hazardous Cargo	13194	6800	7125	8898	8125	8700

Source: Customer Advisory – DELMAS – (CMA CGM Group) Steamer Agent

The significantly higher THC at ICTT is one of the major problems for the slow growth of ICTT. While other reasons include labour problems at ICTT and inconvenience caused due to a distance of about 15 K, between ICTT and Cochin Port CFS which is situated on Willington Island. Major Clearing and Forwarding (C & F) Agents, Steamer Agents, Office of the Customs etc., also situated on Willington Island, Kochi at a distance of about 15 Kilo meter from ICTT.

So these offices are forced to vacate Willington Island so as to relocate themselves in the Vallarpadam area the place where ICTT is located.

Export through ICTT – An Analysis of the Trend in Performance till 2014

The total exports through ICTT; including commodity-wise break-up of such exports, during the period 2011-2014 is shown below in Table III. It is pointed out that there is a gradually falling trend in respect of the total exports of all commodities.

Table III: Commodity-wise exports through ICTT (2011-2014)

Particulars	2011	2011	2012	2012	2013	2013	2014	2014
	TEUs	Kilograms	TEUs	Kilograms	TEUs	Kilograms	TEUs	Kilograms
Cashew	3382	53015325	3580	55599340	4019	6226106	4456	67528172
Coffee	5203	93280518	4445	77234631	3690	65851320	3362	59494250
Coir Products	11068	87495306	11069	87404042	11247	87831247	11548	90433004
Coir Yarn	410	2686333	442	2863222	488	3244687	377	2403011
Cotton Goods	4042	16433427	4140	17286402	4718	18646786	6568	25522408
Jute Products	597	3950907	771	4935551	1018	6284211	879	5428979
Oleoresin	636	5373951	846	6254512	1058	7426881	1028	7705780
Sea Food	13406	155663261	12323	139476072	14785	164306440	14243	158127243
Spices	5880	69658811	6354	71762843	6488	72643257	6473	72212917
Tea	7922	83596551	7279	76035165	7145	74110744	7223	72015986
Cotton Yarn	2527	22629763	4710	43896339	3523	32547856	4217	39158949
Miscellaneous	39438	492919659	41587	521203054	38841	459166368	41558	479410194
Total	**94511**	**1086703812**	**97546**	**1103951173**	**97020**	**1054321903**	**101932**	**1079440893**

Source: Statistical Report of Cochin Chamber of Commerce & Industry, Cochin-3

In respect of the major commodities exported through ICTT, Sea food, Coir products, Cashew, Cotton products, Cotton Yarn have registered a generally increasing trend. It is noted that the overall trend is that declining. In view of the falling trend in the export through ICTT, the exact reasons for such all need to be identified so as to formulate suitable strategies for reversing this discouraging trend and to ensure enhanced performance of ICTT in future. This aspect, the researcher is dealt in PhD thesis of Impact of ICTT on the export of Coffee through Cochin Port Trust.

Major Problems at ICTT for Exporters

Customs formalities are very strict at ICTT when we compared to other major Ports. The Containers can only stack at ICTT after completing the Shipping Bill file and Customs Examination. Let Export order (permission to export the cargo) from Customs Supervisor is essential before the container can stack. But In the case of Mangalore and other southern ports of India, the Container can stack immediately at the terminal. Let Export is required only at the time when the containers are loaded into the vessels. Other problems in ICTT is that cargo to be examined and customs formalities cleared at least 6 hours before vessel berthing (Specific cut-off time is applicable). This is very inconvenient for the exporters. No Cut-off time is applicable in other southern Ports. After Cut-Off time, Special Service Request (SSR) costing Rs 2500/- plus Tax for 20' Container is charged at ICTT. No Cut-off time and hence no need for SSR in Mangalore and other ports. Cargo can be examined even after the berthing of the vessel. Most of the exporters are based in Tamil Nadu, Karnataka and other Southern State of India. So transportation charges would be higher if they export through ICTT located in Cochin. High sales tax and other charges on the one side, lengthy and cumbersome clearance procedures at the Check Post at Walayar near Palakkad on the other side are also a problems that effects ICTT. Frequent labour problems like strikes and lorry strikes are the most problems effects ICTT , Higher THC, Cargo clearance expenses, loading and unloading charges ,other miscellaneous expenses etc are very high at ICTT Cochin are also another major problems in ICTT. Higher THC at ICTT is one of the Major problems for the slow growth of ICTT, and inconvenience caused due to a distance of about 15 Km between ICTT and Cochin Port CFS. Because, offices of major Clearing and Forwarding Agents, Steamer Agents, customs Office are situated on Willington Island, Kochi at a distance of about 15 kilometre from ICTT.

Major Prospects at ICTT for Exporters

ICTT is the first and only transhipment container terminals in India, many exporters still prefer ICTT because transit-time can save. Mother vessel can berth at ICTT, so the container can move directly to the destination. The Union Cabinet relaxed Cabotagelaw under the Merchant Shipping Act, 1958 for transhipment of export-import containers at the Vallarpadam ICTT. The relaxation of Cabotage law, which protects domestic shipping lines by reserving coastal cargo for Indian ships is aimed at attracting more cargo to the ICTT. Coastal cargo is the cargo that moves from ports within India to ports within the country.

Every country has made provisions to protect their country-flagged vessels. Exports through ICTT are expected to pick up in future. There is Vallarpadam rail line with a total length of 9.3 KM in which 4.62 M through Vembanad Bridge which became the longest rail bridge in India. About 80% of the bridge is constructed over the backwaters of Vembanad Lake. There is also a 4 line road between Vallarpadam and Kalamassery (Ernakulam) to handle the heavy traffic of the terminal which is known as N.H 47. These facilities can boost the exporters to divert their cargoes to ICTT. Export and Import cargoes are handling in the area of Wharf. There are two wharves in Cochin Port Trust. One is Ernakulam Wharf and other is Mattanchery Wharf. The import cargoes stuffed in container is unloaded from the ships at berthing pointing in the area of ICTT. The export cargoes stuffed in container is loaded to the vessel at the berthing points in the area of ICTT. The cargoes stuffed in container is stored and kept ready in Container Freight Station (CFS), Public or Private Warehouses for loading to the ships on arrival. There are so many Private Container Freight stations are constructed and operating near Vallarpadam Container Terminal. Radioactive material detectors and vehicles scanners have been installed at ICTT. The Customs Department has launched an export processing centre and Gate Module at ICTT Vallarpadam for speedy export clearance.

The Gate Module was specifically developed for ICTT by the Directorate of Systems, Central Board of Excise and Customs (CBEC) for the efficient and fast clearance of containers. With the introduction of the Gate Module, all export container movement between the Container Freight Station (CFS) can now be tracked. The Customs Export Processing Centre (CEPC) provides a single window system for clearance and will help eliminate the unnecessary container traffic between CFS and ICTT ensuring speedy processing of export.

Suggestions for more effective utilization of ICTT and Its Enhanced Performance

Even though ICTT is the first and only one transhipment terminal in India, and all the facilities are coming under this International Terminal, many exporters especially from southern India prefer other ports like Mangalore, Tuticorin and Chennai. As already noted that, there are many reasons for the poor performance of the ICTT and other ports, in spite of many unique benefits of the former. In view of the foregoing discussions, a few suggestions are made hereunder for the better performance of ICTT from its present level which is not encouraging:

a) Simplifying the Procedural formalities: Procedures like examination by the customs authorities, obtaining their reports, and completion of other customs formalities, Let export order, Special Service Request (SSR) of Rs 2500/- per 20' container, are very lengthy and cumbersome at ICTT. This formalities must simplified by the Customs Authorities.

b) Terminal Handing Charges (THC) is very important for the exporters as they have to spend considerable amounts in the regard. Because of THC has a direct bearing on the operational efficiency and profitability

of the exports. So THC has to go down at ICTT so as to match with those in other ports like Tuticorin, Mangalore, Chennai, Goa, Vizag.

c) Various expenses related to loading and unloading and such miscellaneous charges being very high at ICTT, these need to be brought down.

d) It is appreciable of Kerala state government decision that to materialize the setting up of Walayar-Vallarpadam freight corridor so as to ensure hassle-free, fast, less expensive transit of export items through Kerala Boarder (Walayar). The present system of passing such export goods through Walayar Check-post involves higher cost. Lengthy waiting lines and high charges and undue delays.

e) More effective and frequent dredging of the port is to be ensured in a cost-effective manner so as to attract more mother vessels (large ships) to ICTT.

Given the positive features of ICTT, it has got tremendous potential to come up as the most preferred export destination in India. ICTT is a transhipment hub in India. By projecting the many International terminal facilities are arranged today at ICTT, exporters can use this terminal and save freight charge, transit –time. So It can bring back its lost customers, retain the existing customers and attract new customers into it. In such a case, the prospects of ICTT appear to be very bright in the days to come.

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AN ANALYTICAL STUDY ON THE LINK BETWEEN ENTREPRENEURSHIP AND ECONOMIC DEVELOPMENT

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Abstract

This study is an attempt to analyse the possible link between entrepreneurship and economic development in the case of India. This link has been studied extensively for developed countries, but less so for developing countries. Using the GEM-model as a reference, we expect declining rates of entrepreneurship, as economic development opens up employment possibilities decreasing the number of necessity entrepreneurship. This pattern, however, is not found in the Indian case. Rather, entrepreneurship appears to be an important driver of recent economic growth. This can be explained by the fact that India is very much a service-based economy that facilitates small-scale firms. Although the level of entrepreneurship is increasing over time, the quality of the small firms remains rather stable; the share of registered firms remains equal over time. Given the importance of high-quality entrepreneurship for economic development, it seems that increasing the quality of entrepreneurship should be the main focus of policy measures.

Keywords: E*ntrepreneurship, Liberalisation, Post-liberalisation Period, Information and Communication Technology, Micro, Small, and Medium Enterprises (MSMEs), Economic Development*

Introduction

Before 1991, Indian business success was a function of ambition, licenses, government contacts, and an understanding of the bureaucratic system. Decisions were based on connections, rather than the market or competition. Business goals reflected a continuation of the 'Swadeshi' movement, which promoted import substitution to attain economic freedom from the West. Pre-1991 policies were inward looking and geared towards the attainment of self-reliance. During this era, entrepreneurship was subdued, capital was limited and India had very few success stories. As well, society was risk averse and the individual looked primarily for employment stability.

In 1991, the Indian government liberalized the economy, thus changing the competitive landscape. Family businesses, which dominated Indian markets, now faced competition from multinationals that had superior technology, financial strength and deeper managerial resources. Thus, Indian businesses had to change their focus and re-orient their outlook outward. A few existing Indian business families adapted to

the new economic policy while others struggled. Importantly, a new breed of business was born, one that focused on ICT (Information and Communication Technology) and created wealth for owners and employees.

For the old business houses, success had come from the close-knit joint family structure that fosters family values, teamwork, tenacity and continuity. Under this structure, generations lived and worked together under one roof, reaffirming the Weberian values and trust that have built successful businesses. Wealth from the businesses supported the joint family by providing a social safety net for members. In the structure, businesses and families were intertwined though they were also distinct entities with separate rules. Hence, survival of the family became synonymous with the survival of the business.

Liberalization, however, changed the very nature of the joint family. If large Indian businesses were to succeed, the family would have to re-orient itself to compete in a global, competitive environment. Post liberalization, IT businesses succeeded because they were customer focused and professionally managed. The old, family-managed businesses, which formed the backbone of the economy, needed to evolve and become more institutional, if they were to extend their life cycle (Vishal Jain., 2011).

Objectives of the Study

1. The main objective of this study is to analyse the link between entrepreneurship and economic development in the case of India.
2. Another objective of the study is to assess the contributions Micro, Small, and Medium Enterprises (MSMEs) to the country's inclusive growth and job creation.
3. Finally this paper also tries to assess the role of rural entrepreneurship in the economic and social development of the country.

Methodology of the Study

This is a descriptive study and primarily secondary data has been used for preparing this paper. The secondary information has been collected from various publications, such as books, journals, periodicals, conference paper, working papers and websites.

How the **competency of entrepreneurs affect the economic growth?**

Entrepreneurship is normally driven by individuals with a strong desire to succeed by developing their concept/ vision into a profit making business. Whilst the main driving force is 'Profit', with a capital P they also seek to have control of their own lives and are normally people who resent being told what to do. To be successful the average entrepreneur has to leave the "comfort zone", and take many risks. Borrowing start-up capital for instance normally involves providing the lender with your entire assets including the equity on your home as

security. The entrepreneur's risk taking is what makes the 'commercial world' go around and provides jobs for the more faint hearted wimps who like to be told when and how they should work. Most people need direction and don't like to leave the cosy security of a "safe job", that's an oxymoron if ever there was one. The entrepreneurial businessman in other words provides jobs, wealth and revenue for the government by way of taxes. The role of the entrepreneur is absolutely vital in the 'cut and thrust' of the modern competitive world of commerce and trading.

An entrepreneur can be regarded as a person who has the initiative skill and motivation to set up a business or enterprise of his own and who always looks for high achievements. He is the catalyst for social change and works for the common good. They look for opportunities, identify them and seize them mainly for economic gains. An action oriented entrepreneur is a highly calculative individual who is always willing to undertake risks in order to achieve their goals. Economic development essentially means a process of upward change whereby the real per capita income of a country increases over a period of time. Entrepreneurship has an important role to play in the development of a country. It is one of the most important inputs in economic development. The number and competence of entrepreneurs affect the economic growth of the country.

The economic history of the presently advanced countries like USA, Russia and Japan supports the fact that economic development is the outcome for which entrepreneurship is an inevitable cause. The crucial and significant role played by the entrepreneurs in the economic development of advanced countries has made the people of developing and under developed countries conscious of the importance of entrepreneurship for economic development. It is now a widely accepted fact that active and enthusiastic entrepreneurs can only explore the potentials of the countries availability of resources such as labour, capital and technology.

The role of entrepreneurs is not identical in the various economies. Depending on the material resources, industry climate and responsiveness of the political system, it varies from economy to economy. The contribution of entrepreneurs may be more in favourable opportunity conditions than in economies with relatively less favourable opportunity conditions.

The entrepreneur who is a business leader looks for ideas and puts them into effect in fostering economic growth and development. Entrepreneurship is one of the most important inputs in the economic development of a country. The entrepreneur acts as a trigger head to give spark to economic activities by his entrepreneurial decisions. Entrepreneur plays a pivotal role not only in the development of industrial sector of a country but also in the development of farm and service sector. For the purposes of this estimate, we will define an entrepreneur as anyone who at any point in his or her life has started or owned a

business. One entrepreneur can start more than one business and one business can be started by more than one entrepreneur coming together.

India has one of the fastest growing economies in the world. It also has a significant youth population. So why doesn't the country have a substantial number of entrepreneurs? A 2011 Gallup study of 20 economic entities in Asia showed that India ranked in the bottom quartile on several important indicators of a well-functioning entrepreneurial ecosystem. Entrepreneurs have consistently contributed to the country's vibrant growth-oriented economy since its economic liberalization in 1991. Entrepreneurship has become increasingly important in sustaining India's rapid growth.

Micro, Small, and Medium Enterprises (MSMEs) also contribute to the country's inclusive growth and job creation. The Ministry of MSMEs estimates that between 2007 and 2010, the number of working MSMEs grew at a rate of 4.51 per cent annually, while the number of people employed in the sector grew by 5.29 per cent annually, and production of the sector grew at 11.48 per cent annually. This sector contributed 8.72 per cent of India's GDP in 2009. But as the Gallup study shows, there's significant room for improvement.

Gallup's framework for entrepreneurial ecosystems stresses the mutual interplay between *individual variables* (for example, talent and attitude) and *contextual variables* (for example, the role of government and access to information). It explicitly captures the role of human motivations, perceptions, and behaviors in explaining entrepreneurial decision making as well as the external contextual factors that support entrepreneurship and individual entrepreneurial traits.

About the only official figure we have is the Ministry for Micro, Small and Medium Enterprises (MSME) statement first made sometime in 2007 that there are 13 million registered MSME's in the country. It is a fact that for every small and micro business that has registered with the government, there are at least 15 that have not registered. These include businesses running in small villages, your local vegetable vendor, the local taxi business owner and so on. So the total number of small medium and micro entrepreneurs in the country would be approximately 200 millions. The registrar of companies could give numbers on the number of companies registered. Here, one large group typically register many companies for tax and other reasons. So, that number is not a good indicator for the study. Therefore it is assumed that only 5 per cent of all entrepreneurs own/run large businesses. That is 95 per cent of all businesses are small medium or micro. Therefore, the number of large business entrepreneurs in the country is around 10 million, slightly lower than the number of registered MSMEs. Adding up all these, the total number of entrepreneurs in India is in the range of about 200 million. Out of a

population of 1.2 billions, this is 18 per cent of the population.

India was second among all nations in Total Entrepreneurship Activity as per the Global Entrepreneurship Monitor Report of 2002. But after several years of data, India appears to have a TEA level rather close to the world average. India is ninth in the Global Entrepreneurship Monitor (GEM) survey of entrepreneurial countries. It is highest among 28 countries in Necessity based entrepreneurship, while 5th from the lowest in opportunity based entrepreneurship. The liberalization, which was started in 1991, and the Information Technology boom of the mid-late 90's, has been significant factors, leading to a wave of entrepreneurship sweeping through the country. Indians have entrepreneurial capacity. However the society and government are not very encouraging towards entrepreneurship. To a large extent, the Indian society is risk averse. People usually seek secure and long-term employment, such as government jobs. The physical infrastructure needs to be improved. Social Attitudes, lack of capital, inadequate physical infrastructure and lack of government support are major factors of hindrance. India is the tenth largest economy in the world (ranking above France, Italy, the United Kingdom, and Russia) and has the second largest GDP in the entire continent of Asia. It is also the second largest among emerging nations. The liberalization of the economy in the 1990s has paved the way for a huge number of people to become entrepreneurs. Over the years India and China have followed opposing strategies for development. While China's growth has been fueled by the heavy dose of foreign direct investment, India has followed a much more organic method and has concentrated more on the development of the institutions that support private enterprise by building a stronger infrastructure to support it.

Its corporate and legal systems operate with greater efficiency and transparency than do China's. The Government has encouraged entrepreneurship by providing training and also the facilities to succeed, particularly in the rural areas. One style of innovation that really works in a country as large and diverse as India, is grassroots innovation: this includes inventions for a milieu that is quintessentially Indian. Moreover, in India, the post-liberalization and globalization era has brought with it a growing middle class – roughly estimated to be 350-400 million – and rising disposable incomes. This presents a huge potential, which if tapped can be a veritable gold mine. Entrepreneurs can make the best of this by catering to various demands of this segment. India, with its abundant supply of talent in IT, management, and R&D, has become the hot bed of outsourcing of services from all parts of the globe where companies can reduce their costs, but not their quality. In terms of improvement, there needs to be an increase in the quality and quantity of VC / Angel Investors in India. Also, the Governments need to still continue reducing the administrative burden on entrepreneurs, and

coordinate among their agencies to ensure that the necessary resources are directed where they are needed. The physical infrastructure needs to be improved. Socially, the Indian society is adapting to a more risk friendly environment and also looking for jobs in the private sector.

The employability of management graduates in India has declined in the past five years, as only 21 per cent of MBAs surveyed are 'employable', a study has said. According to the MBAUniverse.com - MeriTrac employability study 2012, which covered 2,264 MBAs from 29 cities and 100 B-Schools, beyond the Top 25, only 21 per cent are employable. The previous study of 2007 by Meri Trac had placed employability index at 25 per cent. However, the number of MBA seats in India has grown almost four fold — from 94,704 in 2006-07 to 3,52,571 in 2011-12 — resulting in a five-year compounded annual growth rate of 30 per cent, but their employability rates have fallen. The students were tested for verbal ability, quantitative ability and reasoning by using internationally standardised tests on behalf of recruiting companies. The index of employability, at 21 per cent mark leaves scope for improvement considering that organisations hire from this talent pool for strategic roles and this is the managerial pool that companies bank on, the "This report clearly brings out the employability gaps across various competencies and highlights the need for scientific examinations and tests to align the candidate skills to employability metrics," Overall average percentage score obtained by MBAs in verbal ability, quantitative ability and reasoning was 52.58 per cent, 41.17 per cent and 37.51 per cent respectively.

While performance on verbal ability seems to be satisfactory, reasoning is an area where there is scope for improvement. Considering that the elements of the reasoning test are crucial to making sound management decisions, this is a result which warrants closer attention. D. Purandeswari, Minister of State for Commerce and Industries, while giving away the CII-Business Line Emerging Entrepreneur Award for 2012 to seven entrepreneurs has stated the significance of entrepreneurship as a catalyst for growth in the country's economy is invaluable. India is seen as a land of ideas and this must be turned into a land of opportunities,. Small enterprises have to be nurtured and provided an opportunity to get bigger. Quoting the Planning Commission, "If we have to create 10 crores jobs over the next 10 years, encouragement of entrepreneurship and self-employment is vital to meeting such goals", this seeks more Government support and encouragement for small and medium enterprises and entrepreneurs. This can be done by creating an environment conducive for their growth, giving access to funds, and working towards cluster development. A number of suggestions have been made to the Government to accelerate the growth. These include extending access to finance, bridging funding gaps, and making initial public offer norms flexible for their entry and creating a

Climate Tech Fund to encourage companies go green. Praising today's youth who are self-driven, the spirit of entrepreneurship is vibrant in the South. "If India is keen to create 10-15 million jobs a year over the next 15 years, there is a need to create the environment for youth to take to entrepreneurship and then scale up. Stressed the need for vigorous promotion of entrepreneurship at a time when economic growth was faltering at sub-five per cent level. There was a need for simplifying regulations, given the fact that the country had been ranked 132 by the World Bank when it came to starting businesses. The situation needs to be dramatically improved and the role of entrepreneurs should not be confined to setting up enterprises, and they should strive to build capacity, generate jobs and income as well. According to her, the current state of under-development was mainly due to lack of adequate entrepreneurs. "The problem is that we do not stretch ourselves enough. But the current entrepreneurs are ready to take the plunge."

According to the World Bank's report "Doing Business 2012: Doing Business in a More Transparent World," India ranks 182 out of 183 countries on enforcing contracts. The time needed to enforce contracts in India is almost triple the average among Organisation for Economic Co-operation and Development (OECD) countries and the cost of doing so is almost double the OECD average. Indian entrepreneurs, often strapped for cash and time, are almost powerless when business partners cheat them. Perhaps this is why Gallup data indicate that 83 per cent of current business owners say they are the sole owner of their business, and only 16 per cent of Indian adults believe they can find someone outside their own family to be a trusted business partner. The lack of judicial infrastructure on enforcement does little to protect the trusting relationship between entrepreneurs and business partners or between entrepreneurs and customers. Lack of trust inhibits collaboration and significantly increases the risk an entrepreneur takes, ultimately slowing the growth of the MSME sector. Limited access to training and funding, difficulties the government poses to starting a business, and lack of trusted business partners are all likely to have negative effects on the optimism and determination of Indian entrepreneurs. Despite these barriers, Indian entrepreneurs still rank fairly high on these individual characteristics compared with residents of other countries in Asia, further indicating that they are resilient and possess the innate talents to succeed if given the necessary support. In addition, India has a large youth population, which tends to be more optimistic and willing to take risks compared to the older population. The 2011 national census shows that more than 50 per cent of the population of India is younger than 25. Factoring the high percentage of young people in India with India's reputation as one of the fastest growing markets in the world, there are plenty of reasons to believe in a promising entrepreneurial future for the country.

Economic Development

Entrepreneurs who are business leaders look for ideas and puts them into effect in nurturing economic growth and development. They play the most important role in the economic growth and development of Indian economy. An entrepreneur plays a pivotal role not only in the development of industrial sector of a country but also in the development of farm and service sector. Entrepreneurship helps in the process of economic development in various ways

Growing unemployment particularly educated unemployment is the problem of the nation. The available employment opportunities can cater only 5 to 10 per cent of the unemployed. Entrepreneurs provide instant large-scale employment to the unemployed which is an unending problem of India. With the setting up of more and more units by entrepreneurs, both on small and large-scale numerous job opportunities are created for others. Small entrepreneurs provide self employment to artisans, technically qualified persons and professionals. As these enterprises grow, they keep providing direct and indirect employment opportunities to many more. Directly, self employment as an entrepreneur and indirectly by starting many industrial units they offer jobs to millions. In this way, entrepreneurs play an effective role in reducing the problem of unemployment in the country which in turn clears the path towards economic development of the nation. Thus entrepreneurship is the best way to fight the evil of unemployment.

A study titled 'Job Trends Across India in 2012' released by the industry body Associated Chambers of Commerce and Industry of India (Assocham) has stated that **Job generation during 2012 saw a 21 per cent decline across various sectors of the economy between January and mid-December.** "A total of over 5.3 lakh jobs were generated during the aforesaid period across India i.e. over 2.8 lakh jobs in first half of the year and over 2.4 lakh jobs during July-December 2015.

Information technology (IT) topped the group with over 2.1 lakh jobs generated in the sector between January-December 15, 2012 across the country as compared to the same period of last year. Academics and education ranked second with over 34,500 jobs generated in the sector followed by insurance (over 27,100 jobs) and banking (24,500). SSI Sector in India creates largest employment opportunities for the Indian populace, next only to Agriculture. It has been estimated that 100,000 rupees of investment in fixed assets in the small-scale sector generates employment for four persons.

The small scale industries sector contributes significantly to the manufacturing output, employment and exports of the country. It is estimated that in terms of value, the sector accounts for about 45 per cent of the

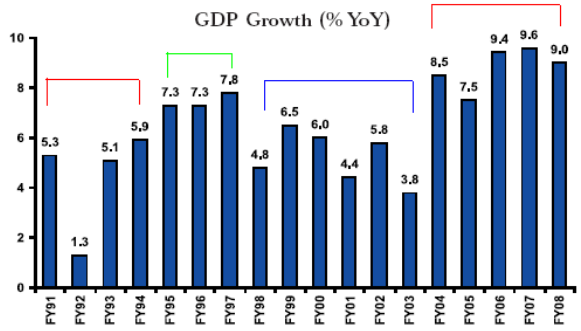
manufacturing output and 40 per cent of the total exports of the country. The sector is estimated to employ about 59 million persons in over 26 million units throughout the country. The production of SSI unit in India was Rs 84,413 crore in 1992-93, which increased and reached up to Rs. 9,82919 crore in 2009-10. The production of SSI units shows continually raising trend during the study period. During 1992-93 SSI units shows 4.71 growth rates in production which has gone up to 11.59 percent in 2009-10. The production of Small Scale Industries increased with an annual average growth rate of 15.15 percent during 1992-93 to 2009-10. The production of SSI shows highest growth rate of 42.49 per cent growth in 2006-07. The total employment from SSI sector in the country as per the third All India Census of SSIs conducted with the reference year of 2001-02 was 249.33 lakh numbers. Units operated with fixed premises are treated as SSIs. As per the estimates compiled for the year 2005-06 the employment was 294.91 lakh persons in SSI sector.SSI Sector plays a major role in India's present export performance. 45 to 50 percent of the Indian Exports is contributed by SSI Sector. Direct exports from the SSI Sector account for nearly 35 percent of total exports. Besides direct exports, it is estimated that small-scale industrial units contribute around 15 percent to exports indirectly.

It is a fact that, internationally some countries are wealthy, some countries are not wealthy and some countries are in-between. Under such circumstances, it would be difficult to evaluate the performance of an economy. Performance of an economy is directly proportionate to the amount of goods and services produced in an economy. Measuring national income is also important to chalk out the future course of the economy. It also broadly indicates people's standard of living.

National Income consists of the goods and services produced in the country and imported. The goods and services produced are for consumption within the country as well as to meet the demand of exports. The domestic demand increases with increase in population and increase in standard of living. The export demand also increases to meet the needs of growing imports due to various reasons. An increasing number of entrepreneurs are required to meet this increasing demand for goods and services. Thus entrepreneurship increases the national income.

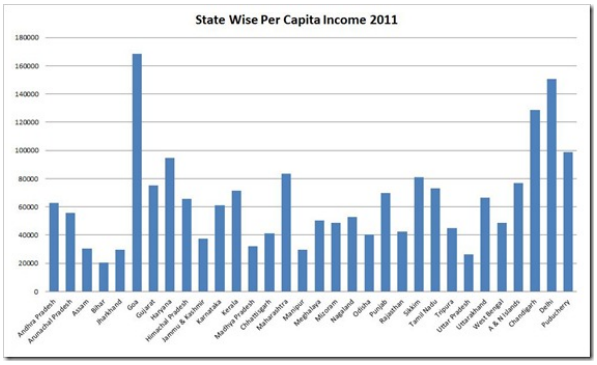
Entrepreneurs are always looking out for opportunities. They encourage effective resource mobilization of capital and skill, bring in new products and services and develops markets for growth of the economy. In this way, they help increasing gross national product as well as per capita income of the people in our nation. Increase in gross national product and per capita income of the people in a country, is a sign of economic growth.

Figure on GDP Growth Rate



Source:http://www.google.co.in/search?q=table+on+India's+GDP+growth&hl=en&tbm=isch&tbo=u&source=univ&sa=X&ei=7yVYUbiVJInVrQevpYHwCQ&sqi=2&ved=0CFMQsAQ&biw=1366&bih=667

Regional imbalances in a country may be natural due to unequal distribution of natural resources and/or man-made in the sense of neglect of some regions and preference for others for investment and infrastructural facilities. In India, apart from uneven distribution of geographical advantages, historical factors have also contributed to regional inequities. India's successive Five Year Plans have stressed the need to develop backward regions of the country. In promoting regional balanced development, public sector enterprises were located in backward areas of the country during the early phase of economic planning. In spite of pro-backward areas policies and programmes, considerable economic and social inequalities exist among different States of India, as reflected in differences in per capita State Domestic Product. While income growth performance has diverged, there is welcome evidence of some convergence in education and health indicators across the states. Entrepreneurs promote development of industries. They help to remove regional disparities by industrializing rural and backward areas. The growth of industries and business in these areas lead to a large number of public benefits like road transport, health, education, entertainment, etc. They help to reduce the problems of congestion, slums and population in cities by providing employment and incomes to them. They help to improve the standard of living in sub-urban and rural areas.



Per Capita Income of Various Indian States: According to the **latest figures released by Government** – Goa leads the country with per capita income of Rs. 1,92,652/-, while Bihar has the lowest with a per capita income of only Rs. 24,681/-. An average Goan earns 6 times more than an average Bihari!. As per latest figures (2012), Delhi comes in second after Goa with PCI of Rs. 1,75,812 followed by Chandigarh (1,28,634 – 2011) & Haryana (1,09,227).

State Wise Per Capita Income Comparison

Sl. No	State/UT	2010-11 (Rupees)	2011-12 (Rupees)	2011-12 % Growth
1	Andhra Pradesh	62912	71540	13.7
2	Arunachal Pradesh	55789	62213	11.5
3	Assam	30569	33633	10
4	Bihar	20708	24681	19.2
5	Jharkhand	29786	31982	7.4
6	Goa	168572	192652	14.3
7	Gujarat	75115	N.A	N.A
8	Haryana	94680	109227	15.4
9	Himachal Pradesh	65535	73608	12.3
10	Jammu & Kashmir	37496	41833	11.6
11	Karnataka	60946	69493	14
12	Kerala	71434	83725	17.2
13	Madhya Pradesh	32222	N.A	N.A
14	Chhattisgarh	41167	46573	13.1
15	Maharashtra	83471	N.A	N.A
16	Manipur	29684	32284	8.8
17	Meghalaya	50427	56643	12.3
18	Mizoram	48591	N.A	N.A
19	Nagaland	52643	56116	6.6
20	Odisha	40412	46150	14.2
21	Punjab	69737	78171	12.1
22	Rajasthan	42434	N.A	N.A
23	Sikkim	81159	N.A	N.A
24	Tamil Nadu	72993	84058	15.2
25	Tripura	44965	50750	12.9
26	Uttar Pradesh	26355	29417	11.6
27	Uttarakhand	66368	75604	13.9
28	West Bengal	48536	55864	15.1
29	A & N Islands	76883	82272	7
30	Chandigarh	128634	N.A	N.A
31	Delhi	150653	175812	16.7
32	Puducherry	98719	95759	-3
All-India Per Capita Net National Income(2004-05 base)		53331	60972	14.3

http://trak.in/tags/business/2012/03/30/average-per-capita-income-indian-states/

India's average Per Capita Income is Rs. 60,972/-, which is one of the lowest in the world. Some European Countries have over 50 times per capita income as compared to India!

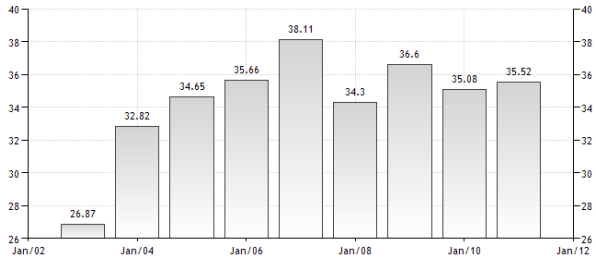
Entrepreneurs help to remove regional disparities through setting up of industries in less developed and backward areas. The growth of industries and business in these areas lead to a large number of public benefits. Setting up of more industries leads to more development of backward regions and thereby promotes balanced regional development. When the industries are concentrated in selected cities, development gets limited to these cities. When the new entrepreneurism grow at a faster rate, in view of increasing competition in and around cities, they are forced to set up their enterprises in the smaller towns away from big cities. This helps in the development of backward regions.

Economic power is the natural outcome of industrial and business activity. Industrial development normally leads to concentration of economic power in the hands of a few individuals which results in the growth of monopolies. In order to redress this problem a large number of entrepreneurs need to be developed, which will help reduce the concentration of economic power amongst the population. Thus it helps in weakening the harmful effects of monopoly. Entrepreneurs play a vital role in achieving a higher rate of economic growth. Increase in the standard of living of the people is a characteristic feature of economic development of the country. Entrepreneurs play a key role in increasing the standard of living of the people by adopting latest innovations in the production of wide variety of goods and services in large scale that too at a lower cost. This enables the people to avail better quality goods at lower prices which results in the improvement of their standard of living.

An entrepreneur is a person who always looks for changes. Apart from combining the factors of production, he also introduces new ideas and new combination of factors. He always tries to introduce newer and newer technique of

production of goods and services. An entrepreneur brings economic development through innovation. Entrepreneurship also helps in increasing productivity and capital formation of a nation. In short, the development of the entrepreneurship is inevitable in the economic development of the country. The Role played by the entrepreneurship development can be expressed as economic development is the effect for which entrepreneurship is a cause. Entrepreneurs promote capital formation by mobilizing the idle savings of our citizens. They employ resources for setting up their enterprises. Such types of entrepreneurial activities lead to value addition and creation of wealth, which is very essential for the industrial and economic development of India. It stimulates impartial redistribution of wealth and income in the interest of the country to more people and geographic areas, thus giving benefit to larger sections of the society. Entrepreneurial activities also ensure equitable distribution of income and wealthy by inculcating the spirit of entrepreneurship amongst people thereby providing them self employment with limited resources.

The Gross capital formation (% of GDP) in India was last reported at 35.52 in 2011, according to a World Bank report published in 2012. Gross capital formation (formerly gross domestic investment) consists of outlays on additions to the fixed assets of the economy plus net changes in the level of inventories. Fixed assets include land improvements (fences, ditches, drains, and so on); plant, machinery, and equipment purchases; and the construction of roads, railways, and the like, including schools, offices, hospitals, private residential dwellings, and commercial and industrial buildings. Inventories are stocks of goods held by firms to meet temporary or unexpected fluctuations in production or sales, and work in progress. According to the 1993 SNA, net acquisitions of valuables are also considered capital formation. This page includes a historical data chart, news and forecasts for Gross capital formation (% of GDP) in India.



Source: http://www.tradingeconomics.com/india/gross-capital-formation-percent-of-gdp-wb-data.html

Entrepreneurs earn valuable foreign exchange through increased exports. India has around $295 billion as foreign exchange reserve. They produce goods and services in large scale for the purpose earning huge amount of foreign exchange from export. Entrepreneurs help in promoting a country's export-trade, which is an important ingredient of economic development. They produce goods and services in large scale for the purpose earning huge amount of foreign exchange from export in order to combat the import dues requirement. Hence import substitution and

export promotion ensure economic independence and development.

India's exports, which had been growing at a compounded annual growth rate of about 20 per cent in the last few years, have dipped by 4-5 percentage points so far during this year. According to ASSOCHAM study India's exports target of USD 500 billion by 2013-14 is unlikely to be achieved as the exports may not even touch last year's level of about USD 304 billion in the current fiscal due to weak demand in global markets,. "If the present scenario in global economy continues, merchandise exports for the current fiscal may even decelerate well below USD 300 billion," During 2011-12, exports grew 21% at USD 303.7 billion over the previous year. As against earlier projections, the economic situations in major markets like the US and Europe have not improved. "This is a matter of worry. The government must work out some urgent measures to arrest the decline. sectors like gems and jewellery, carpets, leather and handloom would face major challenges during the current fiscal. There is a need to identify and undertake certain short- as well as medium-to-long-term measures to grow our exports. In the medium-to-long term, there is a need to change thought processes. Exporters should look to adopt a cluster-based approach to help achieve economies of scale and reduce the unit cost of production. There is a need to create the right environment for attracting high-technology-based manufacturing industries.

Entrepreneurship Induces Backward and Forward Linkages

Entrepreneurs like to work in an environment of change and try to maximise profits by innovation. When an enterprise is established in accordance with the changing technology, it induces backward and forward linkages which stimulate the process of economic development in the country. Linkages are input-output relationships between firms or industrial sectors in the same economy. A firm purchasing inputs from a local supplier is an example of a backward linkage, while a firm selling intermediate inputs to another firm creates a forward linkage. The importance of such linkages with the local economy for economic development has long been recognized in the economics literature. For example, Marshall (1920) argues that input-output relationships between firms are one of the advantages of localized industry, since ‘‘subsidiary trades grow up in the neighborhood, supplying [the firm] with implements and material, organizing its traffic, and in many ways conducing to the economy of its material’’ (271).

In an early view, Hirschman (1958) discusses the importance of linkages between sectors in an

economy in the context of his strategy of unbalanced growth for developing countries. At the heart of this strategy is the suggestion that developing countries should aim at generating imbalances in demand and supply in order to achieve continuing growth. An important part of the unbalanced growth strategy is the potential to develop linkages between sectors in which a leading sector, through linkages with a follower sector, may foster the development of the latter industry.

The issue of local linkages has regained importance in the last decades of the 20th century due to the increasing globalization of the world economy, where many inputs and outputs can be internationally traded, and therefore, inputs can easily be sourced locally or abroad. Given the increasing significance of foreign direct investment and multinational companies in many developed and developing countries alike, a particular focus of interest has been on inter firm linkages between foreign multinationals and indigenous firms, which to some extent echo the role of linkages in Hirschman's earlier work.

Whereas in Hirschman's concept of unbalanced growth ''leading sectors'' (which have the highest potential for linkages creation) induce growth in other sectors, the more recent view on multinationals largely sees these as ''leading firms'' inducing growth in local enterprises. Hence one can think of the former concept as inter sectoral linkages, while the latter are inter firm linkages. Essentially, the inter firm linkage is at the heart of the Hirschman-style inter sectoral linkage, since a sector is composed of a number of firms. The concept of inter firm linkages is a much wider and richer concept, however, and the inter sectoral linkage leading to economic development is only one of many effects of inter firm linkages. See also appropriate technology and foreign direct investment; footloose production; foreign direct investment and labor markets; foreign direct investment under monopolistic competition; foreign direct investment under oligopoly; location theory; multinational enterprises; technology spillovers Contributions of **Entrepreneurs to Overall Development**

Entrepreneurs act as catalytic agent for change which results in chain reaction. Once an enterprise is established, the process of industrialisation is set in motion. This unit will generate demand for various types of units required by it and there will be so many other units which require the output of this unit. This leads to overall development of an area due to increase in demand and setting up of more and more units. In this way, the entrepreneurs multiply their entrepreneurial activities, thus creating an environment of enthusiasm and conveying an impetus for overall

development of the area. Prof. Irma Glicman Adelman, an Irish Economist working in California University at Berkely, in her research work on 'Development Over Two Centuries', which is published in the Journal of Evolutionary Economics, 1995, has identified that India, along with China, would be one of the largest economies in this 21st Century. She has stated that the period 1700-1820 is the period of Netherlands (Holland) , the period 1820-1890 is the period of England, the period 1890-2000 is the period of America and this 21st Century is the century of China and India. World Bank has also identified India would be a one of the leading players of this century after China. India will be third largest economy after USA and China. India will challenge the Global Economic Order in the next 15 years. India, the 10th largest economy (with the GDP of $1.946 trillion) will overtake Italian economy(GDP $2.198 trillion) in 2015, England economy(GDP $2.480 trillion) in 2020, Japan economy(GDP $5.866 trillion) in 2025 and USA economy (GDP $15.676 trillion) in 2050 (China with $8.24 trillion already overtook Japanes economy in 2012 and will overtake USA economy in 2027). India has the following advantages compared with other economies. India is 4th largest GDP in the world in terms of Purchasing Power. India is third fastest growing economy in the world after China and Vietnam. Service sector contributes around 57 per cent of GDP. The share of agriculture is around 14 per cent and Manufacture is 26 per cent in 2010-11. This is a character of developed countries. Expected GDP growth rate is 8 -9 per cent shortly (It has come down from 9.2 per cent in 2006-07 to 6.2 per cent during 2008-09 due to recession. It is only a temporary phenomenon). India has $295 billion as Foreign Exchange Reserve as on today. India had just $1 billion as Foreign Exchange Reserve when it opened its economy in the year 1991. The size of the Indian economy is 4th largest and India ranks 13th among the richest countries in the world, she has the highest number of representatives among the countries in the top 20 list of world's richest persons.

Economic Significance of Rural Entrepreneurs in India

The development of rural entrepreneurs is a complex problem which can be tackled by the social, political and economic institutions. The sooner they are established the better it would be for the entrepreneurial development in the rural sector and the economic growth of the country. Rural entrepreneurship is labor intensive and provides a clear solution to the growing problem of unemployment. Development of industrial units in rural areas through rural entrepreneurship has high potential for employment generation and income creation.

Rural entrepreneurship can fill the big gap and disparities in income rural and urban people. Rural entrepreneurship will bring in or develop infrastructural facilities like power, roads, bridges etc. It can help to check the migration of people from rural to urban areas in search of jobs. Rural entrepreneurship can dispel the concentration of industrial units in urban areas and promote regional development in a balanced way. The age-old rich heritage of rural India is preserved by protecting and promoting art and handicrafts through rural entrepreneurship. The growth of rural entrepreneurship can reduce the social evils like poverty, growth of slums, pollution in cities etc.

Rural entrepreneurship can awaken the rural youth and expose them to various avenues to adopt entrepreneurship and promote it as a career. Rural entrepreneurship will also increase the literacy rate of rural population. Their education and self-employment will prosper the community, thus increasing their standard of living. Many businesses start as one person's idea. The creator is often an entrepreneur who spots a gap in the market or a commercial opportunity. S/he turns the idea into a marketable product or service. There are four main types of business: manufacturing, wholesale, retail and service. For example, Simon Woodroffe opened up his first Yo Sushi restaurant by copying an idea he saw in Japan. The business grew into a chain of successful restaurants with a novel approach to serving Japanese food and drink. Henry John Heinz's first product in 1869 was horse-radish, followed by pickles, sauerkraut, and vinegar. All were delivered by horse-drawn wagons to grocers in and around Pittsburgh. Heinz developed many of the world's best known branded products e.g. tomato ketchup, baked beans, and baby foods. Today's small business sector creates many of the new ideas and innovations future generations will take for granted e.g. ingenious website designs, clockwork radios. Small businesses are vital to the success of the economy. Not only as they provide the success stories of the future, but also because they meet local needs (e.g. hairdresser, financial consultant, emergency plumber). They serve the requirements of larger businesses e.g. for photography services, printed stationery, catering and routine maintenance. Of course, you don't have to set up your own enterprise to be enterprising. Being entrepreneurial simply means developing the right skills, attitudes and initiatives to make an innovative contribution to an organisation**.**

The development of the micro, small and medium enterprises (SME) sector is on the priority of Government Agenda. As per the Results-Framework Document (RFD) for Ministry of

Micro, Small and Medium Enterprises (2012-2013), the Mission of the government is to – "Promote growth and development of globally competitive Micro, small and Medium Enterprises, including Khadi, Village and Coir industries, in cooperation with concerned Ministries / Departments, State Governments and other stakeholders by providing support to existing enterprises and encouraging creation of new enterprises. To endeavor the target cumulative growth of 40%-50% in the number of registered enterprises by the end of 12th Plan and enhance this sector's contribution to GDP from the present 8% to 10% by the end of 12th Plan."

The role of micro, small and medium enterprises (MSMEs) in the economic and social development of the country is well established. As per the Report of the Working Group on Micro, Small and Medium Enterprises (MSMEs) Growth for 12th Five Year Plan (2012-2017), the sector accounts 45% of the manufacturing output and 40% of total exports of the country. The sector provides employment to about 69 million persons through 26 million enterprises throughout the country. Over 6000 products ranging from traditional to high-tech items are being manufactured by the MSMEs in the country. The labour to capital ratio in MSMEs and the overall growth in the sector is much higher than in the large industries. The geographic distribution of the MSMEs is also more even. Thus, MSMEs are important for the national objectives of growth with equity and inclusion.

Multi dimensional contributions of Small Enterprises

Small businesses are well placed to build personal relationships with customers, employees, and suppliers. With a small business you know who you are dealing with; you can 'put a face' to the person you are in contact with. Person-to-person interaction is as important as ever in building strong relationships. In a small business there is little hierarchy or chain of command. Large businesses may have set ways of operating and establish procedures that are hard to change. Small businesses are often far more flexible. It can also reach a quick decision on whether or not it can do what is required.

Small businesses are well positioned to introduce and develop new ideas. This is due to their owners not having to report or seek approval from anyone else. For example, when Anita Roddick set up The Body Shop, she developed a range of environmentally friendly cosmetics in unsophisticated packaging. This would have been frowned on in a conventional cosmetics company. Due to the small scale of operation, small businesses have lower overhead costs. They operate in small premises with low heating and

lighting costs, and limited rent and rates to pay. Low costs result in lower prices for consumers.

Large firms with high overheads must produce high levels of output to spread costs. By contrast, small firms are able to make a profit on much lower sales figures. They can therefore sell into much smaller markets: e.g. a local window cleaner serving a few hundred houses, a specialist jewellery maker with personal clients. The main reason many people choose to set up a small business, is because it gives them independence. They also reap the rewards for themselves; these are two powerful incentives.

Conclusion

The term Entrepreneurship, denotes an owner or manager of a business enterprise who makes money through risk and initiative. While "risk and initiatives" are two bold words for the term, they apply aptly for an Entrepreneur. However, the high reward for these risks more than often compensates, transforming Entrepreneurs into individuals who can bring about a vast majority of changes in our country with their vision and desire to achieve. In that regard, an Entrepreneur can bring certain changes to the society and to our country. Entrepreneurs can and should pivot a very important role in our country's development by creating jobs. It's evident that Entrepreneurs create initiatives, which in turn creates opportunities, which in turn creates jobs. The latest Census reports the unemployment rate as 9.4%, and to further lower this percentage, we need more job opportunities. At a large scale, it should be done by Entrepreneurs. It's worth noting that both the reports prepared by Planning Commission to generate employment opportunities for 10crore people over the next ten years have strongly recommended self-employment as a way-out for teaming unemployed youth. One such example can be pointed to Mr. N.R Narayana Murthy, whose company Infosys now employs over 145,088 employees. However, the most important role that Entrepreneurs can play in the country's development is by creating wealth for the country, which in turn can fund further start ups and budding Entrepreneurs. Entrepreneurial companies offer the greatest opportunity for wealth creation, simply because they have the potential of capturing the market, especially international. Creating and sharing wealth can enable entrepreneurs to do what India's government has failed to do since Independence, such as transforming education and rural India, making wealth an instrument for bringing the revolutions to build the new India. Think of the next Google or Microsoft from India, and the amount of social change it can bring to our country from the wealth generated. Considering

India's increased poverty rate of 37.2%, Entrepreneurs should create wealth overflow in the country for its development.

Lastly, Entrepreneurs should create more innovations for India's development. It's a known fact that Entrepreneurs are the harbingers of new innovations and fresh ideas. And our country, with its increased literacy rate, has a plentiful quality number of innovators, as evident by the increasing number of R&Ds shifts in our country. Entrepreneurs can therefore nurture a great change in the society with their fair set of innovations. Be it technological changes or social changes, the innovative ideas that an Entrepreneur brings in the society contributes towards the betterment of our country by the creation of better products and services. And the thing with innovation is that it creates a ripple effect in such a way that one innovation leads to another, with each innovation contributing some changes towards the society. Concluding on, creating jobs, generating wealth and nurturing innovation are some of the very crucial job roles that Entrepreneurs should play, all aimed towards sustained development of our country.

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RUBBER CULTIVATION AND INSTABILITY IN PRICES IN INDIA- CHALLENGES AHEAD

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Abstract

India is one of the largest producers of natural rubber in the world. State wise analysis of cultivation and production of natural rubber shows that Kerala is the major cultivator and producer of natural rubber in India. Natural rubber cultivation and production in India have increased significantly in the last two decades. Prices of natural rubber have shown high volatility and instability in recent years. Synthetic rubber is a byproduct of crude oil. Decline in the prices of crude oil is the major reason for the decline in prices of natural rubber.

Keywords: Natural Rubber, Synthetic Rubber, Price Instability, Crude oil, Plantation crops

Rubber is one of the most important cash crops in India. Natural Rubber is produced from the latex of rubber trees, an exotic deciduous rain forest tree species of family Euphorbiaceous. India ranks fifth in terms of production of natural rubber in the world after Thailand, Indonesia and Malaysia. Area, production and productivity of natural rubber have increased significantly over the years in India. Natural rubber is a strategic raw material and caters to a wide range of industries manufacturing a variety of products. Rubber enjoys an important place among the plantation crops in India.

Thailand is the largest producer of natural rubber in the world. The total production of Thailand is 41.7 lakh tonnes in 2013. Indonesia is the second largest producer with a production of 31.8 lakh tonnes. Thailand produces 37.37 percent of the global production of natural rubber followed by Indonesia with 28.5 percent. Malaysia produces 8.26 lakh tonnes with a share of 7.61 percent of the global production. India is the fifth largest producer of natural rubber in the world with a production of 8.9 lakh tones in 2013. Indonesia is the largest cultivator of Natural rubber in the world with an area of 34.56 lakh hectares in 2011. Thailand is the second largest cultivator of Natural rubber in 2011 with an area of 27.65 lakh hectares in 2011. India is the sixth largest global cultivator of rubber in 2011. Globally more than 80 percent of the Natural Rubber Production is in South East Asia ie., Thailand, Indonesia, Malaysia, India, China and Vietnam.

Table1. Area, production and Production of Natural Rubber in Various Countries

Country	Area (Lakh Hectares) 2011	Production (lakh Tonnes)		Average Yield Per Hectare(Kg)	
		2011	2013	2011	2013
Thailand	27.65	33.94	41.7	1636	-
Indonesia	34.56	29.82	31.8	1085	1104
Malaysia	10.23	9.96	8.26	1500	1400
India	7.35	8.93	8.49	1819	1639
China	10.23	7.27	8.56	1174	1246
Vietnam	8.34	8.12	9.49	1720	1740
World	98.2	110.55	111.56	-	-

Source: Indian Rubber Statistics, Vol.33, Rubber Board, Government of India, 2014.

Trends in Area and Production in India

Rubber plantations in India were introduced by the Europeans. Rubber planting material was brought to India in 1878 from Ceylon. However it was only in 1902 that Natural Rubber cultivation was started in a commercial scale in the country. Interestingly the first commercial plantations of rubber were started in 1902 by the Periyar Syndicate at Thattakad near Alwaye in Kerala. The two important factors that were instrumental in the successful introduction of plantation agriculture in the colonial India were British capital initiative along with agro-climatic conditions and the availability of cheap land and labour. Though rubber planting was taken up on a commercial scale in other parts of the country, it was Travancore which became the leading centre of rubber cultivation. Although rubber cultivation had its start on a plantation scale by British planters, subsequent increase in area under the crop is attributable to the enterprise of a large number of Indian proprietary planters belonging to the former native states of Travancore and Cochin, who came into the field later.

Normally rubber trees attain tappable stage in about 6-7 years and yield sharply increases year by year, reaching a peak after 14 years of planting and are productive for about 25 years. Although started in a modest scale rubber plantations in India have recorded a phenomenal growth after the post independence period. Rubber plantations in India consist of organized and unorganized sector. The organized sector comprises well organized estates and the unorganized sector represents thousands of small holders. Rubber plantations of over 20.23 hectares (50 acres) under a single ownership are treated as estates and those whose area range up to 20.23 hectares are treated as holding. The rubber plantation industry is predominantly of the small holders which accounts for more than 80 percent of the area and almost 75 percent of the total production of natural rubber in the country.

Area under Natural Rubber has increased significantly over the years. From 524075 hectares in 1995-96 rubber cultivation has increased to 778400 hectares in 2013-14. The percentage increase is estimated to be 48.53. Production of rubber has also increased significantly over the years. From 5.07 lakh tonnes in 1995-96 production increased to 774000 tonnes in 2013-14. The percentage increase is estimated to be 52.70. Productivity of natural rubber has increased substantially during the period 1995-96 to 2013-14. From 1422 kg/ha. average yield per hectare increased to 1629 kg/ha in 2013-14. The percentage increase is estimated to be 14.55.

Table 2. Area, Production and productivity of Natural Rubber in India

Year	Area in Hectares	Production in Tonnes	Productivity in Kg/hectares
1995-96	524075	506863	1422
2000-01	562670	630405	1576
2005-06	597610	802625	1796
2006-07	615200	852895	1879
2007-08	635400	825345	1799
2008-09	661980	864500	1867
2009-10	687000	831400	1784
2010-11	711560	861950	1806
2011-12	734780	903700	1841
2012-13	757520	913824	1813
2013-14	778400	774000	1629

Source: Indian Rubber Statistics, Vol.33, Rubber Board, Government of India, 2014.

State Wise Cultivation Natural Rubber in India

In India, rubber is predominantly grown in the tropics where an equatorial monsoon climate prevails. The rubber growing regions of India are classified under two major zones viz. the traditional and non-traditional based on the agro-climatic conditions. Kerala, a traditional region that enjoys an equatorial monsoon climate and has an ideal geographic feature, is the leading producer of natural rubber in India.

Kerala and Tamil Nadu constitute the traditional area. The non-traditional area consists of the Northeast states of India such as Tripura, Assam, Nagaland, Manipur, Mizoram, Arunachal Pradesh and other states such as Karnataka, Andaman and Nicobar Islands, Goa, Maharashtra, Orissa, West Bengal and Andhra Pradesh. In 2011-12, 73.43 percent of the area under cultivation in India was in Kerala. It is to be noted that more than 83 percent of the area under cultivation was in Kerala in 2003-04. During the last two decades cultivation of natural rubber in Tripura has increased substantially. In 2011-12, 8.8 percent of the area under cultivation of rubber in the country was in Tripura. In fact Tripura is the second largest cultivator of natural rubber in 2011-12. Karnataka occupies the second position and Tamil Nadu the third position in the cultivation of natural rubber in the country in 2011-12.

Table 3. State Wise Area, Production of Natural Rubber in India

State	2003-04		2005-06		2010-11		2011-12	
	Area	Production	Area	Production	Area	Production	Area	Production
Kerala	479602	655135	493800	739225	534228	770580	539565	798890
Tamil Nadu	18633	22520	18815	23555	19767	25160	19790	25220
Karnataka	20460	14070	23153	14940	38110	23705	41588	27890
Tripura	30770	-	34189	16322	59285	30850	64480	32045
India	575980	711650	597610	802625	711560	861950	734780	903700

Source: Indian Rubber Statistics, Vol.33, Rubber Board, Government of India, 2014.

Movement of Prices of Natural Rubber

Prices of natural rubber showed a lot of variations in the last two decades. A lot of factors influence the movement of natural rubber prices. Prices of synthetic rubber, crude oil prices, domestic demand, production of natural rubber in other producing countries, variations in the climatic conditions, political decisions, labour problems, lack of quality and quantity of

yields etc. influences the domestic price of natural rubber. Natural Rubber is an agro commodity, which is used in manufacturing industrial products. The various stakeholders- planters, dealers, processors, consumers and politicians often battle over its cost of production and fair pricing especially when prices crash or boom. They are eager to work a mechanism out where the growers can get a fair price for their produce and the consumers can buy with an affordable price. Many efforts have been taken over the years to arrive at a fair price agreeable for both the producer and consumer but have not been succeeded, since the cost of production varies from country to country, region to region and plantation to plantation due to the topography, weather, management style, labour cost and the like. Rubber being a plantation crop with a long gestation period, growers cannot respond to changing prices by reducing production or vice versa. Since farmers have made a huge investment in the initial period, switching to other crops in the middle of the economic life of their plantation would involve huge losses. The prime concern of a consumer shall be the availability of natural rubber at a globally competitive price. Natural Rubber prices have ever been a matter of serious dispute between the growers and manufactures in India and the world. Good price is the best incentive for planters to stick on to natural rubber cultivation and its further expansion amid many other options available today. The remunerative price for natural rubber demanded by the growers is often considered too high and unaffordable by the manufacturers. The dispute continues creating rivalry between these two important stakeholders of the rubber industry. A mutual cooperation is essential in these for the industry's growth, especially in these years of global economic competition. Price is the most important factor, which reflects the whole developments taking place in the respective commodity market. Therefore, the most important thing that can be given to any farmer is to give a remunerative price for their produce.

Market price of indigenous natural rubber had increased remarkably over the last two decades. The period from 1994 to 1998 was the most turbulent in domestic price trend of natural rubber. In June 1995 RSS-4 price shot up sharply to Rs.61.71 per/kg from Rs.25.99 per/Kg in March 1995. The probable reason for this sudden price hike was the decline in world production of natural rubber in main rubber producing countries. Immediately after 1996, India's import of natural rubber also increased. The maximum natural rubber import during 1991-92 to 2003-04

took place in that year. Simultaneously in global market, natural rubber price rose in anticipation of future supply tightness and shortage of some grades. The price of natural rubber showed an increasing trend in 1994 and this trend continued up to 1997. After 1997 the price showed a decreasing trend, which continued up to 2002. From 1997 onwards the rubber plantation industry has been passing through a period of great strain and stress due to the fall in the price of natural rubber. This has raised many doubts about the future prospects especially because this steep fall was just after the unprecedented rise in price level scaled in the mid- periods of the last decade of the 20th century. The other major rubber producing South East Asian countries earned more domestic currency by exports from the devaluation of their currencies. Hence a decline in the price of natural rubber in the world has an adverse effect mostly on India.

Wide monthly fluctuations are there in the market price of natural rubber. This may be due to the fluctuations in production of natural rubber in different months. The domestic market price of natural rubber has decreased to 30.36 Rs/Kg in 2000-01. However it has showed wide fluctuations after that. The average monthly spot price of RSS-4 grades rose to 38 percent during the period of January 2005- January 2006. During the year 2006, the rise was sharp and volatile. The average monthly rubber spot price increased by 45 percent during January- June 2006, tackling bullish crude prices, rise in international prices on account of falling stocks and consumption demand from China and India. The rise in the natural rubber export demand also contributes to its price rise. However the price failed to sustain at higher levels and dropped to Rs.81.69 Rs/kg in September 2006 on softer crude oil prices and withdrawal of industrial buyers from the market on account of higher prices. The domestic prices of natural rubber reached an all time peak of 238.68 Rs/Kg in April 2011. However it has declined and stood at 132.57 in 2014-15.

After the opening up of the Indian economy in 1990s, India's domestic rubber market started showing links to the international market. Probable determinants of volatility in natural rubber prices in domestic market are state administered procurement programmes, inconsistent import and export policies and global market trend.

The fall in natural rubber prices during the year 2011 has attracted wide attention of the media and hectic parleys between the stakeholders and the concerned authorities. The monthly average price of RSS-4 grade fell from

a peak of Rs.238.68 per kg in April 2011 to Rs.152.69 in January. The role of steady increase in rubber imports has been considered pivotal in prompting the downtrend in prices. In fact, the volume of imports has registered a three- fold increase from 77,762 tonnes in 2008-09 to 2, 62,753 tonnes in 2012-13. In this process, the import intensity of the domestic rubber consumption has reached an unprecedented level of 27.01 percent in 2012-13. Hence, it is logical to link the fall in prices to the surge in imports and the need for explicit policy measures to replenish market sentiments.

By 2013, natural rubber prices have dropped below Rs.160 a kg, owing to a slowdown in production in the automobile segment, especially trucks and buses. An increase in natural rubber production in the last three months also led to the fall in prices. The price of the benchmark RSS-4 grade fell to Rs.157 a kg at the local market. However, international prices were much higher than the Indian prices. By the end of 2014, the prices of natural rubber were down by almost 70 percent since the highs of early 2012. The relative price weakness reflects a slowdown in demand in emerging economies, particularly China, as the majority of natural rubber is used for tyre production. Rubber prices are volatile and are influenced by many factors. Over the past decade natural rubber prices have increased three to four fold, from less than $1 per kg to above $4.5 and then declined to about $2.09 per kg. The price volatility of natural rubber prices, as a general rule, tends to be more volatile than other mainstream commodities.

Rubber prices, which ruled around Rs.220 per kg in January 2011 has touched a low of Rs.123 per kg in 2014 in the domestic market due to lower demand for the commodity in the wake of general economic slowdown and lower price in international market. The continuing slowdown in demand from the domestic tyre industry, which consumes over 50 percent of the total natural rubber production in the country coupled with a bearish trend in overseas market, is adding to the pressure on prices, according to rubber experts.

With prices becoming unremunerative in the face of rising cost of production, mainly because of high wages of tappers and rising cost of fertilizers, growers have also started staying away from production. In fact, price fall in the recent past has been mainly owing to a demand recession for rubber at home and abroad arising out of the world economic downturn and a fall in demand for rubber products. A close analysis of

the rubber consumption across the continents shows that only Asia had a positive growth in the year while all other continents had negative growth. This was the main reason for rubber price decline. With a full-fledged economic recovery not in the sight for the time being, the dull sentiments in the global natural rubber market are likely to continue throughout 2015.

It is well known that the prices are determined by the interaction of demand and supply in a free market economy. The rubber goods manufacturing industries enhanced consumption and have played a major role in price rise. Consumption of NR is increasing at a rate between 10 to 12 percentages while the production is declining due to various factors. When the NR production was 825345 tonnes during 2007-08 the consumption moved up to 861000 tonnes. At this period 89700 tonnes of NR was imported to bridge the gap. But it was inadequate because 60280 tonnes of NR from indigenous production was exported in the same time. Having a gap of 35655 tonnes between production and consumption, only 29240 tonnes could be bridged by import. Although the shortfall was less at 6415 tonnes, it was large enough to engineer price rise.

The rubber market used to move up and down based on the demand and supply situation. The role of speculators in bringing about price swings had been more talked about since the introduction of Futures Trading. Futures Trade was introduced in India in 2003. People believed that there had been attempts of profiteering by sale of futures contracts at lucrative margins, noticing the overall shortfall in supply. The price swings abroad have helped them to confidently make higher or lower quotes. Most of the transactions were paper transactions as the futures contract purchased was often sold before the delivery date. No transfer of physical stock was involved. Trading without exchange of commodities often resulted in violent fluctuations.

The stability in prices does not mean a fixed price to rule for a given period of time. It only means that the demand factor would be made stable to match the supply side of the rubber economy. In other words, when the supply increases, there would be a number of factors working to the advantage of the market to push up the demand. It may be at home or abroad. In the era of globalisation, the basic determinant of price changes is not only the conditions of supply and demand, but it is also the international price prevailing in the liberalized market. Thus though price is

essentially decided by demand-supply balance or imbalance the international price has a say in influencing the NR price during the post liberalisation period.

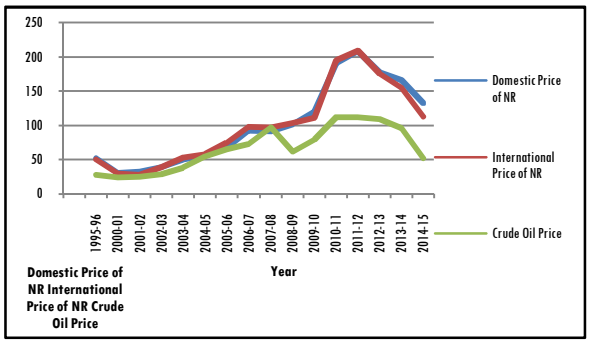
For many applications, natural rubber can be replaced by synthetic rubber. Hence large production of low priced synthetic rubber can affect the prices of natural rubber as it forms a substitute and competes in the same market place. However, since synthetic rubber is dependent on oil prices, a higher price of oil leads to a higher rise in price of synthetic rubber making it unfavourable among consumers. Oil prices have a large impact on the rubber industry. Synthetic rubber which acts as a substitute to natural rubber requires oil for its manufacturing. Traditionally, synthetic rubber has been cheaper to produce. However with declining oil prices, the cost of making synthetic rubber has gone down. This has again decreased the demand for natural rubber which in turn has pushed its prices downwards. Global economic conditions such as recession affect the prices of rubber. Rubber prices had dipped to its lowest level in the past 30 years due to reduced demand and an increased supply from the South East Asian countries especially Vietnam which had doubled its production from 155000 tonnes in 1995 to 320000 tonnes in 2001.

Table 4. Trends in Prices of Natural Rubber in India

Year	Price (Rs/ Kg)		Oil Price($/bbl)
	Kottayam (RSS4)	Bangkok (RSS3)	
1995-96	52.04	50.16	28.5
2000-01	30.36	29.58	24.44
2001-02	32.28	27.93	25.02
2002-03	39.19	39.15	28.83
2003-04	50.40	52.78	38.27
2004-05	55.71	57.51	54.52
2005-06	66.99	74.32	65.14
2006-07	92.04	97.79	72.39
2007-08	90.85	96.75	97.26
2008-09	101.12	103.79	61.67
2009-10	119.98	111.13	79.5
2010-11	190.03	195.55	111.26
2011-12	208.05	209.15	111.67
2012-13	176.82	175.76	108.66
2013-14	166.02	155.25	96.22
2014-15	132.57	112.71	52.50

Source: Indian Rubber Statistics, Vol.33, Rubber Board, Government of India, 2014.

Figure 1. Trends in Domestic Price of NR, International Price of NR and Crude Oil Price



Conclusion

Thus the foregoing analysis clearly revealed that area, production and average yield per hectare of natural rubber has increased substantially over the last two decades. Share of the small holding sector in the production of

natural rubber is found to be significant. Prices of natural rubber showed lot of instability and variability. The decline in crude oil prices was a major factor for the decline in natural prices. Suitable price stabilization policies should be adopted by the government to improve the productivity of natural rubber and also to prevent the high volatility in prices.

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IMPORTANCE OF THINKING STYLES IN AUGMENTING ACADEMIC EFFICACY

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Abstract

Thinking Styles can affect learning, hence styles of thought are important in education from several points of view. The theory of mental self-government provides different modes of rendering teaching more effective through style differentiated instruction for those who teach and assess students at any level. As per the theory, the styles can be tuned towards Thinking Styles that contribute to achievement .Hence teachers must be careful to take facilitative measures or use instructional strategies to bring up these Thinking Styles in the learners.

Key words-Thinking styles, Theory of mental self government

Thinking Styles are defined as the preferred ways of using the abilities that one has. To manage the activities, individuals choose styles with which they feel comfortable and the styles are distinct from abilities, and involve preferences, not necessarily conscious, in the use of whatever abilities one has. Styles are not connected solely with ability, but rather, preferred ways of expressing or using one or more abilities (Sternberg, 1997). Individuals have a style profile, meaning that they show varying amounts of each style, but they are not locked into any one profile. People can vary their styles to suit different tasks and situations. Styles further vary over the course of a lifetime, and change as a result of the role models they emulate at different points in their lives. People do vary in their flexibility to shift styles, and in the strengths of their preferences. Thus, when we speak of individual differences in Thinking Styles, we are speaking only of differences, not of better and worse.

The General Principles of Thinking Styles

The general principles of Thinking Styles (Sternberg, 1997) are

- Styles are preferences, not abilities. There is a difference between how creative a student is (ability) and how much the student likes to be creative (style).
- Styles can vary across tasks and situations. People vary their styles, at least somewhat, to fit what they are doing. They do not have one fixed style.
- A match between styles and abilities creates a synergy that is more than its parts.

- People have profile of styles, not just a single style.
- People differ in strengths of stylistic preferences. Some people strongly prefer certain styles; others have only weak preferences.
- People differ in stylistic flexibility. Some people easily can switch among styles; others cannot.
- Styles are socialized. Styles are learned through interactions with the environment.
- Styles can vary across the life span—they are not fixed. People may change their styles over the years.
- Styles are measurable. We measure styles using various techniques.
- Styles are modifiable. People are not "stuck" with certain styles unless they want to be.
- Styles are teachable.
- A style which is valued in one time and place may not be valued in another. The very style that leads to success in one school or one job may lead to failure in another.
- Styles are not "good" or "bad", but rather matters of fit between learner and teacher or learner and material. What one teacher considers a good style, another may consider bad, and vice versa.

The Theory of Mental Self-Government

The theory of Mental Self-government (Sternberg, 1997), holds that styles can be understood in terms of constructs from human notions of government. The basic assumption of the theory of Mental self-government is that people, like societies, govern themselves and their mental processes and establish systems and organizations for this governance. These different ways of managing our activities are our Thinking Styles. Thus Thinking Styles are our preferred ways of governing or managing our activities. The Theory of Mental Self-Government views people as self-organizing systems that actively shape their environment as well as themselves. People influence and respond in varied ways to the environment, depending to a large extend upon their styles of responding.

In this theory, Sternberg proposes thirteen Thinking Styles grouped within five dimensions of Mental self-Government-Functions, Form, Level, Scope and Leaning. Function refers to how mind copes with the world. Like a government, the mind legislates, plans, implements, executes, judges or evaluates. Hence he identified three distinct Thinking Styles in the functioning of mind, the executive, legislative and judicial.

Table 1: Characterization of Thinking Styles

STYLES OF MENTAL SELF-GOVERNMENT		
Thinking Style	**Characterisation**	**Example**
• **Functions**		
(1) Legislative	Likes to create, invent, design, do things his or her own way, have little assigned structure	Like doing science projects, writing poetry, stories, or music, and creating original artworks
(2) Executive	Like to follow directions, do what he or she is told, be given structure	Like to solve problems, write papers on assigned topics, do artwork, form models, build from designs, learn assigned information
(3) Judicial	Like to judge and evaluate people and things	Like to critique work of others, write critical essays, give feedback and advice
• **Forms**		
(4) Monarchic	Like to do one thing at a time, devoting to it almost all energy and resources	Like to immerse self in a single project, whether art, science, history, business
(5) Hierarchic	Likes to do many things at once, setting priorities for which to do when and how much time and energy to devote to each	Like to budget time for doing homework so that more time and energy is devoted to important assignments
(6) Oligarchic	Like to do many things at once, but has trouble setting priorities	Like to devote sufficient time to reading comprehension items, so may not finish standardized verbal-ability test
(7) Anarchic	Likes to take a random approach to problems; dislike systems, guidelines, and practically all constraints	Writes an essay in stream-of-consciousness form; in conversations, jumps from one point to another; starts things but doesn't finish them
• **Levels**		
(8) Global	Likes to deal with big picture, generalities, abstractions	Writes an essay on the global message and meaning of a work of art
(9) Local	Likes to deal with details, specifics, concrete examples	Writes an essay describing the details of a work of art and how they interact
• **Scope**		
(10) Internal	Likes to work along, focus inward, be self-sufficient	Prefers to do science or social studies project on his or her own
(11) External	Likes to work with others, focus outward, be interdependent	Prefers to do science or social studies project with other members of a group
• **Leaning**		
(12) Liberal	Likes to do things in new ways, defy conventions	Prefers to figure out how to operate new equipment even if it is not the recommended way, prefers open-classroom setting
(13)Conservative	Likes to do things in tried and true ways, follow conventions	Prefers to operate new equipment in traditional way, prefers traditional classroom setting

Form refers to the preferred ways of approaching and dealing with a problem. The theory specifies four forms- the Monarchic, Hierarchic, Oligarchic and Anarchic. The levels of Mental self-government are global and local. Sternberg classified the Scope into internal and external on the assumption that government needs to deal with internal or domestic affairs. Leaning encompasses liberal and conservative Thinking Styles.

Thirteen Thinking Styles in Sternbeg's Theory of Mental Self-Government and their Key characteristics are presented in the Table.1

Scope of Thinking Styles in Education

Thinking Styles can affect learning, hence styles of thought are important in education from several points of view. The theory of mental self-government provides different modes of rendering teaching more effective through style differentiated instruction for those who teach and assess students at any level. The key principle is that for students to benefit the most from instruction, at least some part of the instruction should match their styles of thinking even though it is not possible to provide a perfect match all the time. If we want students to show what they truly can do, a match of instruction and assessment to styles is essential. Studies reveal that certain Thinking Styles have sufficient influence on the achievement of students and it is possible to develop these Thinking Styles in students and teachers can do much with the knowledge of students Thinking Styles. As per the theory, the styles can be tuned towards Thinking Styles that contribute to achievement (Gafoor & Lavanya, 2008). Hence teachers must be careful to take facilitative measures or use instructional strategies to bring up these Thinking Styles in the learners.

Students need to learn, and the world does not always provide people with a perfect match to their preferred ways of doing things. Hence flexibility in Thinking Styles is as important for students as it is for teachers. But if we want students to show what they truly can do, a match of instruction and assessment to styles is very important. If a teacher wants to reach and truly interact with a student, he or she needs the flexibility to teach to different styles of thinking, which means varying teaching

styles to suit different styles of thought on the part of students.

According to Sternberg (1997) there are various methods of instruction that are most suited for the different Thinking Styles. The following is a list of the various methods of instruction and the styles that are most compatible with these methods

- Lecture with executive
- Thought-based questioning with judicial/ legislative
- Problem solving of given problems with executive
- Projects with legislative
- Small-group recitation with executive
- Small-group discussion with judicial
- Reading for details with executive
- Reading for main ideas with executive
- Reading for analysis with judicial
- Memorization with executive

Teachers can reach more students by varying their activity prompts in teaching and assessment. Hence it is necessary that teachers must accommodate an array of thinking and learning styles, systematically varying teaching and assessment methods to reach every student by using the full range of styles that are available.

Thus it can be concluded that Styles matter. They are often confused with abilities, so that students are thought to be incompetent, not because they are lacking in abilities, but because their styles of thinking do not match the styles of the people creating the assessments. Hence especially in teaching, teachers need to take into account students' styles of thinking if they desire to reach them. This means differentiating instruction in a way that helps students, at least some of the time, capitalize on their stylistic preferences. So Teachers need to carefully consider how their practices in educational settings may deprive opportunities of able people, while giving opportunities to those who are less able. For attaining this aim, teaching should be differentiated to help each child capitalize on strengths and compensate for or correct weaknesses.

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AN ANALYTICAL STUDY ON THE TRENDS IN PRICES AND DEMAND FOR GOLD IN INDIA

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Abstract

Gold is considered as the most trusted asset for centuries. It is the best instrument of investment by the common people to hedge their portfolio investment. Gold prices were on steep rise during the last decade. Its prices have been gone up by more than 300% till 2010. After 2011 the rate of increase in the price of gold steadily falls down from a peak of $1,900 an ounce. Recently international gold prices steeply came down to 1077 US Dollar, the lowest rate of all the last five years. The paper studies the various factors contributing the fluctuating trend of gold and its repercussions in India during last decade (2002 to 2015). Demand for the yellow metal in India was 481 tons during the July-December period in 2012, but since then, it has declined steadily. In the second half of 2014, demand was 439 tons. Demand for gold stood at 346.2 tons during the first six months of 2015. The paper discusses the factors influencing high demand for gold in India irrespective of price rise. Since the market for gold in India is demand driven, it is met by imports. India's import of gold has increased from 471 tons in 2000-01 to 1079 tons in 2011-12 and 1017 tons in 2012-13 which translates into a fourteen fold rise roughly over a decade. What is of particular concern is the sharp increase in imports since 2008-09 ie since the post recession period which resulted in heaps of current account deficit. The paper gave a glimpse about the trends of import of gold during the specific time period.

Keywords: Trends in gold prices, Trends in gold demand, Trends in import of gold, Post recession period, Current Account deficit, Exchange-Traded Funds (ETFs) etc.

Introduction

Gold has a unique status in the economic world as a precious metal with wide uses, a store of wealth, and for a long time the measure of economic power of nation. Gold has been used in rituals, decoration and jewelry for thousands of years. Its unusual chemical properties, high density, superb malleability, imperishable shine and its genuine rarity contribute to it being the most coveted commodity in nearly every culture. Government and investors have traditionally held gold as a hedge against inflation and to provide security at times of international crisis. Gold has both private and government demand. Private demand is further divided using different criteria. Like most of the commodities, the price of gold is driven by the demand and supply of gold including demand for speculation. The world gold

council forecasts India's gold demand to reach 900-1000 tons in 2015. India is a country in which gold market is created by the demand for gold which is met by imports of gold. The gold market is not supply driven as there are a minimal number of gold mines in the country. There are various factors affecting prices of gold and this paper is an attempt to analyse the price and demand trends in gold with a special focus on Indian economy.

Objectives of the Study

The major objectives of the study are-

1. To study the factors behind fluctuating trends in the gold prices with special reference to India
2. To understand about the factors behind the stable demand for gold in India irrespective of price fluctuation.
3. To analyse the trends in investment demand for gold during the post recession period.
4. To examine the import trends of gold in India

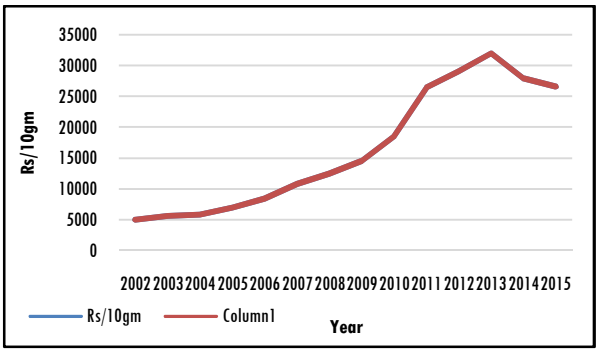
Methodology of the Study

This study is basically descriptive in nature. Secondary data from various sources such as articles, e-journals, websites, newspapers are used for the analysis. Statistical tools like, bar diagram, pie diagram are used accordingly. The period considered for the study ranges between the years 2002 to 2015.

Factors Affecting changes in the price of Gold with special reference to India

The world economy is experiencing a steep rise in the prices of gold during last few years. Now we are going to study the factors that are contributing towards this rise. The below mentioned are the various factors which are contributing towards rise in the prices of the gold. The price of gold is determined by several factors. It is an important commodity in certain products such as jewelry. It is also seen as an important way to invest wealth – especially in times of economic uncertainty. The world consumption of new gold produced is about 50 % in jewelry, 40 % in investments, and 10 % in industry (excellent as conductor and resists corrosion)

Gold Price from 2002 to 2015



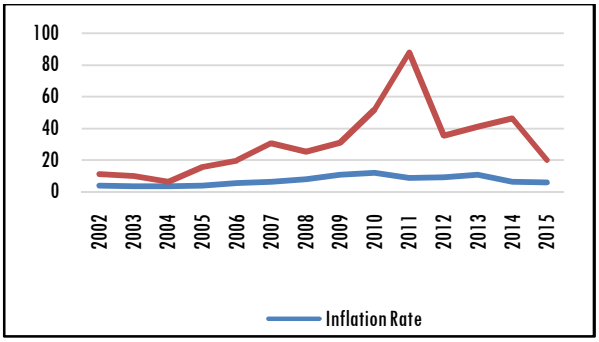
(Source: World gold Council)

Markets like India have strong demand for using gold in jewelry. Economic growth in India increases disposable income and therefore demand for gold. As gold is a luxury good (income elasticity of demand > 1) then a rise in income in India could lead to a bigger impact in the

percentage increase in demand for gold. India was the top consumer of the metal in 2014 and the second biggest after China in first quarter of 2015. Higher domestic gold inventories is also have an impact on the price movements of yellow metal.

Gold is commonly believed to be a hedge against inflation. If gold prices rise faster than the general price level, investment in gold is seen as a superior hedge against inflation .Gold's history as a monetary asset makes it an attractive store of value in periods of high inflation or rising inflationary expectations. To be a hedge against inflation, gold would have to be negatively correlated with inflation. As gold pegged to the US Dollar US interest rates affected gold prices. Whenever interest rates fall, gold prices increase and when the inflation is on the rise, gold prices also increase. Therefore in periods of high inflation, people will seek to switch out of cash and into physical assets which retain their value. It also depends on the real interest rate. However, if you get a situation of high and volatile inflation, you are more likely to have negative real interest rates. In India prices of gold was rising and imports was also at a high rate due to a high inflation rate of 13%. A relative high interest rate at banks kept gold as an inflation proof on investment. The investment demand is the key factor behind the increase in price of gold between 2006 and 2011. But now the fall in the inflation rate in India leads to fall in the interest rate which gives a loss to investors of gold upto 24%.

Inflation rate and Gold price (%)



(Source: World Gold Council)

Economists have long recognized the role of currency valuation in pricing commodities, particularly imported commodities, such as oil and gold. Gold has inverse relationship with the dollar. Recently in USA in great financial turmoil the dollar has weakened against many currencies, thus it is expected that there will be increase in the gold prices. Dollar is de-facto currency exchange all around the world. USA was on financial depression and gold had been substituted as a safe haven for investment. But recently as a revival from recession, the value of US Dollar gain its strength and may lead to a rise in interest rate. The current downswing in Indian gold prices is directly related to the strengthening of the US dollar in recent times. This will adversely affect the investment demand for gold. With gold prices falling, gold ETFs are facing redemption which is forcing them to sell the yellow metal. This has pushed gold prices into a vicious cycle. It is reported that the investment came down to 684.6 tons in the prominent gold based ETF, the SPR gold trust. Central banks usually keep some of their reserves in gold. Gold

doesn't give any interest so Central banks may prefer bonds which give some interest. But, if they decide to hold more reserves in gold, demand and price will rise. Recently, China and Russia have indicated they will seek to hold more reserves in gold. The economic boom in China had led to huge demand for gold. But since the country is now facing an economic slowdown, in the first six months of 2015, demand has fallen by about 24%, leading to lower prices. One of the reason for steep fall in price of gold is that China dumped a huge amount of gold in the market, causing the price of the precious metal to fall drastically. The level of US government borrowing can have an impact on the price of gold. If markets feel the US debt is projected to get out of control, there is a greater chance that the dollar will devalue and dollar assets will fall. This means people may sell dollar assets (e.g. US treasury bills) and buy gold instead.

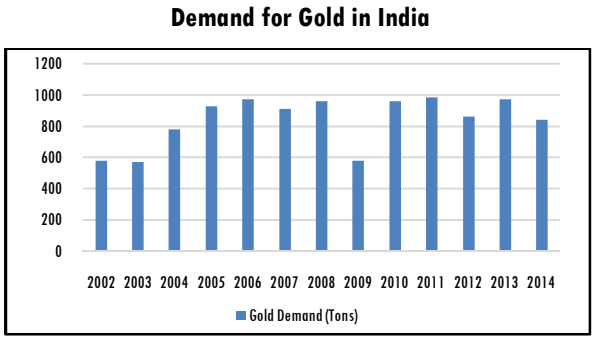
Supply factors Affecting the price of Gold with special reference to India

A change in supply could alter the price of gold. The mining of the gold ore has been on the lower side from the past few years. There is steep rise in the price of gold and whereas the quantity extracted has been volatile, rather on a lower side .There has been decrease in of nearly 40% in production of gold. Gold behaves less like a commodity than like long-lived assets such as stocks or bonds. That characteristic makes expectations particularly important because, like the stock market, gold prices are forward-looking, and today's price depends heavily on future demand and supply. There also has been increase in monetary and non-monetary demand of gold thus pushing price of gold. Demand for gold in India is also sluggish as concerns over a weak monsoon still remain. Nearly two-thirds of India's gold demand comes from rural areas where jewelry is a traditional store of wealth for millions who have no access to the formal banking system. Gold is negatively correlated with the stock, bonds and real estate. During any of the financial and non financial crisis investors like to invest in gold. High uncertainty in international commodity markets amid geopolitical developments in the aftermath of Greek debt deal and the historic nuclear agreement between Iran along with the world powers too weighed on bullion trade.

Factors behind high consumption pattern of gold with special reference to India

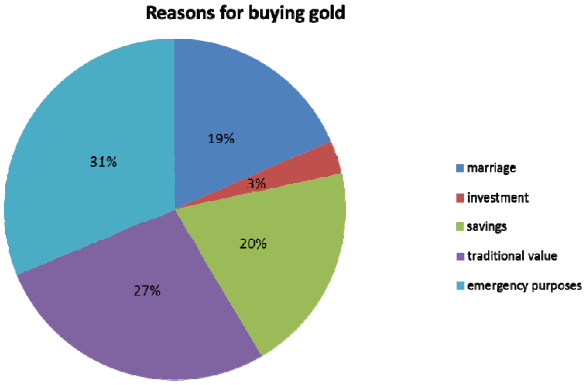
India is one of the biggest markets for gold and gold loans. Reasons for this are spread across various social, economic and cultural dimensions. According to World Gold Council, India accounts for 10% of total world gold stock, of which rural India accounts for 65% of the total gold stock. For Indians, gold is not just a commodity, but an auspicious metal that they buy for various purposes on different occasions. There has always been a high demand for gold in India, irrespective of prices. In South India especially in Kerala, people purchased kilograms of gold for their

daughter's wedding as part of 'sthreedhan' which is considered as blanket for her future.

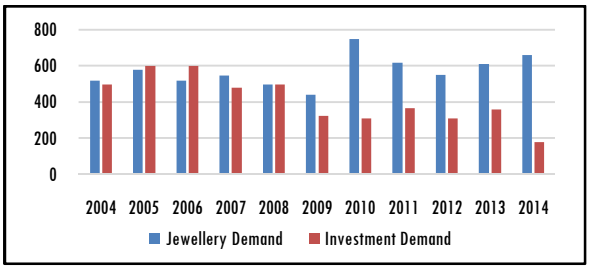


Source: (World gold Council)

During 2001- 2012, the annual demand for gold remained relatively stable at around 700 to 900 tons despite constant rise in prices during the last ten years. According to the World Gold Council, India consumed 963 tons of gold in 2010, amounting to one-third of global demand. In the financial year ending March 31, 2012, India imported $58 billion of gold compared with $38 billion over the previous 12 months. Gold demand in India declined 14 per cent to 842.7 tons in 2014 as compared to the previous year, mainly due to government policies putting restrictions on imports, according to the World Gold Council (WGC).The overall demand stood at 974.8 tons in 2013. In value terms, the precious metal's demand dipped by 19 per cent to Rs 208,979.2 crore in 2014 as compared to Rs. 257,211.4 crore in 2013. During festivals like 'Akshaya Tritiya' and 'Diwali' ,buying gold is a ritual in India. In the western India, more than 5,000 people ranging from farmers to middle-class professionals flock buy gold during these special occasions. After selling up, their first instinct is to invest in gold.



As observed, 31% of people buy gold for use during emergency situations. This is because gold loans are easily available with minimal procedural requirements. Gold is also considered as one of the most liquid assets, since it can be easily converted back to cash and hence the resale value of gold is quite high compared to other types of asset. The second most common reason for buying gold is that gold has a very high traditional value in India. This includes buying gold during festivals, marriages, etc. There are various festivals in India during which buying gold is considered auspicious. This is true especially in the case of South India where people are gripped with what we can call a 'gold mania'.20% of respondents save in the form of gold. This is indeed a prudent decision as the value of gold has seen an upward trend over the last few years. Therefore, Indians prefer investing and saving in the form of gold, as gold is considered to be a safe asset. Lastly, a total of 19% of the sample size cites buying gold for marriage purposes Jewelry and Investment demand in India



Source: World Gold Council

Total jewelry demand in India for 2014 was up by eight per cent at 662.1 tons as compared to 612.7 tons in 2013. In value terms, jewelry demand in 2014 was Rs. 208,979.2 crore, a fall of 19 per cent from Rs. 257,211.4 crore in 2013. In 2013, India imported 1,017 tons, up from 471 tons in 2000–01. The government's target of bringing this down to 700 tons a year seems ambitious considering how intertwined the metal is with India's social fabric.

Gold as an earning asset during the post financial crisis period

Ever since global financial crisis erupted, there seems to be an escalation in gold price. The augmentations of official gold reserves across many countries have been perceived as one of the important cause of spiraling gold prices. India also officially purchased 200 tons of gold from IMF in 2009. It was reported that India's purchase of gold was among the factors that impacted gold price in the world market and also boosted price expectations. It is found that gold is seen as a safe haven during bad times. In fact this phenomenon was observed even during the financial crisis as large number of central banks restored in buying gold during the crisis.

It was after the 2008 global financial crisis that gold became the most preferred vehicle for investment, with prices doubling in four years. Gold was not considered much as a hedge against inflation but as an insurance against uncertainty. When the economy is faltering and the future looks bleak, gold becomes a preferred asset. After the 2008 crisis, there was hardly any asset that could conserve the value of investment. Property prices were down, stock markets had crashed, and interest rates were down to near zero. Gold came to the rescue as an earning asset. Gold prices in India shot up from 13,662 rupees ($221) for 10 grams at the beginning of 2009 to nearly 31,000 rupees ($502) at the beginning of 2013. Thereafter, prices started to decline. In just one year, gold prices dropped 8 percent. That appeared to be the end of the metal as a safe investment. International gold prices also declined as the uncertainty which dogged the world economy gradually diminished. The U.S. economy improved, and unemployment figures dropped to 6.5 percent – well below the target set by the Federal Reserve .Gold was no longer in

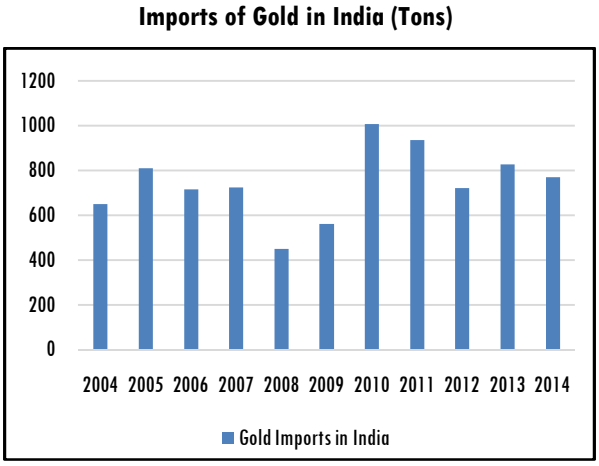
demand as an insurance against uncertainty because business confidence had returned. There was a shift to other assets like stocks and bonds. Indians traditionally invest in gold by buying gold jewelry. But other gold investments including gold exchange-traded funds (ETFs) are rapidly gaining in popularity as investors seek a safe haven and become more aware of the benefits of investing in gold in a non-material form as opposed to holding it as jewelry. Disinvestment in gold in exchange-trade funds, forced prices down by 28 percent. The year 2013 was bad for gold in India as the prices fell by 6 percent .That was still small compared to the fall in international prices, mainly because of the weakening of the rupee. Lower international prices inflated demand for gold in India, bloated the current account deficit and forced the government to raise import duty by 10 percent. In value terms, gold investment demand saw a fall of 53% at Rs 44,847.1 crores from 95,460.8 crores in 2013. The investment demand dropped mainly because of the adoption of government policies that lead jewelers not selling bars and coins. Total gold recycled in India also declined by 23.5% in 2014. Imports consequently dropped, though it made gold smuggling and import via non-resident Indians more rewarding to keep up market supply. India had imposed some rules on gold imports over the last two years to curb overseas purchases of the yellow metal, which were hurting its current account deficit. Due to certain restrictions, imposed by the government sales of bars and coins have faced a lot of troubles and a part of investment demand has moved to jewellery. India's jewellery demand, which rose 22 percent to 150.8 tons in the January-March quarter, has been a key driver in boosting appetite for the precious metal in 2015.

Trends of gold imports in India

Gold is the second-largest import item for India after petroleum. The demand for gold in India is very healthy, but supplying Indians with gold has always been a problem. That's because less than 4 tons of gold are produced in India every year. This output provides less than 1% of India's annual gold demand. So to solve the supply problem, India must import its gold. There has been a sharp increase in India’s gold imports in the recent past, which has raised concerns about its implications for trade deficit. India’s current account deficit (CAD) reached a record 4.8% of GDP, in part due to high gold imports 2013 . Nearly 95% of our annual gold demand is met by imports. Approximately 65% of gold Indian gold imports come from South Africa and

Australia. It also imported it from countries such as Switzerland and the United Arab Emirates. However, many experts counter that while buying gold should be curbed in the short term, it might not necessarily be an inherently bad thing for the economy. While current account and trade deficits are negatively affected by importing gold but buying and storing gold is like saving money. This creates room for the government to spend more without creating inflationary pressure. The rise in India's import of gold has been on account of both price and quantum factors. International gold prices on average rose by 27.2 per cent in US dollar terms. As far as quantum of gold import is concerned, it is estimated to have increased by 9.2 per cent in 2011-12 (12.0 per cent in 2010-11). As shown in the figure volume of gold import has surged in recent years despite sharp increase in gold prices. It implies that gold imports of India are relatively price inelastic. Uptrend in gold imports is particularly evident during the post-global financial crisis period. Similarly, increasing preference for gold is reflected in a steep rise in gold import–GDP ratio in the past few years. Since 2009-10, gold import-GDP ratio has remained significantly above the trend .It needs to be noted that India exports a certain portion of its gold imports in the form of re-exports of gold jewelry, etc. However, gold re-exports as a percentage of total gold imports has declined from around 41 per cent to 29 per cent, which may be a concern for India's trade balance. A large portion of gold imports is not used for creating exports. Increasing domestic consumption of gold import is clearly a concern for external sector sustainability. When the global financial crisis erupted in 2008, the investors were standing at the margin and disinclined to invest in various assets including gold for some quarters in 2008 and 2009 as there was gloom and uncertainty from the crisis related developments. This has led to postponing of the demand for gold investment by investors as they cling on to bank deposits. But, from the mid 2009 onwards investors have started re-entering the gold market in a big way and the pent up demand for gold resulted in large gold imports thereafter. India's gold imports in 2012 is estimated to drop by around 25% from last year as high prices, poor liquidity, high inflation and a hike in customs duty has dampened buying sentiment. There is a liquidity crisis because of high interest rates and the monsoon was not very good in some states so purchasing power will be low. In 2011, India imported 933.4 tons of gold, down 7% from an all-time high of 1,006.3 tons in 2010, according

to World Gold Council. India's overall gold demand was slightly lower in 2014, which was due to the restrictions on imports in place for most of the year.



Source: Smaugld

Conclusion

The paper studies various factors contributing towards fluctuations in gold prices with special reference to India. It is observed that factors like inflation and interest rates, Government borrowings, uncertainty in international commodity market have strong correlations with fluctuations in gold prices. The increase in the official gold reserves of gold across many countries has been viewed as one of the important cause for spiraling gold price. Gold has become an essential element of foreign reserves because of its unique abilities to meet liquidity and safety requirements. The paper also examines factors behind the stable consumption pattern of gold in India irrespective of price fluctuations. Indians had an appetite for gold. One of the reason is its resale value is quite high compared to other assets. The second reason for demand for gold is its traditional value associated with marriage and festivals. Easy availability of loan requirements seems to be another reason for it. After the 2008 crisis, there was hardly any asset that could conserve the value of investment other than gold. Gold investments including gold exchange-traded funds (ETFs) are rapidly gaining in popularity as investors seek a safe haven and become more aware of the benefits of investing in gold in a non-material form as opposed to holding it as jewelry. Yet the appetite for investing in gold remains strong in India. In order to meet this huge demand there arise a need to import from gold producing countries. Gold import is found to be moderately inelastic with respect to gold price in long run. In short run gold demand shows high elasticity with respect to price. There has been a sharp increase in India's gold imports in the recent past, which has raised concerns about its implications for trade deficit. It forced the government to raise import duty. As a result of the adoption of government policies the investment demand dropped mainly. Imports consequently dropped, though it made gold smuggling and import via non-resident. Durably lowering the demand for gold as a store of value will only be achieved through low inflation, raising real interest rates on deposits, and ensuring macroeconomic stability.

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AN OBSERVATORY STUDY OF LABOUR COST INVOLVED IN PEPPER CULTIVATION

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Abstract

Black pepper (Piper nigrum) is most often referred as the 'king of spices' is largely cultivated in India. It is widely cultivated in States namely Kerala, Karnataka and Tamil Nadu. Malabar Grade Black Pepper has a premium brand image in the international market and it is exported to more than seventy countries of the world. The agro-climatic conditions prevailing in the state are suitable for the cultivation of pepper. Idukki District is the major producing centre of pepper in the state and Wayanad and Kozhikode are the other important pepper tracts of the state. Pepper is cultivated both as an intercrop and as a pure crop. Pepper is a perennial vine and continuous cropping over a number of years can result in depletion of soil fertility and consequent decline in yield and therefore it is necessary to fertilise the crop regularly and judiciously. It is a fact that cost of cultivation is escalating year after year. Many of the pepper growers in the state are in distress. Around 75 per cent of the total cost of pepper cultivation is labour cost. Hence the rising wage level and the shortage of workers are the serious concerns of the pepper growers. In this context, this study is an attempt to evaluate the various cost aspects of pepper cultivation and the estimation of human labour involved in it.

Keywords: Spices, Black pepper, Cultivation practices, Establishment cost, Maintenance cost, Labour cost, Bearing period, Amortized establishment cost.

Introduction

Kerala is famous for black pepper from olden days. In the present day, agricultural production in Kerala is mainly focused on several cash crops. Pepper is an important item of cash crop and its cultivation has a significant role in the agricultural economy of the state. The agro-climatic conditions prevailing in the state are suitable for the cultivation of pepper. It is believed that black pepper originated in Kerala. Pepper is popularly known as 'black gold' and it holds a prime position in the spices economy of Kerala. During 2009-2010 the state continued to hold the monopoly in pepper production by producing 42459 tonnes of pepper in an area of 175868 hectares of land and it is considered as the king of Kerala's spices.

Pepper is a plant of humid tropics requiring adequate rainfall and humidity. Idukki District is the major producing centre of pepper in the state and Wayanad and Kozhikkodu are the other important pepper tracts of the state. Kochi and Sulthan Butchery are the primary markets for black pepper in Kerala. The products developed

from pepper broadly fall into four categories: black pepper, white pepper, green pepper and oil and oleoresin of pepper.

During 2009-2010, the total area under spices cultivation in the state was 2.5 lakh hectares and the total volume of production was 1.21 lakh tonnes. Total area under pepper cultivation was 1.71 lakh hectares, which constituted 68 per cent of the total area. The percentage share of other spices in total area were cardamom (17 per cent), ginger (2 per cent), turmeric (1 per cent), nutmeg (6 per cent).Area wise share of garlic and cloves were less than one per cent. In the case of total spice produce, 35 per cent was constituted by pepper. Of the total spice produce, the share of other spices were cardamom (6 per cent), ginger (24 per cent), turmeric (5 per cent), garlic (5 per cent), tamarind (16 per cent), Nutmeg (9 per cent and the share of clove was only nominal. Table-1 shows the area and production of various spices in Kerala during 2009-2010

Table-1 Spice wise Distribution of Area and Production of Spices in Kerala During 2009-2010

Item	Area	Share in%	Production	Share in %
Pepper	171489	68.29	42459	34.91
Cardamom	41593	16.56	7800	6.41
Ginger	5408	2.15	28603	23.52
Turmeric	2438	0.97	6066	4.99
Garlic	336	0.13	5712	4.70
Tamarind	12715	5.06	19627	16.14
Cloves	1206	0.48	84	0.07
Nutmeg	15931	6.34	11269	9.27
TOTAL	251116	100	121620	100

(Source: Spices Board)

Importance of the Study

Kerala contributes a major share in the production and export of black pepper from India. Recently, the volume of pepper production and its exports are showing a deceleration trend. Many factors are responsible for this. The domestic price of pepper is also highly fluctuating in the era of globalisation and trade liberalisation. This has created some problems in the pepper economy of Kerala. It is said that cultivation of pepper is unprofitable in a totally inconsistent price structure. At the same time cost of cultivation is escalating year after year. Many of the pepper growers in the state are in distress. Around 75 per cent of the total cost of pepper cultivation is labour cost. Hence the rising wage level and the shortage of workers are the serious concerns of the pepper growers. In this context, this study is an attempt to evaluate the various cost aspects of pepper cultivation and the estimation of human labour involved in it.

Objectives of the Study

The objectives of the study are:

1. To analyse the various cost aspects of pepper cultivation
2. To calculate the number of man days involved in pepper cultivation
3. To assess the imputed value of family labour involved in pepper cultivation

Methodology of the Study

The study was conducted on the basis of both primary and secondary data. The various aspects of the cost of cultivating pepper and the estimation of human labour involved in it were studied with the help of primary data. Primary data were collected through a sample survey

method, by using a properly planned interview schedule. The primary data regarding pepper growers were collected from five selected Panchayats of Idukki district, namely Vathikudi, Konnathadi, Nedumkandam, Kattapana, and Upputhara. Idukki district was selected purposely for the study because it covers major part of the area under pepper cultivation in Kerala. These five Panchayats were also selected purposely on the basis of the largest area under pepper cultivation. These Panchayats have maximum production potential in pepper. The entire study was based on a total of 200 samples of pepper cultivators. The period of primary data collection was from February 2009 to May 2009.

Pepper Cultivation Practices

Black pepper is an important spice which is produced by the pepper plant grown as vine. This plant needs supporting trees for climbing. Arecanut, jack, mango, 'murikku' and 'kalasu' trees are used as standard for pepper. The most widely practiced form of propagation is with the use of cuttings. They are selected from the terminal area of the main shoot of a strong, healthy and highly productive parent plant. Normally pepper plants are planted during monsoon season in the pits of 50 cm. depths, at a spacing of 2.5 m. x 2.5 m. and live standards are commonly used, accommodating 1000 vines /hectare. The planting density varies in between 800 and 1200 pepper plants/hectare.

Pepper is a sensitive crop which requires special attention of the farmers. Pepper plants when young, needs shade either natural or artificial. As the plant grows the shoots are tied to standard as often as required. Manuaring the soil around the plants twice a year is practiced by the farmers. That is the first half before the monsoon and second half after monsoon in October-November. During the first few years, pepper grows relatively well. Thereafter attempts are required to combat the upsurge of diseases and nutrient problems. Therefore, proper utilization of fungicides and mineral fertilizers are essential. The use of organic manure and cattle manure can develop the basic facility to encourage the quicker growth of pepper plants.

Monitoring and Maintenance of Pepper Crop

Weeding and light digging are practiced at the time of manure and fertilizer application. Time to time weeding and cleaning at the base region of black pepper plant are done by the farmers depending upon the weed growth. During the harvesting time, the ground beneath the plants must be kept clean, in order collect all the ripe berries that have fallen down. Careful maintenance is essential for acquiring a reasonable yield. Vines must be regularly tied back and pruned.

Harvesting and Post- harvesting Works

Pepper vines start yielding from third year on wards. They take 6 to 8 months of period from the stage flowering to ripping of fruits. January to March is the harvesting times. Pepper berries are

harvested when their colour is greenish yellow. Berries are separated from the spikes by rubbing them between the palms of hands and trampling them under the feet. After separation, the berries are sun dried for 7 to 8 days until the characteristic black colour and wrinkled shape appeared. About 100 kg of green pepper can produce approximately 35 kg. of black pepper.

Basic Farm Management Practices

Basic crop management after planting for pepper crops includes weed control, pest and disease management, fertilizing, irrigation during dry periods, training of wines and pruning. Pruning the tips or stems of young plants promotes the development of dense canopies. Harvesting of pepper and the post harvesting practices such as threshing the spikes, cleaning, drying, grading etc are the other major practices related to pepper cultivation. All these works require more human effort.

Cost Aspects of Pepper Cultivation.

This is an attempt to find out the cost of labour required for the cultivation of pepper. The profitability of pepper growers mainly depends upon two factors, the market price of pepper and the cost of labour. Labour cost of cultivation implies that total amount of expenses incurred for man days involved in the cultivation practices per one hectare of land. Pepper is a perennial crop. The life span of pepper plant is expected to be 20-25 years. Therefore, the cost of cultivation of pepper was studied by using two approaches namely;1) Establishment cost and 2) Maintenance cost. Labour cost is the relevant item among these two.

Establishment cost is the cost incurred during the first four years of a pepper plantation. The costs incurred under this category comprises land preparation, digging of pits, planting ,plant protection measures, inter cultural operations, cost of vines, standards , plant protecting chemicals, and other miscellaneous expenses. Labour used for the cultivation practices include both hired labour and family labour. Hired labour means labour hired from outside on payment of wages. Hired labour includes both male and female workers and their wages were also different. Labour cost was computed on the basis of the actual wage paid by the cultivators in the study area. During the survey period February 2009 to May 2009, the overall average wage of male workers was Rs.301.58 and that of female workers was Rs.182.31 per day. These wage rates were considered for imputing the cost of family labour in each group.

The analysis of the cost incurred in the first year shown that the maximum cost was incurred for labour input which was 42.30 per cent of the total expenditure. This higher percentage of labour cost was attributed to the principal operations undertaken in the land in connection with the planting of pepper vines. The contribution of hired labour was much more than that of family labours.

During the second and third years the cost incurred for labour input were estimated as 29.72 per cent and 31.04 per cent of the total establishment cost respectively. For the entire three year period of pepper planting total cost incurred for labour input was Rs.35569.21, which was 32.82 per cent of the total establishment cost. The findings of the study are summarised in table-2.

Table-2 Establishment Cost of Pepper Plants

(Rs. / Hectare)

Sl no.	Item	I year	II year	III year	TOTAL
1	**Variable cost**				
A	**Labour cost**				
1	**Land preparation**	2864.24	0.00	0	2864.24
		(6.33)	(0)	(0)	(2.88)
2	**Opening of pits**	3829.11	341.15	0	4170.26
		(8.46)	(1.31)	(0)	(4.20)
3	**Planting**	3187.52	0.00	0	3187.52
		(7.04)	(0)	(0)	(3.21)
4	**Plant protection measures**	1605.48	140.61	0	1746.09
		(3.55)	(0.54)	(0)	(1.76)
5	**Manure & Fertiliser application**	2395.29	2082.92	2902.66	7380.87
		(5.29)	(7.97)	(10.40)	(7.43)
6	**Inter cultural operation**	2694.41	2528.02	2951.15	8173.58
		(5.96)	(9.67)	(10.57)	(8.23)
7	**Plant protection operations**	1996.06	2196.58	2293.47	6486.12
		(4.41)	(8.41)	(8.22)	(6.53)
8	**Miscellaneous**	569.05	475.98	515.5	1560.53
		(1.26)	(1.82)	(1.85)	(1.57)
	Total labour cost (A)	**19141.16**	**7765.27**	**8662.78**	**35569.21**
		(42.30)	**(29.72)**	**(31.04)**	**(35.82)**
B					**Material cost**
1	**Standards**	4954.19	430.07	0	5384.26
		(10.95)	(1.65)	(0)	(5.42)
2	**Vines**	2871.83	249.43	0	3121.26
		(6.35)	(0.95)	(0)	(3.14)
3	**Manure**	3514.58	3048.14	3757.36	10320.08
		(7.77)	(11.66)	(13.46)	(10.39)
4	**Fertilizer**	0.00	738.67	1113.56	1852.23
		(0)	(2.83)	(3.99)	(1.87)
5	**Plant protection chemicals**	0.00	852.00	1071.26	1923.26
		(0)	(3.26)	(3.84)	(1.94)
6	**Others**	444.16	257.69	344.14	1045.99
		(0.98)	(0.99)	(1.23)	(1.05)
	Total material cost(B)	**11784.76**	**5576.01**	**6286.32**	**23647.08**
		(26.05)	**(21.34)**	**(22.52)**	**(23.82)**
	Interest on working capital@8.5%	2628.70	1134.01	1270.68	5033.39
		(5.81)	(4.34)	(4.55)	(5.07)
	Total variable cost(A+B)	**33554.62**	**14475.28**	**16219.78**	**64249.69**
		(74.16)	**(55.40)**	**(58.11)**	**(64.71)**
II					**Fixed Cost**
1	**Rental value of land**	10000.00	10000.00	10000	30000
		(22.10)	(38.27)	(35.83)	(30.22)
2	**Land tax**	100.00	100.00	100	300
		(0.22)	(0.38)	(0.36)	(0.30)
3	**Depreciation**	577.13	544.35	576.60	1698.08
		(1.28)	(2.08)	(2.07)	(1.71)
4	**Interest on fixed capital@9.5%**	1014.33	1011.22	1014.27	3039.82
		(2.24)	(3.87)	(3.63)	(3.06)
	Total Fixed Cost	**11691.45**	**11655.57**	**11690.88**	**35037.9**
		(25.84)	**(44.60)**	**(41.89)**	**(35.29)**
	TOTAL(I+II)	**45246.08**	**26130.85**	**27910.66**	**99287.58**
		(45.57)	**(26.32)**	**(28.11)**	**(100.00)**

(Source- Primary data & Figures in parenthesis represent the percentage values)

Labour Cost of Pepper Cultivation during Bearing Period

The pepper vines commence bearing during the third year. Thereafter, the amount annually spent by the farmers for the maintenance of pepper plants is described as maintenance cost or cost of pepper cultivation.

Although the vines start bearing from the third onwards, the yield gets stabilized only from the seventh or eighth year after planting. The various cost items that are involved in the cultivation of pepper per hectare are presented in table -3

Table-3 Cost Items Involved in Pepper Cultivation During Bearing Period

(Rs. / Hectare)

Sl.no.	Item	Average
I	VARIABLE COST	
A	Labour cost	
1	Application of manure and fertilizer	3776.44 (7.79)
2	Inter cultural operations	4061.12 (8.38)
3	Plant protection measures	2081.11 (4.29)
4	Harvesting and drying	11466.34 (23.66)
5	Miscellaneous	552.95 (1.14)
	Total Labour Cost	21937.96 (45.26)
B	Material Cost	
1	Mannure	4730.57 (9.76)
2	Fertilizer	1379.24 (2.85)
3	Plant protection chemicals	1454.32 (3.0)
4	Others	375.88 (0.78)
	Total Material Cost	7940.01 (16.38)
	Interest on W.C @8.5%	2539.63 (5.24)
	TOTAL VARIABLE COST (A+B)	32417.59 (68.88)
II	FIXED COST	
1	Rental value of land	10000.00 (20.63)
2	Land tax	100.00 (0.21)
3	Depreciation	589.58 (1.22)
4	Amortized establishment cost	3971.51 (8.19)
5	Interest on fixed cost @ 9.5%	1392.80 (2.87)
Total Fixed Cost		16053.89 (33.12)
Total cost of cultivation(I+II) (Cost –C)		48471.48 (100.00)

(Source- Primary data & Figures in parenthesis represent the percentage values)

It is observed from the table that total cost of pepper cultivation during the bearing period was Rs. 48471.48. Without considering the size of farm groups, at the aggregate level, total variable cost constituted highest proportion (66.88 per cent) while fixed cost constituted 33.12 per cent of the total cost. Among total variable cost, the share of labour cost was 45.26 per cent and the share of material cost was 16.38 per cent of the total cost. Among labour cost, harvesting and drying was the major item of cost accounting for 23.66 per cent of total cost which was followed by intercultural operations (8.38 per cent), application of manure and fertilizer (7.79 per cent), plant protection measures (4.29 per cent) and miscellaneous costs (1.14 per cent).

In the case of material cost the important items were cost of manure (9.76), chemical fertilizers (2.85 per cent) and plant protection chemicals (3 per cent).

Among fixed cost, the rental value of land was the important item of cost amounted Rs.10,000 per hectare (20.63 per cent), followed by amortized establishment cost (8.19 per cent), interest on fixed capital (2.87 per cent), depreciation (1.22 per cent) and land tax (0.21 per cent.

Cost of Hired Labour and the Imputed Value of Family Labour during the Establishment Period

The results of the analysis of the primary data regarding the cost of hired labour and family labour engaged in the establishment of pepper plants per hectare are furnished in table-4

Table-4 Cost of Hired Labour and the Imputed Value of Family Labour During the Establishment Period

Sl.no	Item	I year	Share in %	II year	Share in %	III year	Share in %	TOTAL	Share in %
1	Hired Labour	11081.19	57.89	6230.84	80.24	6084.04	70.23	23396.07	65.78
2	Family Labour	8059.97	42.11	1534.43	19.76	2578.74	29.77	12173.14	34.22
TOTAL		19141.16	100.00	7765.27	100.00	8662.78	100.00	35569.21	100.00

The imputed value of family labour engaged in pepper cultivation during the period of establishment of new pepper plantations was found as the 34.22 per cent of the total labour cost. During the first year the share of family labour was 42.11 per cent and in second and third years these were 19.76 per cent and 29.77 per cent respectively. The total imputed value of family labour was estimated as Rs.12173.14 and the total cost incurred for hired labour was Rs.23396.07

Imputed Value of Family Labour Engaged During the Bearing Period

Cost of labour is the most important item of expenditure in pepper farming. The analysis of the data shown that average total labour cost incurred per hectare during the bearing period was 45.26 per cent (Rs.21937.96) of the total cost of cultivation (Rs.48471.48). Hired labour and family labour wise distribution of labour cost is given in table 5.

Table-5 Imputed Value of Family Labour Engaged During the Bearing Period

Sl.no	Item	Cost	Share in %
1	Hired Labour	14908.68	67.39
2	Family Labour	7029.28	32.61
TOTAL		21937	100.00

(Source- Primary data)

The attempt to work out the labour requirement for the pepper cultivation showed that the family labour constituted around one third of the total labour input used for pepper cultivation during the bearing period. This estimation is made on the basis of the average, irrespective of different farm sizes such as small, medium and large. It was found that both male and female labour was involved in various cultivating practices related to pepper. The total number of work days of both male and female workers which are required for the establishment of pepper plants per hectare during the establishing period and in bearing period were also worked out. For getting clarity for the model, female work days were converted to male work days by considering the average wage of male workers.

The findings of the survey have also revealed that shortage of labour and the escalating wages are the main problems faced by the pepper cultivators. Harvesting and post harvesting practices require skilled and efficient labourers, otherwise it raises the harvesting cost and thereby the profitability of the pepper growers go down.

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STUDIES ON λ CYHALOTHRIN INDUCED CHANGES IN THE LEVEL OF TAURINE AND HISTOLOGICAL ALTERATIONS IN THE BRAIN TISSUE OF FRESH WATER TILAPIA (*Oreochromis mossambicus*)

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Abstract

Taurine is a main ingredient in bile and helps in the digestion of fats and the absorption of vitamins that are fat soluble. It is a necessary amino acid that our body produces naturally. An attempt was made to determine the deleterious effects of λ cyhalothrin –induced in fresh water tilapia (O.mossambicus) with respect to changes in the level of taurine in the liver. Significant ($p<0.05$) elevation in the level of lipid peroxidation was observed in Group IV [pesticide+ acetone 1.1µg/l] fishes as compared to control. Also a concomitant decline was observed in the level of taurine content in Group IV fishes. The role of taurine in modulating calcium homeostasis could be of specific importance for pathological diseases that are characterized by excessive calcium overloads. In Group IV fishes λ cyhalothrin might have inhibited the taurine mediated biological processes such as cell membrane stabilization, antioxidation and osmoregulation in the hepatic membrane. This might be a possible reason for the λ cyhalothrin induced toxicity. Brain has been used as the key organ to understand the toxic impact of λ cyhalothrin in O.mossambicus. The histopathological observation made in brain tissue indicates that λ cyhalothrin may act as a potential neurotoxin in fishes.

Keywords: λ cyhalothrin, o.mossambicus, taurine, lipid peroxidation, brain, hepatic membrane, histology.

Introduction

λ cyhalothrin, is a mixture of highly active isomers of cyhalothrin. cyhalothrin is a pyrethroid insecticide. Pyrethroids are synthetic insecticides derived from natural pyrethrins, which are produced by a species of chrysanthemum. Pyrethroid use in agriculture and urban pest control has been increasing steadily because of the phasing out of organophosphate insecticides, the potential risk of which to aquatic systems has become a concern. Because of their lipophilic nature, pyrethroids are readily taken up by biological membranes and tissues. Fish is used as a bio indicator for detecting the changes in the aquatic ecosystem. Tilapia is an exotic species introduced in India in 1952. It is found greatly in back waters, rivers and ponds of kerala. It can tolerate a wide range of environmental conditions like salinity and it is resistant to diseases. Taurine has been demonstrated to function as a direct antioxidant that scavenges or quenches oxygen free radicals, thus inhibiting lipid peroxidation, and as an indirect antioxidant that prevents the

increase in membrane permeability resulting from oxidant injury in many tissues including liver (Chen, 1993). On the other hand, taurine can also function as regulator of intracellular calcium homeostasis (Huxtable, 1992).

Materials and Methods

In the present study, tetraethoxy propane, taurine and trisodium citrate were obtained from M/s. Sigma Chemical Company, St. Louis. MO, USA. All the other chemicals used were of analytical grade.

Fish

Tilapia of length 9-13cm and weight 120-170g were collected from pallathuruthy pond near Medical College Alappuzha, Kerala, India, were selected for the study. Fishes were kept in fibre plastic tanks of 50L capacity containing unchlorinated tap water which is well aerated at normal room temperature (30± 2^{o}C, 12 h light/ dark cycle). The feeding and maintenance of the fish and the physico-chemical characteristics of water used for acclimatization, control and experimentation were as per the procedure of APHA (1995).

Experimental Protocol

Prior to the commencement of the experiment 96hr LC_{50} for λ cyhalothrin was found to be 1.3µg/l. After acclimatization, the fishes were divided into four groups of 10 fishes each. Group I served as control. Group II were normal fishes exposed to acetone alone (vehicle control). Group III and Group IV fishes were exposed to λ cyhalothrin [0.3 µg (dissolved in acetone)/l] lowest concentration and [1.1µg (dissolved in acetone)/l] highest concentration respectively for the induction of oxidative stress. The fibre plastic tanks were covered with nylon nets. Toxicant solution was changed every 24h and the experiment was proceeded for a period of 15 days. At the end of the 15th day, fishes were killed and liver tissue was taken for estimation of taurine and histopathological alterations in brain. Free aminoacid (taurine) in the liver tissue were determined as per the procedure of Ishida *et al.,(*1981).

Result and Discussion

In the present study, a mild (p<0.05) increase was observed in the level of taurine content in Group II (acetone treated) fishes compared to Group I (control) fishes. But a significant decline was observed in the level of taurine content in Group IV (pesticide + acetone treated 1.1 µg/l) fishes when compared to Group I control fishes **Fig 1.** Taurine is a conditionally essential amino acid and is either derived from food/feed biosynthesised in the liver. Taurine is involved in various important biological and physiological functions, which include cell membrane stabilization (Heller-Stilb *et al.,* 2002), antioxidation (Atmaca 2004), detoxication (Birdsall, 1998), osmoregulation (Timbrell *et al.,* 1995), neuromodulation, brain (Renteria *et al.,* 2004) and retinal development (Wright *et al.,*

1986). In fish, taurine is one of the main osmoregulators (O'Flaherty *et al.,*1997). Lipid peroxidation refers to the oxidative degradation of lipids. In the present investigation, on exposure of λ cyhalothrin induced significant (p<0.05) increase in the level of lipid peroxidation in the liver tissue of Group IV (pesticide + acetone treated 1.1 µg/l) fishes as compared to Group I (control). There were no significant alterations observed in the level of lipid peroxidation in Group II (acetone treated) and Group III (pesticide + acetone 0.3µg/l) fishes as compared to Group I control fishes **Fig 2.**

Histopathological observations in brain tissue of fishes reveal the following aspects:

a) **PLATE 1** Group I control fishes shows no significant changes.

b) **PLATE 2** Group II acetone treated fishes shows that some neurons are completely lysed and there are areas of encephalomalacia. The 2nd photograph shows neurolysis.

c) **PLATE 3** 1st and 2ndphotographic view of brain tissue of λ cyhalothrin administered fishes of Group III (pesticide + acetone 0.3µg/l) shows slight demylenation of the brain. The 2nd photograph also shows neurolysis, encephalomalacia and promatolysis.

d)**PLATE 4** histology of the brain tissue sections of Group IV (pesticide+ acetone1.1µg/l) fishes shows no significant changes in the 1st photograph where as in the 2nd photograph shows neurolysis, vacoulation of the neurons and slight demylenation.

Taurine has been demonstrated to function as a direct antioxidant that scavenges or quenches oxygen free radicals, thus inhibiting lipid peroxidation, and as an indirect antioxidant that prevents the increase in membrane permeability resulting from oxidant injury in many tissues including liver (Chen, 1993). On the other hand, taurine can also function as regulator of intracellular calcium homeostasis (Huxtable, 1992). In the present study the stabilizing impact of taurine on cellular membrane has been proposed to be connected with the interaction between taurine and polyunsaturated fatty acids in the membrane, which brings about the increasing similarity of taurine for its carrier transport and the interaction between taurine and the areas associated with anion transport and water influx. The role of taurine in modulating calcium homeostasis could be of specific importance for pathological diseases that are characterized by excessive calcium overloads. In Group IV fishes λ cyhalothrin might have inhibited the taurine mediated biological processes such as cell membrane stabilization, antioxidation and osmoregulation in the hepatic membrane. This might be a possible reason for the λ cyhalothrin induced toxicity.

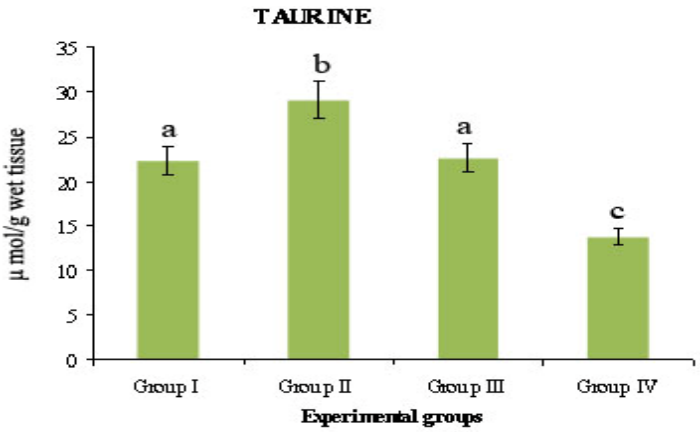

Fig 1 Level of taurine content in liver tissue of control and experimental groups of fishes. Results are mean±SD for 10 fishes; one-way ANOVA ($p<0.05$;Duncan's multiple range test). Values expressed:µmol/g. Values that have a different superscript letter (a,b,c)differ significantly with each other

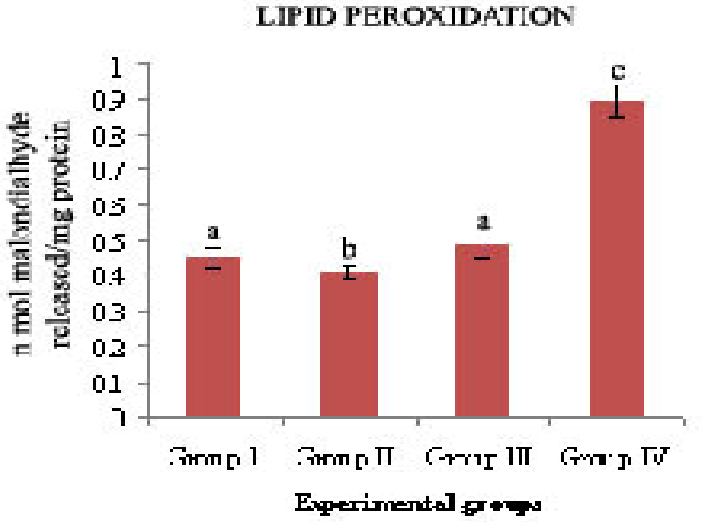

Fig 2 Level of LPO content in liver tissue of control and experimental groups of fishes. Results are mean±SD for 10 fishes; one-way ANOVA ($p<0.05$:Duncan's multiple range test). Values expressed: LPOµ mol malondialdehyde released/mg protein. Values that have a different superscript letter (a,b,c)differ significantly with each other

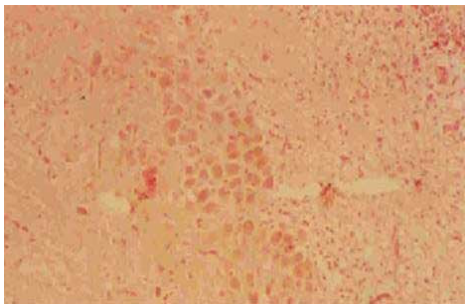

Plate.1 The architecture of normal brain tissue in Group (I) control fishes (Haematoxylin and Eosin 100x)

(1) (2)

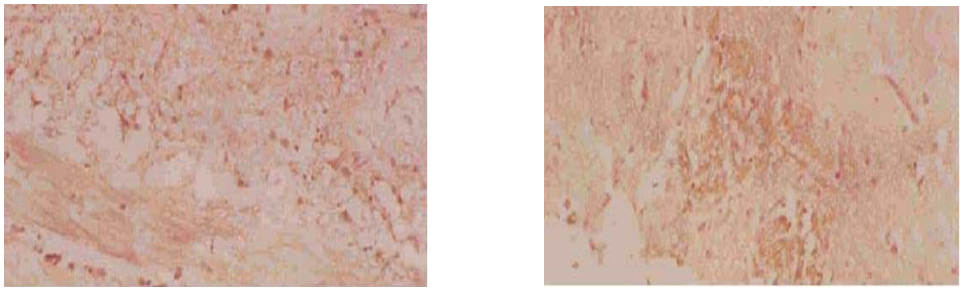

Plate. 2 Architectural view in the brain tissue of λ cyhalothrin administered fishes Group (II) acetone treated (Haematoxylin and Eosin 100x)

(1) (2)

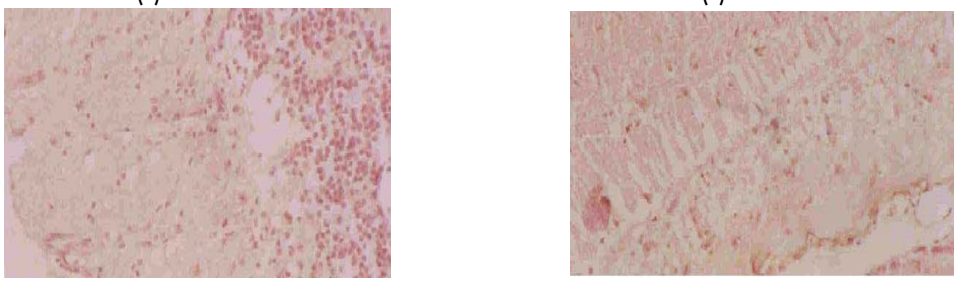

Plate. 3 Photographic view of brain tissue of λ cyhalothrin administered fishes Group (III) pesticide + acetone 0.3µg/l (Haematoxylin and Eosin 100x)

(1) (2)

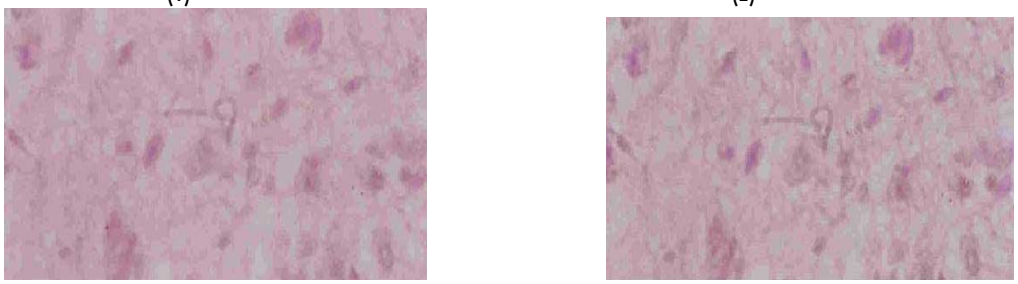

Plate.4 Histology of the brain tissue sections of Group (IV) pesticide +acetone 1.1µg/l λ cyhalothrin administered fishes (Haematoxylin and Eosin 100x)

Conclusion

The present experimental trials revealed that λ cyhalothrin may also be neurotoxic, evidenced by the histological changes. These findings agreed with earlier reports by Omitoyin *et al.,* 2006 in *clarias gariepinus* exposed to glyphosate

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A SURVEY OF GROUND WATER QUALITY STATUS OF PUTHENVELIKKARA PANCHAYATH IN ERNAKULAM DISTRICT OF KERALA STATE, INDIA

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Abstract

Open dug wells are important ground water extraction structures in the costal belt of Kerala and the ground water is the most common source of drinking water in these areas. Off late, these precious resources are getting contaminated high various effluents and anthropogenic activities. Quality of water is an important criterion for evaluating the suitability of water for drinking and irrigation. In the present investigation ground water samples of dug wells from 18 wards of Puthenvelikkara Panchayath were studied for a period from January 2014 to April 2014. Temperature, pH, EC, Ca, Mg, TDS, Alkalinity, iron, DO, BOD are within the permissible limit. Chloride in 11 of the samples, acidity in all the studied samples, total hardness in 5 of the samples and carbon dioxide in 60% of the samples exceeds the permissible limit. The results of the present study suggest that even though the contamination problem is not alarming at present, ground water quality of the study area may deteriorate with time.

Keywords: ground water, drinking, irrigation ,alkalinity, hardness

Introduction

Ground water is one among the Nation's most important natural resources. It is one of the major sources for drinking water, agriculture, industry, as well as to the health of rivers, wetlands, and estuaries throughout the country. Large-scale development of ground-water resources with accompanying declines in ground-water levels and pollution has led to concerns about the future availability of groundwater to meet domestic, agricultural and industrial needs (Datta, 2005).

Ground water is an invisible natural resource. It is present beneath our feet, in the dark pores and fissures of sands and rocks of the upper portion of the Earth's crust. Due to this hidden dimension, the general public is much less familiar with groundwater than with more visible components of the water cycle, such as rain and surface water. Without groundwater, the face of the planet would look different. Groundwater is used to meet 23% of all irrigation demands, to feed 53% of all public water supplies and to cover 97% of all rural domestic water demands. Now a days, this precious natural water resource is contaminated in many ways, hence the study of

groundwater quality and its spatio- temporal distribution are important for drinking, irrigation and industrial water supply, and for sustaining the ecology of streams and wetlands. (Jeyavel Rajakumar etal 2010).

Kerala is one among the most thickly populated state in India. As a result of the measures to satisfy the needs of the huge population, the river, pond, wells, tanks and streams of Kerala have been increasingly polluted from the industrial and domestic waste and from pesticides and fertilizers. Industries discharge hazardous pollutants like phosphates, sulphides, ammonia N, fluorides, heavy metals and insecticides into the water bodies. Recent trend is much alarming i.e. depositing the chemicals from factories, E. waste (computer waste) and other biological wastes (chicken waste) in open wells and ponds.

Open dug wells are important ground water extraction structures in the coastal belt of Kerala and ground water is the most common source of drinking water in these areas. In general, ground water quality of Kerala is very good. Of late, these precious resources are getting contaminated by various effluents and anthropogenic activities. Open wells of Kerala have the problem of bacteriological contamination and studies have shown that fecal contamination is present in 15% of drinking water wells. This could be due to poor or poorly maintained sanitation facilities. Majority of the population have access to piped water but only have proper sanitation facilities. (Shaji E 2011).

The chemical composition of groundwater depends upon the soluble products of rock weathering and decomposition and changes with respect to time and space in addition to the polluting agents. Improper disposal of liquid wastes, defective well construction and failure to seal the abandoned well cause the contamination of groundwater through the natural processes of infiltration and percolation. Contamination of groundwater may also occur by the movement of wastewater through large openings and fissures in rocks. In addition to these factors, seawater intrusion causes groundwater deterioration in coastal areas. The quality of groundwater can be viewed as the resultant of all the processes and reactions that act on the water from the moment it condensed in the atmosphere to the time it is discharged by a well or spring and varies from place to place and with the depth of water table. (Jain etal. 995)

The effectiveness of groundwater quality management and protection relies on enforcement and a comprehensive, targeted monitoring program. Since monitoring often must be under taken over the long terms, it often suffers budget

cuts or is neglected due to lack of resources. However, if baseline trends are not known, early response to potentially adverse impact is not possible. Monitoring is a key activity to enable identification and protection groundwater from pollution. It is in this context a groundwater quality assessment dug wells of Puthenvelikkara Panchayath is Ernakulam District is under taken.

Study Area

Puthenvelikkara is a panchayath in Paravur Taluk, Ernakulam in the Indian State of Kerala. It is located between 10^0 10' 0'N latitude of 76^0, 14' 0' East longitude and covers a total area of 19.87 km^2. It is surrounded by waters: rivers and lagoon and has a population of 32,213 as per 2001 census and has 18 wards. It is on the banks of rivers Periyar, Chalakudy and Kottappuram lagoon. It has been a centre of agricultural production with paddy fields.

Materials and Methods

Groundwater samples were collected from dug wells of 18 wards of Puthenvelikkara Panchayath during the period from January 2014 to April 2014. Samples were collected in clean polythene bottles without any bubbles. The bottles were rinsed before sampling and tightly sealed after collection and lapelled in the field. The temperature of water samples was measured in the field itself at the time of collection. After the collection of samples, they were properly labeled indicating source, date, time of collection and other records. The water samples were brought to the water testing laboratory and kept in refrigerator at 4^0c for further analysis. Water quality parameters such as pH, Total dissolve solids Electrical conductivity, TDS, Acidity, Alkalinity, Acidity, Total Hardness, Calcium, Magnesium, Chloride, Free CO_2, Iron, DO, BOD, and COD were analyzed using standard procedures.

Results and Discussion

In the present investigation, a comparative study of general parameters of water samples from 17 wards of Puthenvelikkara Panchayath were analyzed. The results are given in table 1 and compared with the standards prescribed by ISI, WHO 1984, US public health service and Kerala Pollution Control Board.

Temperature

The temperature of the water body ranged from 27.9°C to 2°C. In general the temperature of the shallow ground water approximates that of the mean annual temperature of the air. The dominant factor controlling groundwater temperature was found to be the geothermal gradient. Temperature is basically important for its effect on certain chemical and biological activities in organisms in aquatic media Rita et al. 2011.

pH

pH is considered as an important ecological factor, which provides an important piece of information in many types of geochemical equilibrium or solubility calculations. It is an important parameter in water body since most of the aquatic organisms are adapted to an average pH and do not withstand abrupt changes. The pH of the water samples studied in the present investigation varied between the permissible limits of 6.5 and 8.5 (BIS 1991) except for one sample.

Electrical Conductivity

The EC of water samples ranged from 1.02 10^{-3} to 7.8 x 10^{3} siemen. Minimum value was recorded from sample 10 ad maximum from sample 17. It indicated the presence of ionic salts in drinking water sources and a rise in conductivity indicates pollution.

Calcium

The Calcium forms the principal cation in most of the natural freshwater samples, as it is an essential constituent in the igneous rocks. The extreme mobile nature in hydrosphere is responsible for the occurrence of calcium as one of the major constituents in ground waters. The presence of other cations like potassium and sodium also influences the concentration of calcium. The calcium concentration in the present study ranges from 33.6 - 77.9mg/L. ISI specified maximum value of Ca is 75 mg/L.

Magnesium

The source of magnesium in ground water is due to ionic exchange of minerals in rocks and soils by water. Magnesium and calcium together are major contributors to hardness of waters. ISI specified maximum permissible value of Mg is 30mg/L. In the present study magnesium varies from 18.5 to 82.03 mg/L. According to KSPCB the relaxation allowed value for Mg is 100mg/L. So in all the studied samples the value is within permissible limits.

Chloride

Chloride occurs in natural water with widely varying concentration. Chlorides gain access to natural water through many ways particularly because of solvent power of water, which dissolves chloride from top soil as well as from deeper formations. The higher concentration in certain waters is due to the lateral movement from the source. The higher concentration of chloride above 250 mg/L makes the water salty in taste. The concentration of chloride in the study area varies from 112-671mg/L. In eleven of the samples, chloride concentration exceed the permissible limits. According to BIS the permissible limit of chloride is 250 mg/L.

TDS

In the present investigation TDS value varies from 0212-0.542 mg/L. The maximum permissible limit of total dissolved solids in drinking water is 500mg/L according to WHO and BIS standard. The TDS values in all the samples are within the permissible limits. Water containing high TDS concentration may cause laxative or constipation effects besides taste Krishnamoorthi 2010.

Acidity

Acidity is the quantitative capacity of aqueous to media to react with OH ions or to accept electrons. Acidity of water lowers dissolved CO_2 content thereby reducing photosynthetic activity. The observed values are in the range between 10-50 mg/L. The permissible limit of BIS value is less than 1mg/L.

Alkalinity

The overall range of alkalinity for the studied samples ranged from 40-300mg/L. The desirable limit of alkalinity in potable water is 200mg/L (BIS 1991). The maximum permissible limit is 600mg/L. The measure of alkalinity provides an idea of natural salts present in water. The cause of alkalinity is the minerals that dissolve in water from soil. The various ions that contribute to alkalinity include bicarbonates, hydroxides, phosphates, borates and organic acids. These factors are characteristics of the source of water and natural processes taking place at any given time. (Murugappan et.al 2010).

Total Hardness

The total hardness of water samples analyzed was found to vary in the range 24- 428 mg/L. As per Bureau of Indian standards 10500-1991 specifications, the desirable limit of total hardness is 300 mg/L and the maximum permissible limit is 600mg/L. Out of the 17 samples studied in the present investigation, in five of the samples the value exceeded the limit of 300 mg/L.

COD

The COD values ranged from 1500 mg to 17600 mg/L. It measures the organic and inorganic content as indicators of the amount of dissolved oxygen that will be removed from the water column and sediment, due to bacterial or chemical activity. Desirable limit is less than 10mg/L. (Ramesh Babu 2009). The permissible limit of COD is 750mg/L.

Iron

Iron is an essential element in human nutrition. Anaerobic groundwater may contain Fe at concentrations up to several milligrams/litre without discoloration or turbidity in the water.

Taste is not usually noticeable as iron concentration below 0.3 mg/L, although turbidity and colours may develop in piped systems at levels above 0.05 to 0.1mg/l. Long time consumption of drinking water with a high concentration of iron led to liver diseases. In the present study iron concentration varies from 0.008 to 0.023mg/L. ISI prescribed limiting value of iron is 0.3mg/L. 1 mg/L is the relaxation allowed by KSPCB and USPH.

BOD

It is the amount of oxygen consumed by micro organisms in stabilizing the organic matter. BOD depends on oxidisable organic matter present in aquatic body. The 5 day BOD value is expressed in milligram/L varies from 0.2 to 0.37 mg/L. The permissible limit for BOD as per WHO 1992 is 5mg/L. The water from all the samples from the study area have BOD value much less than permissible limits Nima K.P. 2013.

Dissolved Oxygen

It is one of the most important parameters in water quality assessment and reflects the physical and biological processes prevailing in waters. The concentration of dissolved oxygen range from 5.2 to 8.2 mg/L. The optimal value for good quality water is 4-6 ml/L of DO. The WHO standard of DO is > 5ml/L. In all the studied samples, it is in conformity with the standards. The amount of dissolved oxygen is an index of productivity in aquatic systems. The photosynthetic and respiratory activities have profound influence on dissolved oxygen concentration. Dissolved oxygen level can also be correlated with the photosynthetic activity. Low oxygen concentrations are generally associated with heavy contamination by organic matter. The value of DO showed negative correlation with temperature. There is an inverse relationship between temperature and dissolved oxygen.

Free CO_2

Free CO_2 in water forms carbonic acid (H_2CO_3), which dissociates into H^+ and HCO_3^- ions. This brings a change in pH of water as H^+ ions set free. HCO_3 reacts with calcium to calcium bicarbonate, which is soluble in water. If free CO_2 is not available at this stage Calcium carbonate gets, which is soluble in water. If free CO_2 is not available at this stage, calcium carbonate gets converted in to insoluble calcium carbonate. Thus free CO_2 is dependent on the temperature and controls the pH and concentration of bicarbonates, carbonates and calcium. In this investigation free CO_2 ranged from 0.791 to 4.494 mg/L. The acceptable range of CO_2 for most finfish is less than 2mg/L. In more than 60% of the studied samples it is well above the permissible limit.

Table 1. Physico Chemical Parameters of dug wells of Puthenvelikkara Panchayath

No		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Temperature (^{0}C)	28.4	28	28	28.1	29	27.9	28	28.3	29	27.8	28.1	28.1	28.7	28	29	28.2	28.1
2	pH	8.26	7.57	7.32	6.66	7.22	7.36	6.15	6.70	7.30	7.58	7.12	6.94	7	6.56	7.34	6.78	6.68
3	Electrical Conductivity (siemen)	1.3 x10^{-3}	1.11 x10^{-3}	2.4 x10^{-3}	1.2 x10^{-3}	2.6 x10^{-3}	4.2 x10^{-3}	1.78 x10^{-3}	1.7 x10^{-3}	2.8 x10^{-3}	1.02 x10^{-3}	7.4 x10^{-3}	4.2 x10^{-3}	3.2 x10^{-3}	2.1 x10^{-3}	1.88 x10^{-3}	1.3 x10^{-3}	7.8 x10^{-3}
4	TDS	0.091	0.112	0.323	0.103	0.472	0.234	0.542	0.043	0.271	0.021	0.311	0.051	0.067	0.031	0.081	0.0931	0.068
5	Acidity	12.5	17.5	50	15	12.5	25	20	32.5	37.5	45	50	40	10	35	37.5	17.5	12.5
6	Alkalinity	60	90	70	110	65	60	80	145	100	125	150	150	35	300	130	150	40
7	Total hardness	231	428	97	142	306	232	110	24	340	200	310	270	40	122	140	305	140
8	Calcium	76.2	51.3	44.2	33.8	62.4	71.4	77.8	39.2	46.2	50.04	38.1	65.4	56.7	33.6	77.9	39.4	56.7
9	Magnesium	19.2	25.2	82.03	19.1	31.4	68.6	19.4	22.3	18.6	74.22	24.3	58.8	60.4	18.5	19.6	59.8	58.2
10	Chloride	216	562	221.2	112	432	671.3	474	173	265.2	371	148	321.6	138	621.4	435	610	371
11	Free CO_2	2.69	1.49	3.196	0.791	2.596	0.898	4.494	3.296	2.397	2.996	3.795	0.799	2.497	4.89	2.996	1.697	3.096
12	Iron	0.021	0.037	0.002	0.017	0.004	0.0121	0.008	0.010	0.004	0.032	0.021	0.011	0.007	0.023	0.004	0.006	0.013
13	DO	7.4	8.1	6	7.7	6.2	5.2	6.2	8.1	6	7.1	6	8.2	6.4	8.3	5.6	7.2	5.3
14	BOD	0.35	0.7	0.24	0.4	3.1	1.6	3.4	1	0.8	0.2	0.36	0.6	1.4	0.6	0.37	3.2	0.8
15	COD	7000	16000	12000	4600	5200	12000	10400	9200	17600	7000	11000	4400	14000	5200	1500	4100	4400

All the parameters are in mg/l except temperature (^{0}C), pH, EC (Siemen)

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TiO_2-REDUCED GRAPHENE OXIDE NANOCOMPOSITES WITH HIGH PHOTOCATALYTIC ACTIVITY FOR THE REMOVAL OF RHODAMINE B FROM WATER

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Abstract

Photocatalytic methods for environmental remediation have been an active field of research for over three decades. However, the effectiveness of this approach can be enhanced several-fold when the inorganic semiconductor active material is combined with other complementary components. In this study TiO_2-reduced graphene oxide (RGO) composites were prepared by a simple and environmentally benign one-step hydrothermal methodusing the titanium dioxide precursor $TiCl_4$ and graphene oxide (GO). Hydrolysis of $TiCl_4$ and mild reduction of GO were simultaneously carried out under hydrothermal conditions. The graphene nature of RGO in the composite was confirmed by X-ray diffraction (XRD), UV visible absorption spectroscopy, Raman spectroscopy and Transmission electron spectroscopy (TEM).The photocatalytic performance of the TiO_2-RGO composites was evaluated for the photodegradation of Rhodamine B in an aqueous solution. The TiO_2-RGO nanocomposites exhibited much higher photocatalytic activity than pure TiO_2.The presence of RGO sheets as a two- dimensional (2D) platform for the deposition of titanium dioxideimproved the adsorption of Rhodamine B. As the graphene oxide in the composites has a very good contact with the TiO_2 nanoparticles it enhances the photo-electron conversion of TiO_2 by reducing the recombination of photo-generated electron–hole pairs.

Keywords: TiO_2, reduced graphene oxide, nanocomposites, Rhodamine B, photocatalysis.

1. Introduction

Over the last decade semiconductor mediated photocatalysis have been investigated as an efficient Advanced Oxidation Process (AOP)for the removal of aqueous contaminants or air pollutants. Generally, photocatalysis by semiconductors is the result of the interaction of photo generated electrons and holes with the substrate. These electrons and holes can participate in reductive and oxidativere actions that lead to the decomposition of pollutants. Among various oxide semiconductor photocatalysts, Titanium dioxide has attracted interest of many researchers in recent years because of its applicability for all the three classes of water contaminants viz., organic, inorganic and microbiological with a minimal risk of the production of harmfulbyproducts.[1.-3] Titanium dioxide has been proven to be the most suitable photocatalyst because of its chemical inertness, strong oxidizing power, long-term stability against photo andchemical corrosion, suitable band gap

energy and electronic andoptical properties. Also titanium dioxide is photocatalytically stable, relatively easy to produce and is able to efficiently catalyzereactions. Undesirable recombination of electrons and holes, and low efficiency under irradiation in the visible region are the two main drawbacks associated with the use of TiO_2 for environmental applications. Efforts have been made to extend the light absorption range of TiO_2 from UV to visible light and to improve the photocatalytic activity of TiO_2. For example, doping, combining with metal oxides, semiconductors, and carbon materials.[1-7] In particular, there is growing interest in the combination of carbon based materials and TiO_2 to enhance photocatalytic performance.

As a rising star of carbon family, graphene has become the focus of considerable interest because of its unique electronic properties and other excellent attributes, such as high chemical stability, large theoretical specific surface area (2630 m^2/g), high Young's modulus (~1.0 TPa), high thermal conductivity (~5000 W/m/K), excellent mobility of charge carriers (20,000 $cm^2\ V^{-1}\ s^{-1}$) and relatively good optical transparency.[8]On the basis of this understanding, graphene can be combined with TiO_2 because the ¶-¶ conjugation net and the conductivity made graphene an efficient electron acceptor, when the semiconductors were excited, the electrons at the interface could be transferred to graphene and stabilized by the conjugation net, retarding the charge recombination. Graphene also provides a favorable absorption of dye through ¶-¶ conjugation between thedye and aromatic regions of graphene owns pristine mechanical performance to stabilize the catalysis and offers the two-dimensional plane to deposit catalyst. It seems reasonable to envision that the novel TiO_2–graphene nanocomposite with high interfacial contact and potential could be much more promising to improve the photocatalytic performance of TiO_2. Furthermore, grapheneis easy to produce from inexpensive natural graphite through intermediates product "graphene oxide".[9, 10]The presence of oxygen-containing functional groups in GO and reduced GO makes them as excellent supporters to anchor TiO_2 nano crystals for the synthesis of TiO_2-graphene. Moreover anchoring wellorganizedTiO_2 nanostructures on GO sheets can efficiently utilize the combined merits of TiO_2 and GO to obtain a photocatalyst with superior performance. Several synthetic techniques such as chemical reduction using hydrazine, UV assisted photoreduction,[11] sol−gel method,[12] Chemical Vapour Deposition,[13] solvothermal method[14]have been employed for the preparation of TiO_2−graphene composites. This work demonstrated a simple and environmentally benign one-step hydrothermal methodto synthesize TiO_2/Reduced Graphene Oxide (RGO) nanocomposite using the titanium dioxide precursor $TiCl_4$ and graphene oxide (GO). Hydrolysis of $TiCl_4$ and mild reduction of GO were simultaneously carried out under hydrothermal conditions. The most notable aspect

of this approach is the use of an aqueous solution and lack of harsh chemicals (such as hydrazine) during synthesis. Accordingly, the proposed approach is highly energy-efficient and environmentally benign, making it truly green. The catalysts show enhanced photocatalytic activity toward the degradation of the rhodamine B dye under UVlight irradiation.

2. Materials and Methods

2.1. Materials

Graphite powder (<20 μm, synthetic), $NaNO_3$ (99.0%), H_2SO_4 (95.0%), $KMnO_4$ (99.3%), and H_2O_2 (34.5%) were purchased from Merck, India. Titanium tetrachloride ($TiCl_4$) was purchased from Sigma-Aldrich. All the chemicals were used as received and without further purification. In all experiments deionized water was used.

2.2. Synthesis of Graphene Oxide.

Graphene oxide (GO) was prepared from graphite powder using a modified Hummer's method.[16]In brief, first, 0.5 g of powdered flake of graphite and 0.5 g of $NaNO_3$ were added into 24 mL of H_2SO_4 and were stirred until dissolved. Then, 3 g of KMnO4 was added slowly, preventing the temperature of the suspension from exceeding 20°C. After the mixture was stirred continuously for 1 h at 35 °C, 40 mL of distilled water was slowly added to dilute the mixture and the temperature was raised to 90 °C. To reduce the residual permanganate and manganese dioxide to colourless soluble manganese sulfate, 5 mL of 34.5% $H_2O_2$was added and the suspension was filtered with distilled water until pH 7.0. The obtained yellow-brown suspension was exfoliated to produce single layer graphene oxide using an oil bath. Finally, a brown dispersion of homogeneously exfoliated graphene oxide was obtained.

2.3. Synthesis of Titanium dioxide-Reduced Graphene Oxide (RGO) Composites.

In a typical reaction, the water dispersion of graphene oxide was sonicated for 15 min under cold conditions. The resulting dispersion was centrifuged at 6000 rpm for 5 min and the supernatant was collected and kept in a refrigerator. Then, 0.2 mL of $TiCl_4$ was added to the 31.0 mL of ice-cooled solution under vigorous stirring. After stirring for 1.5 h at room temperature the brown solution (total volume 31.2 mL) was transferred to a 50 mL Teflon lined stainless steel autoclave for hydrothermal reaction at 180 °C for 8 h. The autoclave was cooled naturally. The resulting black product was collected by centrifugation and washed with deionized water and ethanol. It was then dried at 60 °C. TiO_2-RGO composites with weight % of 1, 2, 5&10 RGO were prepared. In this way, nanocomposites of graphene and titanium dioxide were synthesized. Meanwhile, individual titanium dioxide and RGO for control were synthesized separately following the same procedure.

2.4. Photodegradation Experiment

A stock solution of 1000ppm of Rhodamine B was prepared by dissolving

1000mg/L in double distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions. Photodegradation experiments were carried out by using a 400 W medium pressure mercury vapourlamp (Philips UV-C). The reacting system wassurrounded by a cooling jacket to maintain the reaction temperature constant during reaction, as heat is generated because of irradiation. Reaction mixture was stirred magnetically. Experiments were carried out with 50mL of the dye solution of desired concentration (*Co* = 10 mg/L) prepared in double distilled water. A known amount of photocatalyst was added in solution. Catalyst was removed by centrifugation at6000rpm before analysis. Suspension keptunder identical conditions in the dark was used as the reference in each case to assess the contribution from adsorption towards the reduction in the dye concentration.

2.5. Analysis

The degradation of dye was monitored by measuring the absorbance of dyes in JASCO V670 spectrophotometer. Degradation of Rhodamine B was monitored at 554 nm. The equilibrium adsorption capacity was calculated from the relationship:

$$q_e = (C_0 - C_e)\, V/m$$

where $C_0$and C_e are the initial and residual concentrations of Rh B in ppm, $q_e$is the adsorption capacity in mg/g, V is the volume of Rh B solution in L, and m is the adsorbent mass in g.

3. Results and Discussion

3.1. Characterisation of the Catalysts.

The nanocomposites prepared with different ratios of graphene oxide (GO) were characterized by X-ray diffraction (XRD), UV visible absorption spectroscopy, Raman spectroscopy and Transmission electron spectroscopy (TEM).

3.1.1. X-ray Diffraction

Wide angle powder X-ray diffraction (XRD) pattern of the sample was recorded on a Rigaku D/MAX-diffractometer using CuKα radiation. The XRD pattern of synthesized TiO_2 is shown in Fig.1.

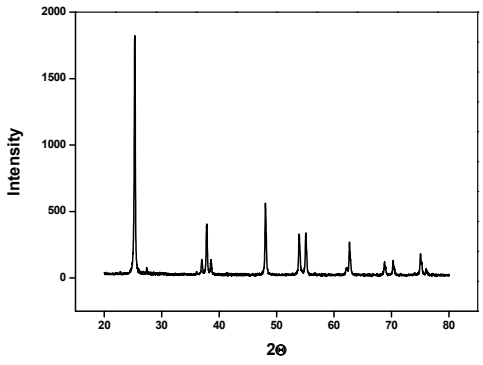


Fig 1. XRD of TiO_2

As shown in the diffractogram, pure titanium dioxide synthesized by the hydrothermal route shows good crystallinity. The peaks of 2θ values at 25.3, 37.9, 48.0, 54.4, 56.6, 62.8, and 68.9° can be indexed to (101), (004), (200), (105), (211), (204), and (116) planes of anatase titanium dioxide respectively.[17]The XRD pattern of TiO_2-

RGO is compared with GO and is shown in Figure2.

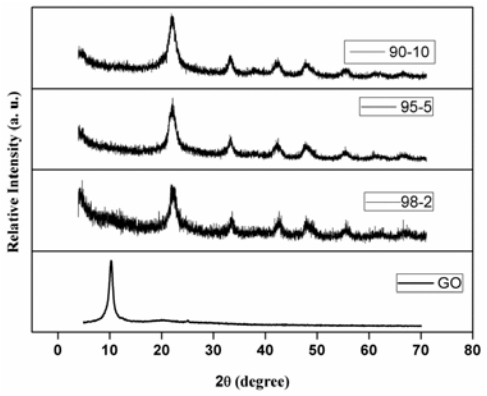


Fig 2: The XRD pattern of GO and TiO_2-RGO

The characteristic peak at 9.7^0 is assigned to the(001)plane of GO, while after reduction of GO to RGO, the diffraction peak at 9.7^0disappears and two broad bands at 25.9^0 and 42.9^0 are observed which are assigned to graphene (002) and (100) planes. Therefore GO is reduced to RGO by the hydrothermal process[18].

3.1.2. UV-Visible absorption Spectrum

The UV-visible absorption spectrum of GO and TiO_2-RGO were recorded on a JASCO V670 spectrophotometer and is shown in figure3.

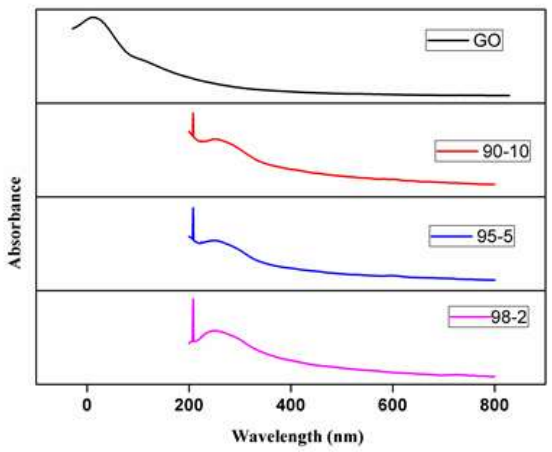


Figure3: The UV-visible absorption spectrum of GO and TiO_2-RGO

The optical absorption onset shows a red shift in the case of composites which shows a much stronger UV visible light absorption than pure GO. The shift of the absorption edge of the TiO_2−RGO composites was possibly ascribed to be due tothe interaction between $TiO_2$and RGO.[17]

3.1.3. Raman Spectroscopy

Raman spectra were obtainedat room temperature from DXR Raman microscope with 633 nm laser excitation and CCD detector. Figure 4 displayed the Raman spectrum of the composite. The typical features of GO in Raman spectra were the D band located at 1348 cm^{-1} and the G band at 1588 cm^{-1}. G band was common to all sp^2 carbon form and provided information on the in-plane vibration of sp^2bonded carbon atoms .The D band suggested the presence of sp3 defects. For the RGO-TiO_2 composite, D and G bands could also be observed in the range 1200−1800 cm^{-1}. [19]

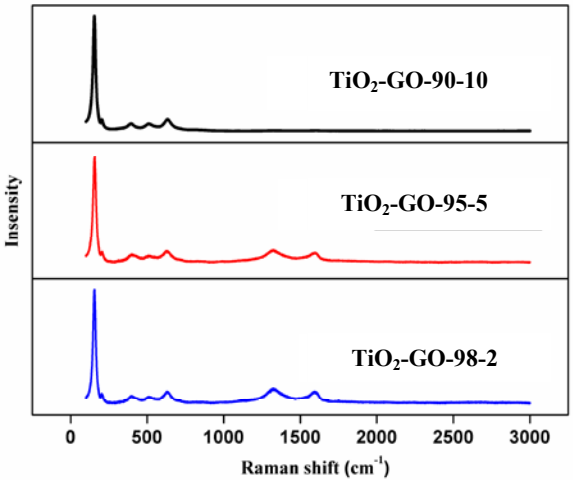


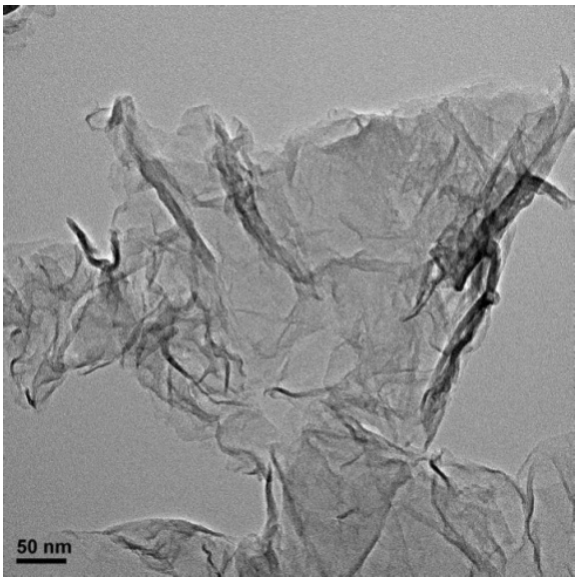
Figure 4: Raman spectrum of TiO_2-RGO nanocomposite

The characteristic D and G bands at 1332 and 1590cm^{-1} of GO was broadened in

the composites illustrating the presence of RGO that originated from the solvothermal reduction of GO.[20]The sharp peak at 143cm^{-1} is attributed to the anatase phase of TiO_2.

3.1.4. Transmission Electron microscopy

Transmission electron microscopic (TEM) image was achieved with Philips CM 200 transmission electron microscope operating at 20–200 kV range. In the TEM images of GO(figure5a) the morphology of GO consisting of thin stacked flakes and having a well-defined layer structure at the edge, can be clearly seen. TiO_2 nanocrystals onto RGO layers are proven by TEM(Fig 5b). It reveals a homogeneous dispersion of TiO_2 in the RGO matrix. The TiO_2 nanoparticles are not simply mixed up or blended with RGO rather they have been entrapped possibly inside the RGO sheets.



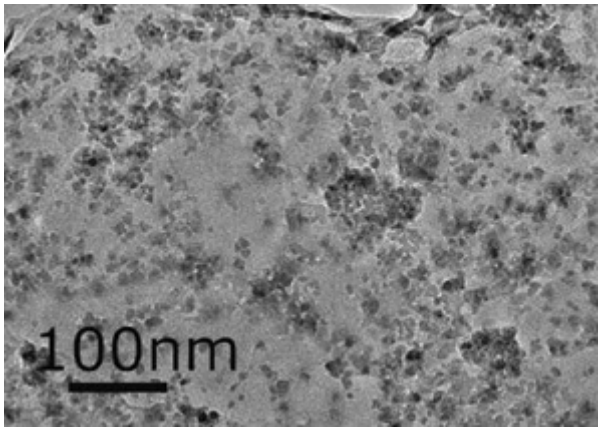


Figure 5: (a) TEM images of GO (b) TiO_2-RGO(5wt%RGO)

3.2. Photocatalytic Degradation of Rhodamine B on TiO_2 and TiO_2-RGO

To evaluate the photocatalytic activity of TiO_2−RGO nanocomposites obtained in this work, a model reaction of RhB is employed for photodegradation experiments under UV light exposure. The dye solution with the catalyst was kept in the dark to assess the contribution of adsorption towards the degradation. Figure 6 shows the absorption of RhB by different composite catalysts in the dark as obtained by the UV−visible absorption measurement of the corresponding samples. The result clearly shows that the dye absorption increases with an increase in the amount of RGO in the catalyst, which is associated with the increased surface area of the catalyst as revealed in Table 1.

Table 1: BET specific surface area of the composites

Samples	BET surface area(m^2g^{-1})
TiO_2	79.3
TiO_2-1 wt%RGO	98.2
TiO_2-2 wt%RGO	118.5
TiO_2-5 wt%RGO	155.7
TiO_2-10 wt%RGO	168.2

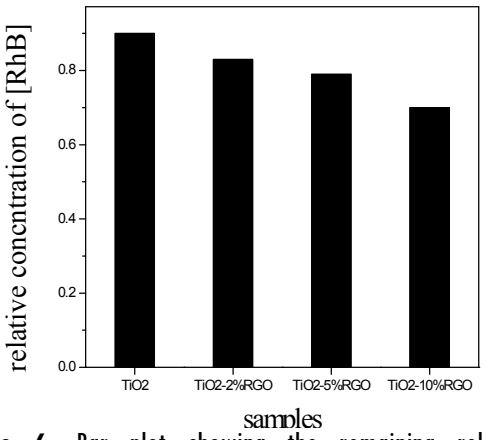


Figure 6: Bar plot showing the remaining relative concentration of RhB after dark absorption by TiO_2–RGO nanocomposites.

Dye also may be absorbedby π–π interactions between the aromatic region of RGO and the dye molecules. Figure7(a)&(b) displays the photodegradation efficiencies of RhB with different catalysts after 120 min of UVexposure. Without the use of a catalyst, the concentration of RhB change only very slightly(less than 5% during

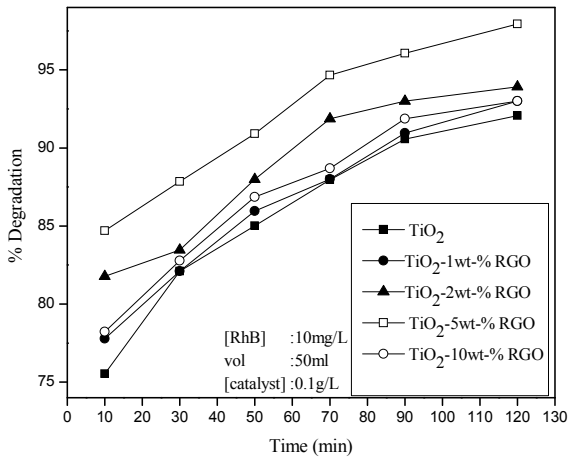


Figure 7: Photodegradation of the RhB dye under UV light

1 hour exposure). A similar phenomenon is displayed by RhB in the presence of RGO. Therefore, RGO does not act as a photocatalyst independently. However, in the presence of a TiO_2–RGO nanocomposite catalyst, photodegradation is remarkably enhanced. The photocatalytic efficiency is maximized at the optimal RGO content in the catalyst. The catalyst with a RGO-concentration of 5weight % (TiO_2–5 weight % RGO) shows the best catalytic activity in UV light. After 120min, 98% of RhB is photocatalytically degraded by the catalyst. In the nanocomposites, dye molecules are adsorbed by both components TiO_2 and RGO. The incorporation of RGO in TiO_2 will increase the surface area. Higher surface area promotes increased dye adsorption. At the same time, some active sites of the catalyst (TiO_2) are disadvantageously occupied by RGO. This leads to a decrease in the number of the active sites of the catalyst, resulting in reduced photocatalytic activity. These two competing factors are compromised with each other upon 5 weight % loading of RGO, at which the screening of active sites counterbalances the effect of increased surface area. Therefore, the nanocomposite of TiO_2–5 weight % RGO shows the best photocatalytic activity. On the other hand, below 2 weight % concentration, the contribution of dye adsorption by RGO may not be sufficiently high as compared to the case of TiO_2–1 weight % RGO composite. Therefore, the photocatalytic activity decreases for reduced RGO loading below 1 weight %.

3.3. Optimisation of the Process Variables

The photocatalytic efficiency is maximized at the optimal RGO content in the catalyst. The catalyst with a RGO-concentration of 5weight % (TiO_2–5 weight % RGO) shows the best catalytic

activity in UV light. So this concentration is selected for optimizing the process variables. As shown in figure 7approximately 85% decolorisation of the dye is achieved in 10 minute time in presence of TiO_2-5weight% RGO catalyst. The degradation in presence of TiO_2-5weight%RGO is about 10% more compared to TiO_2. The photogenerated superoxide/ hydroperoxide (O_2-./HO_2.) radicalsinitiate degradation of the dye. Repeated attacks by the O^{2-} / HO_2 radicals on the pollutant nuclei can lead to the mineralization producing mainly CO_2 and water.

3.3.1. Effect of Catalyst Loading

The effect of catalyst loading on the photocatalytic degradation of the dye is tested using pure TiO_2 and TiO_2-5weight%RGO composites keeping all other reaction parameters constant (Fig.8). The optimum loading is taken as 0.100 g/L in the case of both TiO_2 and TiO_2-RGO.

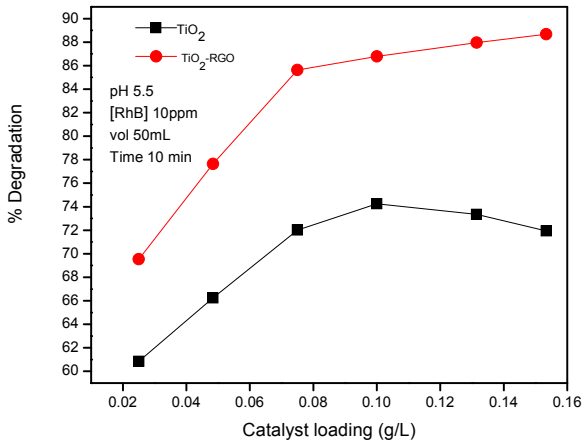


Figure 8: Effect of catalyst loading

3.3.2 Effect of Initial Concentration

Studies on the effect of concentration of Rhodamine in the range of 2-20 mg/L on the rate of photocatalytic degradation in presence of TiO_2 as well as TiO_2-RGO showed that the degradation remains steady or decreases at high initial concentration. The results are shown in figure 9.

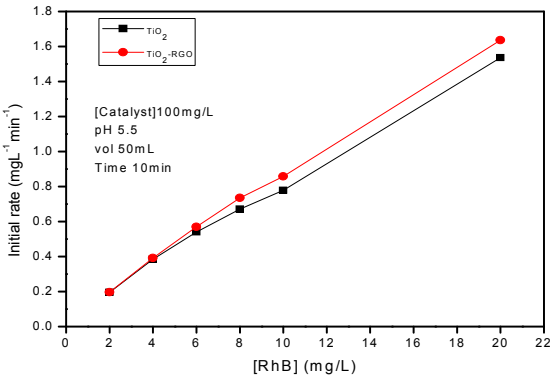


Figure 9: Effect of initial concentration of Rhodamine B on photocatalytic degradation in UV light.

Since the degradation is accelerated by both catalyst and light, the negative effect at increasing concentration implies that at higher concentration, the dye is inhibiting the action of catalyst and/or light. At higher concentration there will be better adsorption of the dye on the surface of the catalyst. This will inhibit the direct absorption of light by the catalyst thereby affecting its ability to generate free radicals and reactive oxygen species. In the absence of continued significant degradation, the adsorbed dye will not leave the surface sites. This prevents the adsorption of new molecules and continued degradation. Thus it is clear that light absorption and number of adsorption sites are the two factors affected by higher concentration of the dye.

3.3.3. Effect of pH

The pH is an important factor in the case of wastewater and hence its effect on the

photocatalytic degradation of the dye is investigated. The results are shown in figure 10.

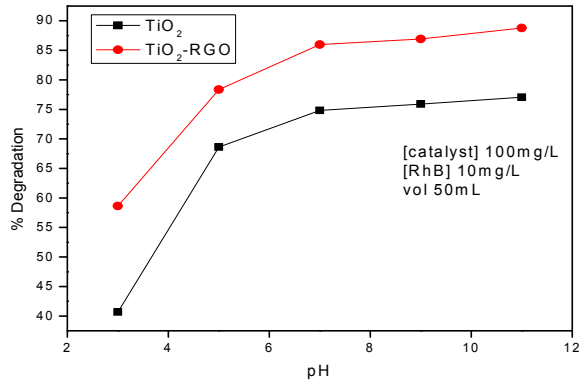


Fig 10: Effect of pHin UV light

The degradation increases with increase in pH, the rate of increase being more in the alkaline range. The variation is not due to any change in the absorption of light as the λmax for the dye changes very little (552-554 nm) in the pH range of 1-13 even though rhodamine exists in two principal forms in water, ie cationic (RhB+) or zwitter ionic (RhB±).[21] At pH value less than the Point of Zero Charge (P_{ZC}) of TiO_2 (6.5), the surface will be positively charged. The effect of pH on the ionization state of the TiO_2surface is as follows:

$$TiOH + H+ \rightarrow TiOH_2 + (1)$$
$$TiOH + OH- \rightarrow TiO- + H_2O (2)$$

In the acidic range the dye will be in cationic form (RhB+). Hence due to electrostatic repulsive forces, the adsorption of the dye on the catalyst is less. Thus the surface promoted degradation is less and the observed degradation is primarily taking place in the solution. At higher pH value, the RhB+ gets deprotonated and its zwitter ion is formed (figure 11).

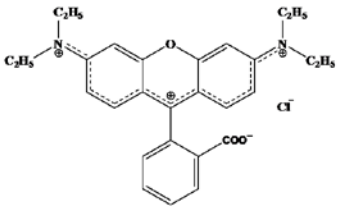


Figure11: Zwitter ionic form of Rh B

This can get adsorbed onto the negatively charged catalyst surface resulting in increased degradation of the dye. Further, under alkaline conditions, more OH radical formation is possible from the abundant hydroxide ions, which also enhances the degradation.

3.4 Kinetics of the photodegradation

The reaction kinetics of the photodegradation of TiO_2 and TiO_2-RGO nanocomposite obeyed a Langmuir– Hinshelwood pseudo-first-order model.

$\ln(C_t/C_o) = -kt$, where k, C_0, and C_t are apparent rate constant, initial concentration, and concentration after a time t respectively. The rate constant calculated for the composite was 0.01865 min^{-1}, which is ~2 times greater than that of TiO_2 (0.01027 min^{-1}).

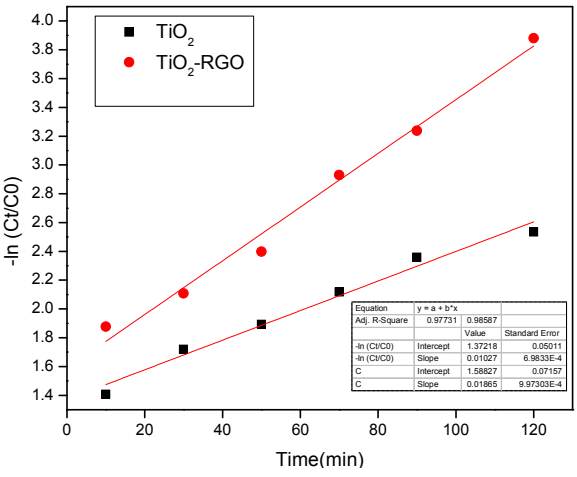


Fig 12:(a) Plot of pseudo first order model

Three reasons may account for the enhanced catalytic activity of the TiO_2–RGO nanocomposites. First, composites with substantially enhanced specific surface area can provide more active sites and adsorb more reactive species. Second, due to its two dimensional π-conjugation structure, RGO can act as an electron acceptor, thereby allowing for the photoexcited electrons of TiO_2 in the composites to be quickly transferred from the conduction band of TiO_2 to RGO. This eventually decreases the rate of recombination of the photogenerated electron–hole pairs, which yields an enhanced photocatalytic activity of the composites. Lastly, the recombination of photogenerated electron–hole pairs can be mitigated via accepting electrons by surface hydroxyl groups in both TiO_2 and RGO. The chemical oxygen demand(COD) was also determined to confirm the mineralization of the dye. A reduction in COD value of the RhB to 3.2 mg/L after 2 hour irradiation in presence of TiO_2-RGO nanocomposite confirmed the mineralization of the dye.

3.5 Conclusions

TiO_2-Reduced graphene oxide composites were successfully prepared by a facile and environmentally benign one-step hydrothermal method using the titanium dioxide precursor $TiCl_4$ and graphene oxide (GO). Hydrolysis of $TiCl_4$ and mild reduction of GO were simultaneously carried out under hydrothermal conditions. The graphene nature of RGO in the composite was confirmed by X-ray diffraction (XRD), UV visible absorption spectroscopy, Raman spectroscopy and Transmission electron spectroscopy (TEM).The photocatalytic performance of the TiO_2-RGO composites was evaluated for the photodegradation of Rhodamine B in an aqueous solution. The TiO_2-RGO nanocomposites exhibited much higher photocatalytic activity than pure TiO_2.The presence of RGO sheets as a two- dimensional (2D) platform for the deposition of titanium dioxide improved the adsorption of Rhodamine B. As the graphene oxide in the composites has a very good contact with the TiO_2 nanoparticles it enhances the photo-electron conversion of TiO_2 by reducing the recombination of photo-generated electron–hole pairs.

$TiO_2$and TiO_2-RGO nanocomposites are good photocatalysts capable of mineralizing the dye Rhodamine B in presence of UV light. TiO_2-RGO is more effective than TiO_2 alone for the removal of the pollutant. The photocatalytic efficiency is maximized at the optimal RGO content in the catalyst. The catalyst with a RGO-concentration of 5weight % (TiO_2–5 weight % RGO) shows the best catalytic activity both in UV and sun light. After 120min, 98% of RhB is

photocatalytically degraded by the catalyst. The degradation in presence of TiO_2-RGO is about 10% more compared to TiO_2 in in UV light. This is due to the inability of pure TiO_2 to get activated significantly in sun light while TiO_2-5weight%RGO continues to absorb light resulting in the formation of electron-hole pairs and subsequent activation of adsorbed oxygen. The comparative advantage of RGO incorporation is not that significant in UV irradiation because TiO_2 itself is very active in this region. Higher pH favours the removal of Rhodamine B while increase in concentration of the dye decreases the % removal. There is an optimum for the catalyst loading beyond which the rate of degradation stabilizes or decreases. Simple decolorisation of the dye solution does not result in mineralisation as seen by the measurement of COD which takes longer time to disappear. The degradation is proceeding through many stable intermediates which also get degraded further and mineralized, though slowly. The reaction kinetics of the photo degradation of TiO_2 and TiO_2-RGO nanocomposite obeyed a Langmuir– Hinshelwood pseudo-first-order model. The rate constant calculated for the composite (TiO_2-5wt%RGO) was 0.01865 min^{-1}, which is ~2 times greater than that of TiO_2 (0.01027 min^{-1}).

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GREEN SYNTHESIS AND CHARACTERIZATION OF SILVER NANO PARTICLES AGAINST FOOD BORNE PATHOGENS

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Abstract

Synthesis of silver nanoparticles using leaf extract is a cost-effective, non-toxic, and environment friendly noval method for the synthesis of nanoparticles. In this study, silver nanoparticles were synthesised using Averrhoa bilimbi leaf extract and examined their anti-bactericidal effect against food borne pathogens Escheria coli and Listeria monocytanes. Silver nanoparticles is characterized by means of UV-Visible spectroscopy and SEM analysis. The anti-bacterial effect of silver nanoparticles is determined by microtitre plate assay. Silver nanoparticles show potential anti-bacterial effect. The anti- bactericidal effect increases with increase in the concentration of nanoparticles. The promising results of silver nanoparticles suggests its usage as an effective antibacterial agent to enhance food safety. These nanoparticles can be incorporate with food package materials to prevent the attack and contamination by the food borne pathogenic bacterias and hence corroborate the food safety.

Keywords: Silver nanoparticle, UV-Visible, SEM

Introduction

Nanotechnology is manipulation of matter to at least one dimension sized from 1 or 100 nanometers. Nanochemistry or nanotechnology is related with the production and the reaction of nanoparticles and their compounds[1-10]. Nanotechnology is being used in developing countries to treat diseases and prevent health issues. Now a day's different methods for the synthesis of metal nano particles are under consideration due to their useful applications in different fields. Conventional methods are uneconomical, time consuming and harmful to environment and to other lives. The aleternative biosynthesis of nanoparticles are free from these drawbacks[11-13]. It is a quick, cost effective, environmentally friendly and a one step method for the synthesis of nannoparticles. Therefore green chemistry and chemical processes [14-19] are increasingly integrated in science and industry for sustainable development. Biosynthesis of nanoparticles gained lots of interest due to the use of mild experimental condition such as temperature, pH, and pressure. Since 19th century, silver based compounds have been used in many antimicrobial applications. Silver is well known for its antimicrobial effect in medicine and industrial products. Silver nanoparticles helps in diagnostics,

in therapies and have wide applications in medical fields. Because of the antibacterial property of silver nanoprticles it can effectively use as an anti bacterial agent. Historically silver has been extensively used for both hygienic and healing purposes. Silver was of particular interest due to its distinctive physical and chemical properties.

The major biological systems which help for the synthesis of nanoparticles are bacteria, fungi, and plant extract. The plant extract mediated process is a simple one step method for the synthesis of silver nanoparticles [20-25]by the reduction of aqueous silver ions using leaf extract at room temperature without using any additive. Biosynthesis of silver nanoparticles using *Averrhoa bilimbi* leaf extract *(*Family; oxalidaceae) and to explore the antibacterial activity against food borne pathogenic bacteria. *Averrhoa bilimbi* is a common plant found in Asia. The bilimbi leaf extract was selected as it is of high medicinal value and it does not require any sample preparation and hence is cost effective. and its easy availability with high healing power. The Green synthesis provides advancement over chemical and physical method as it is cost effective, environment friendly, easily scaled up for large scale synthesis and in this method there is no need to use high pressure, energy, temperature, and toxic chemicals.

Materials and Methods

Fresh leaves of *Averrhoa bilimbi* were collected and washed with distilled water.The plant leaves were chopped in to small pieces. Then 5g of leaf pieces were boiled with 50 ml of nuclease free water for 10 minutes in microwave oven. The extract was cooled at room temperature. Then the extract were filtered through filter paper to get clear solutions.

The aqueous solution of 50mM silver nitrate was prepared and used for the synthesis of silver nanoparticles. 20 ml of silver nitrate and 20ml of the leaf extract was mixed in separate conical flasks. Incubation under dark for 24 hours. Silver nanoparticles formation was investigated.

The *E.coli* bacteria was isolated from decayed fish sample on Eosin Methylene Blue agar. *Listeria monocytogene* bacteria from milk sample on PALCAM agar. Then these plates were incubated at 27° C for 48 hours.

The bio reduction of silver ions in aqueous solution were characterised in Perkin-Elmer UV-Vis spectrophotometer. The UV-Vis absorption spectra of the sample were recorded and numerical data were plotted. The silver nanoparticles suspension was air-dried on the specimen grid and was observed with a JEOL JEM -6480LV Scanning Electron Microscope.

For microtitre plate assay, a sterilized microtitre plate was used. The details of the content are given in the Table 1. The absorbance of each well indicated the growth of the bacteria.

Table 1

Sl.No	Particulates	Treatments
1	40ml distilled water +150ml nutrient broth+40ml bacterial broth	Bacterial Control
2	40ml distilled water +150ml nutrient broth+10ml silver nanoparticles	Regaent Control for test 1
3	40ml distilled water +150ml nutrient broth+20ml silver nanoparticles	Reagent Control for test 2
4	40ml distilled water +150ml nutrient broth+30ml silver nanoparticles	Reagent Control for test 3
5	40ml distilled water +150ml nutrient broth+10ml silver nanoparticles+40ml bacterial broth	Test 1
6	40ml distilled water +150ml nutrient broth+20ml silver nanoparticles+ 40ml bacterial broth	Test 2
7	40ml distilled water +150ml nutrient broth+30ml silver nanoparticles+ 40 ml bacterial broth	Test 3

Results and Discussion

The bacterial cultures were isolated from milk sample (*Listeria monocytogene*) and from decayed fish sample (*Escherichia coli*). Isolated colonies of bacteria were obtained on nutrient agar. Bacteria isolated from the samples were identified by means of cultural characteristics, Gram staining.

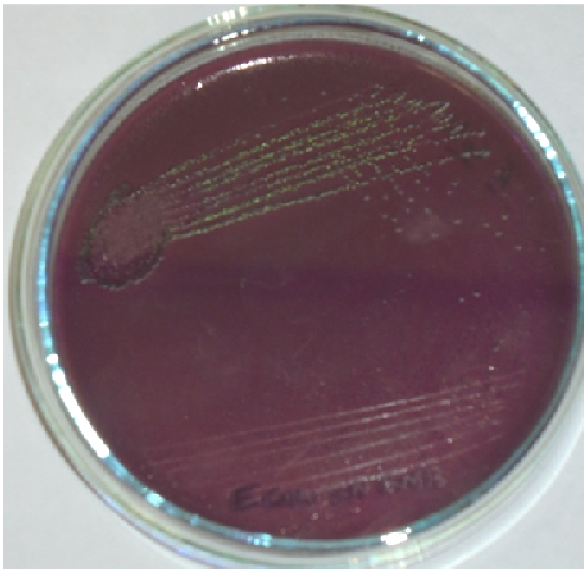

Figure 1: E.coli on agar plate

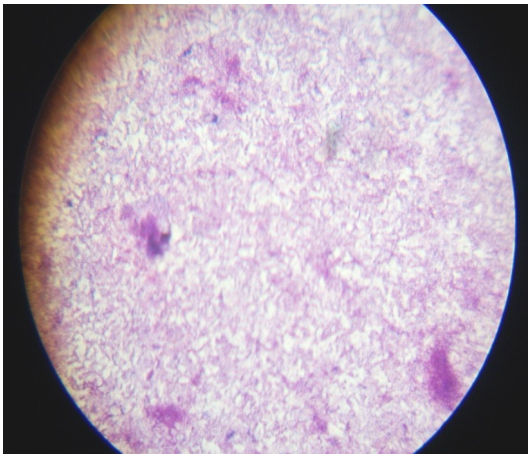

Figure 2: Gram staining of E.coli (G-ve)

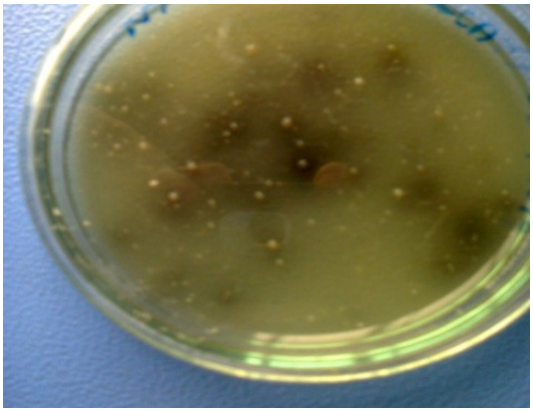

Figure 3: Listeria on agar plate

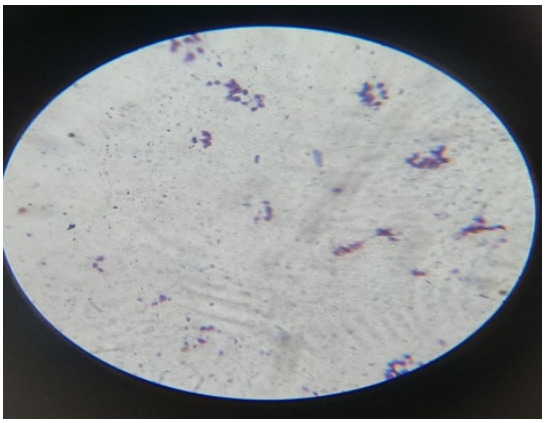

Figure 4: Gram staining of Listeria (G+ve)

Absorbance of silver nanoparticles from wavelength 200-600 nm was read. It was observed that the absorbance peak was centered

near 350nm. The UV-VIS absorption spectra of the silver nanoparticle are shown in Figure 5

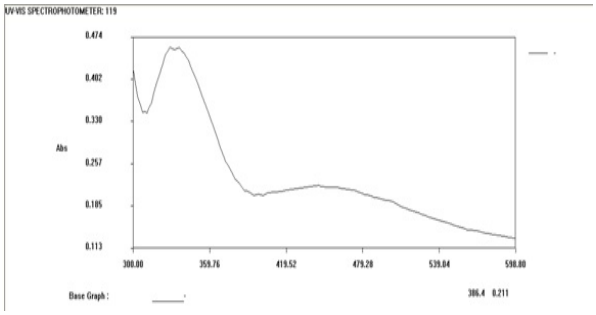

Figure 5: UV-Visible spectrum of nano particles

The SEM image of silver nanoparticle synthesized by "Green synthesis" process by using 50% of plant extract and 50mM $AgNO_3$ concentration is shown in the figure 6. It gave a clear image of highly dense silver nanoparticles. The silver nanoparticle was flat in shape with particle size ranging from 90 nm to 93 nm. The larger silver nanoparicles may be due to the aggregation of the smaller ones. The SEM image showing silver nanoparticles synthesized using bilimbi extract confirmed the development of silver nano structure.

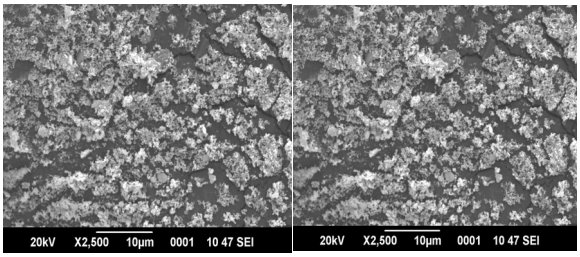

Figure 6 & 7: SEM image of silver nanoparticles

Antimicrobial Assay of Green Synthesized Silver Nanoparticles

By Microtitre Plate Assay

Table 2: Antimicrobial assay of nanoparticles

	1	2	3	4	5	6	7
E.coli	0.621	0.186	0.230	0.260	0.571	0.588	0.598
Listeria	0.630	0.175	0.225	0.276	0.535	0.545	0.595

Bacterial Growth:

Bacterial growth can determined by subtracting the values of test (serial no: 5 to 7 in table:1) from the values of controls (serial no: 2 to 4 in table :1).

The results are tabulated in the table : 3

Table 3: Bacterial growth

	10µl nano particle	20µl nanoparticle	30µl nanoparticle
E.coli	0.385	0.358	0.338
Listeria	0.360	0.320	0.319

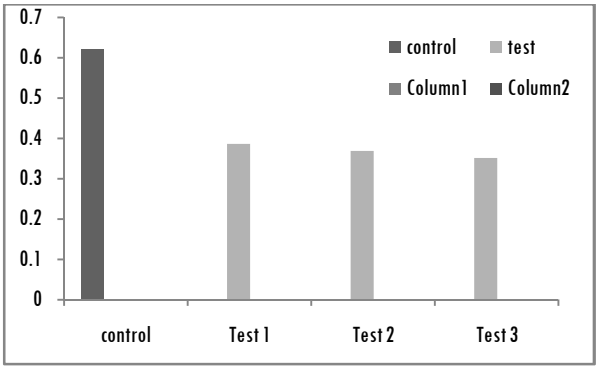

Figure 8 Comparison with control and test (for *E.coli*)

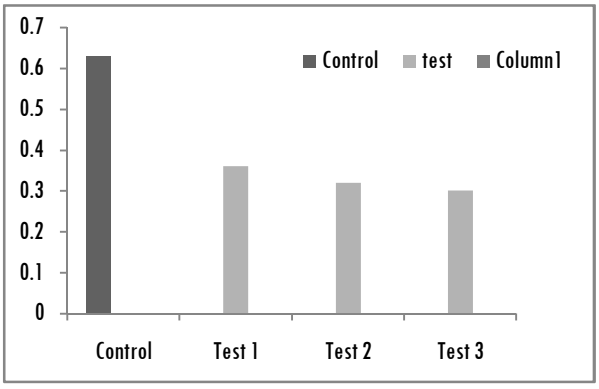

Figure 9 Comparison with control and test (for *Listeria)*

The present study deal with the green synthesis of silver nanoparticles and its antimicrobial activity against the isolated food pathogens, *E.coli and Listeria.* The isolated

organism was confirmed by microscopical characteristics and growth on specialised media. The antibacterial efficiency of *Averrhoa bilimbi* plant extract on *E.coli and Listeria* was done. The silver nanoparticles were synthesized from plant extracts showing highest antibacterial activity against these pathogen. It is possible that these extract may take a role as an adjuvant to the use of antibiotics or as a replacement of current antibiotics.

Conclusion

In this study silver nanoparticles were successfully synthesized using *Averrhoa bilimbi* leaves. The present study represents a clean, non toxic as well as eco friendly procedure for synthesizing silver nanoparticles. This technique gives us a simple and efficient way for the synthesis of nanoparticles with tunable optical properties governed by particle size. From the nanotechnology point, this is a noteworthy development for synthesizing silver nanoparticles economically. This study also support the claim of the usefulness of the plant extract in treating diseases. Nanotechnology has grown to be an important research field in all areas. For several years, Scientists have constantly explored different synthetic methods to synthesize nanoparticles. On the contrary, the green method of synthesis of nanoparticles is easy, efficient and eco-friendly in comparison to chemical mediated or microbe-mediated synthesis. This study was conducted for the Green synthesis of silver nanoparticles from *Averrhoa bilimbi.* *E.coli* and *Listeria* from food sample was isolated and confirmed by microscopic evaluation. From this study it is found that, when the concentration of the silver nitrate solution increases the formation of the nanoparticles became very effective. The silver nano particles formed immediately in that leaf extract mixture which contain 50mm silver nitrate solution. Characterization of the synthesized silver nanoparticle was done using UV visible spectrometer and scanning Electron Microscope. Antimicrobial assay of synthesized silver nanoparticles was carried out against the test organisms. The antibacterial assay of green synthesized silver nanoparticles against the food pathogens was performed. The silver nanoparticles showed good zone of inhibition against these bacteria compared to the control kept and it is found that the zone of inhibition increased with the increase in the concentration of silver nanoparticle used. The green synthesized Silver nanoparticles hence found to be having high antibacterial activity against these bacteria.

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SAHODARAN AYYAPPAN AS A SOCIAL ACTIVIST

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Abstract

Sahodaran Ayyappan, the well known personality rendered great services in social, religious and literary areas of Kerala. Sree Narayana Guru was the insptring force for him. Guru's deeds and words enlightened his path and there was a strong relationship existed between that guru-sishya. All the activities that made Sahodaran as a social leader and a historically important person, starting from Misrabhojana, was done by utilizing the power produced by a spiritual dynamo called Narayana Guru. Ayyappan's activities prove that he upheld the philosophy of Guru.

Keywords: Sahodaran Ayyappan, universal brotherhood, revolutionary, misrabhojana, rationalistic, spiritual dynamo.

Sahodaran Ayyappan, an outstanding personality of Kerala, was known for thegreat services he rendered in four major realms : social, religious, literature and politics. His extensive activities have attributed him a central position in the religious and political fields. He used literature as a weapon to support his religious/social reforms in society and for the propagation of his revolutionary ideas.

All of his biographers have clearly stated the role of Sree Narayana Guru as an inspiring force and leading light behind him in all his social activities. For centuries, India had been a fertile soil for varna system (chathur varnya) In the Brahmin centred society many Indians suffered under cruelties like slavery and untouchability. In that scenario, Sree Narayana Guru empathised with the oppressed and revolted against the caste/ religious centred system that resulted in tremendous changes in the society.

With his great historical Aruvippuram consecration in 1888, the Guru ignited the minds of the people with enough confidence and established that all had equal rights to worship God. The down trodden, whose minds were buried under the cluctches of slavery were enlightened and consequently, they acquired purity and discipline in their lives. The Guru made several consecrations of idols through out the length and breadth of Kerala for the lower caste of the society and gave guidance for the establishment of educational institutions, libraries, industries, vocational training centres etc. for them. He aimed at total upliftment of society. With this view in his mind he abolished unwanted customs and superstitions.

The Guru awakened the people with his inspiring message "Independence through education and strengthen through organisation" His words and activities greatly influenced the people and it brought dominant changes in the society.

Ayyappan met Sree Narayana Guru in this social context, when the Guru's relentless activities were effecting a wind of social change. Naturally the Guru exerted great influence on him. The extent of this influence is evident from his later statement

"The Guru was a spiritual dynamo that created a peaceful social revolution and we were mere wheels that rotated, utlizing the power produced by the dynamo."

When Ayyappn moved to Madras for his higher education he met the Guru for the first time and came to know more about him (before that he had only a glimpse of the Guru in the house of his elder brother Achuthan Vaidyar). Ayyappan went for higher studies with the money acquired from pledging his share of family property.

He desired to join Medical College. However, paucity in funds forced him to opt for Philosophy and he joined Madras Christian College. Soon he realised that he was a misfit in the campus and changed his academic track. Next, he selected Sanskrit

Honours and shifted to Presidency college. The affluent life style of his peer group created such an inferiority complex in his mind that he lost interest in his studies. He became an introvert and refused to leave the room, he was lodged in. It was during this time that Sree Narayana Guru visited him. The Guru's speech impressed all. He spoke on the importance of cleanliness, purity of mind and purity of body. He also stressed on the need for destroying caste system and fostered the idea of universal brotherhood for the purification of mind. This speech touched the very soul of his mind.

Due to unfavourable circumstances Sahodaran Ayyappan discontinued his studies and returned to his native place. Backhome, he found the thoughts and ideas of Sree Narayana Guru, spreading like wild fire., Ayyappan too began to get involved in certain social issues. When the Guru visited Cherai for the consecration of

Gowreeswara Temple, one of his followers introduced Ayyappan to him as the younger brother of Achuthan Vaidyer. The Guru, then invited Ayyappan to visit Adwaithasramam, Aluva. Here the two discussed the violence of communal a trocities.

The Guru, on learning about Ayyappan's discontinued studies advised him to complete his education. The Guru then wrote a letter is his own hand to Kumaranasan informing him about the financial crisis of Ayyappan. As instructed by the Guru, Kumaranasan gave Ayyappan Rs. 100/- With this he joined Maharajas College, Trivandrum for his B.A Course. During this period, Ayyappan stayed with Kumaranasan at Kaithamukku. Thus, he could build a strong relationship with Asan, who was then secretary of SNDP Yogam

Ayyappan visited the Guru while he was studying in Maharaja's college, Trivandrum. As a dynamic person he was very much liked by the Guru. More than devotion, Ayyappan had respect and admiration for the Guru. At times, Ayyappan

was surprised by certain moves of the Guru. Once he got irritated when the Guru rested in the house of an Ezhava land lordReading his mind, the Guru said "Do You know that there in no one in this world who is beyond reformation? Our dharma should be to try to istil goodness in everyone1". This incident has been recorded in all of his biographies.

Ayyappan was so fortunate that he got the opportunity to travel along with the Guru to several places. The Guru protected him like a guardian. Eventhough the Guru was a pure vegetarian, knowing Ayyappan's taste,he gave instructions to his host and made arrangements to serve fish curry for him2.

Ayyappan was blessed with knowledge from the Guru,while he was travelling along with him " Man/Human being should be good which ever religion he follows" was one of the most famous statements made by the Guru during their conversation.

Later,Kottukoyikkal Velayudhan reported this conservation in Deshabhimani and it was also published in Kerala Kawmudi. These reports give us solid proof about how strong a relationship existed between them.

Despite his respect for the Guru, Ayyappan unhesitatingly expressed his views that were apparently contradictory with the views of the Guru. But they were similar in content and thought. This is illustrated from the speech he made at Koorkkanchery Maheswara temple in a Programme organised by Yukthivadi and Sahodhara Organisation. He revealed his revolutionary ideas such as " there is no need of temple and religion. God is unnecessary for human beings". He went on to establish his views in a more rationalistic way. Understanding the crux of the speech, the Guru supported his views saying that " what Ayyappan said is true"3- "No caste, No religion, No God for humanbeings. But Dharma ethics, ethics alone is most appropriate and needed". These lines written by Ayyappan, share the same idea of the Guru.

In Ayyappan, Guru saw the most suitable follower after his life span. But herefused to accept this great responsibility due to fear.Later, he regretted this decisions4.

Several statements made by Ayyappan reveal the influence of the great Guru. The greatest revelation was, Ayyappan the rational, referring to the Guru as 'lord' in a requiem after the Guru's samadhi.

'Jaathi Nirnayam' was written as a message by the Guru on Ayyappan's request to signify the meaninglessness of caste system. This was published later as "thirunal Sandeshm" in 1096, malayalam era in the first page of his journal. Another famous work of the Guru, "Jaathi lakshanam" was also written on his request and published in the magazine 'Sahodaran' with a beautiful interpretation by Ayyappan.

Inspired by the Guru, Ayyappan endeavoured to bring changes in the society Misrabhojana is a typical example for this.

Scholars say that once the guru reminded him of the urgent need to abolish the caste system from the minds of his followers than mere preaching of it. As a result he conducted Misrabhojana in 19175. This sparked a thundering roar in the society. As an after effect he had to face bitter experiences. The People who participated in Misrabhojana were severely tortured mentally and physically by the orthodox. They even tried to manhandle Ayyappan. He founded ' Sahodara sangham,' an organization with the supporters of misrbhojana. The Vijnana Vardhini Sabha' in Cherai was against this organisation, and they spread rumours in the name of Sree Narayana Guru. At last Sree Narayana Guru himself came up with a message justifying Misrabhojanam. This is known as Mahasandhesham, which reads- "Irrespective of religion, appearance and language, human beings are one and the same and therefore there is no harm in marriages and panthibhojanam between them"6. It gained him whole hearted support from society. Later the Ashramam became the stage for anniversary celebrations of Sahodara Sangam. These all show the depth of teacher - disciple student relationship and it also unveiled the inherent support the Guru gave to Ayyappan.

In a speech Ayyappan made at the formation of the Sangam he stated that the Guru had come not for erecting a temple for the ezhavas but for giving his great messages to the society. Ayyappan upheld the philosophy of the Guru that the eradication of caste system will be achieved only through love and not with competition.

Sahodaran Organization influenced the growth of other organizations like yukthivadi organisation,trade union,socialist organisation etc in the society. Public speaking, a common feature of our society was actually started by Ayyappan. Like public speaking he used the news paper as a mouth piece to fight against caste system and to foster the idea of religious brother hood. With this in mind, he arranged the Misrabhojana in 1917. The orthodox hindu groups turned against Ayyappan and there were even attempts to break the holy bond that existed between the Guru and Ayyappan. But the latter, continued the Sahodara Sangham to create and improve social awareness. Ayyappan encouraged intercaste marriages and organized several activities to support these concepts. Hence, he enjoyed the patronage and the blessings of the Guru in all his endeavours.

Through the journal 'Sahodaran' Ayyppan protested against the employment system that existed in 1941 under the reign of Kerala Varma. The key positions were occupied by the kings men and relatives only. He wrote about the necessity of education and the need for educational institutions for vocational training, trade in the society in his columns. He used his pen as a weapon to fight against injustice and corruption. He emphasised and welcomed the historical Temple Enry Proclamation.

V.T Bhattathirippad claimed that the Sahodaran journal helped the upper caste Namboothiris to think practically and they became involved in the issues of the human race, irrespective of caste differences7.

The journal alsotaught the upper castes to share the sorrows and joys of the people at large. In this way, his jounal lighted a lamp in the Namboothiri community for reformation and rejuvenation.

Ayyappan and his companions strove to abolish uncouth rituals like animal sacrifice and poorappattu organised in the kodungallur temple annually. Some devotees used this occasion to drink liquor. The drunken pilgrims entered the temple singing bharnippattu to satisfy the goddess. They also killed cocks as sacrifice and ate it with liquor in the temple premises.

During his tenure as the Minister of Cochin State, Ayyappan played a vital rolein the enactment of government order to abolish this animal sacrifice. He gathered a group of like minded young men and led a procession against such ill practices.

His agitation agaisnt social evils clearly reveals the great influence of Sree Narayayana Guru.

Ayyappan had decided to form trade union along with the Sachodara Sangam.

In 1935, he presided over the trade union conference, in Alleppey. He was the master brain behind the formation of Adi Vypin Thozhilali Sangam (First Vyppin trade union), the first Trade Union in Kerala and the other organizations such as Ochanthuruthu trade union, Travancore Labour Association and Cochin Labour union. The main objective of these Organisations was to solve the problems of labourers and to draw the attention of the government to Labour issues. These organisations offered legal support too for the labourers.

Ayyappan through the columns of his news paper Velakkaran and journal Sahodharan fought against caste discrimination and argued for the need for responsible government and right of Labourers. He introduced the great idea of socialism to the people of Kerala through his writings.

Ayyappan supported the Abstention Movement, demanding equal representation in the Legislative Assembly and employment opportunities for Ezhavas, Christians, and Muslim communities in Travancore. As the President of S.N.D.P yogam, he passed the resolution for responsible government. The historical Temple Entry Proclamation was another great movement lead by the yogam under the leadership of Ayyappan.

When Ayyappan was elected Minister in Travancore Cochin State, he used all opportunities for the welfare of the people. Under his responsibility, he implemented several social reforms in several areas like protection of back ward community, Panchayath Village

reconstruction, Registration,Village court etc. In general Sahodharan Ayyappan used his ministership to serve the people.

Ayyappan planned to connect Ernakulam and Vypin islands with bridges8. He became instrumental for the enactment of several legislations like Adult franchise, Cochin Makkathayam Thiyya Act, the Cochin Civil Marriage Act-intended to reform the realm of marriage. By this act people, could enjoy complete freedom in respect of marriage without the consideration of caste and religion. As Minister of Public Works Departments, he introduced several developmental programmes throughout the state. He did not show any reluctance to surrender his own land for 70 ft. Road construction programme in Ernakulam.

After rejecting Ministership, in his later life, Ayyappan started a social welfare centre in Sree Narayana Giri and encouraged his wife Parvathy to be an active partner in it. He founded Sree Narayana Sevika Samajam for women empowerment which runs schools, libraries, orphanage, press, old age home etc.

Ayyappan was a staunch follower of Sree Narayana Guru, who questioned superstitions in a rationalistic way and revolutionised the society. Sree Narayana Guru's rationalistic thoughts enabled him to act against ill practices and socio religious restrictions. He wanted to mould a rationalistic generation in Kerala through his daily Yukthivadi. His poetry illustrated his emphasis on rationalistic thoughts. The reader can identify his rationalistic thoughts and revolutionary ideas throughout his poetry. He used his poems for the propagation of his ideas.

Ayyappan utilised different methods like public speaking, social activities, and writings to reform the society. He has succeeded in strengthening and liberating the people of Kerala through his well-planned and organised activities.

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VO(ll), Cr(lll), Mn(ll) and Fe(lll) COMPLEXES OF (z)-3-((1H-indol-3-yl) methyleneamino) BENZOIC ACID

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Abstract

Potential azomethine class of ligand (z)-2-((1H-indol-3-yl)methyleneamino)benzoic acid and its VO(II), Cr(III), Mn(II) and Fe(III) complexes were synthesized and characterized by elemental analysis, magnetic, conductance and spectroscopic techniques like UV, IR, ^{1}H NMR and ^{13}C NMR. Analysis established that the Schiff base is acting as monovalent bidentate ligand. Octahedral geometry was shown by Cr(III), Mn(II) and Fe(III) complexes while VO(II) complex displayed distorted square pyramidal geometry. All the complexes and ligand were assayed for their antibacterial activity against gram positive as well as gram negative bacteria.

Keywords: Schiff base, Metal complexes, Antibacterial studies

Introduction

Metal complexes of Schiff bases play an important role in the development of coordination chemistry [1-3] Schiff base ligands and transition metal complexes derived from them have been found increasing applications in chemical, biological and industrial fields. Transition metal complexes of Schiff bases derived from aminoacids are useful in catalysis, organic synthesis and medicine as antibiotics, anti-allergic, and antitumor agents [4]. In the present course of investigation, a novel Schiff base (z)-3-((1H-indol-3-yl) methyleneamino) benzoic acid (IMABA) and its transition metal complexes of VO(ll), Cr(lll), Mn(ll) and Fe(lll) were synthesized and characterized. Antimicrobial activity of the Schiff base and the metal chelates were examined using plate disc method [5-14].

Experimental

Preparation of Schiff base and complexes

An ethanolic solution of 3-aminobenzoic acid (2mM) was mixed with a solution of 3-formylindole (2mM) and refluxed for four hours in a water bath. The resulting solution was concentrated and cooled and the precipitate formed was filtered, washed with ethanol and dried. M.P: 146^{0}C. Complexes were prepared by mixing ethanolic solutions of metal acetate (2mM), 3-aminobenzoic acid (2mM) and 3-formylindole (2mM). Ferric chloride (2mM) solution was used for the synthesis of Fe(III) complex. The resulting solution was refluxed for 3 hours, concentrated and cooled in an ice bath. The complex formed was filtered, washed with ethanol and dried.

Physicochemical measurements

Metal percentage was calculated by standard methods. Magnetic susceptibility measurements were done on Sherwood, UK (Mark 1) magnetic susceptibility balance at room temperature [15-17]. Percentage of carbon, hydrogen and nitrogen content of the Schiff base ligand and it's metal complexes were determined by microanalysis using Elementar make Vario EL III model CHN analyzer. Molar conductance studies were conducted in DMSO solvent at a concentration of 10^{-3}M. Cell constant was maintained as 1 in all investigations [18]. Shimadzu FTIR spectrometer and 1800 UV-Visible spectrophotometer were utilized for spectral studies. ^{1}H NMR and ^{13}C NMR spectral studies of ligands and chelates were recorded in DMSO-d^6 on a Bruker AVANCE III HD. Mass spectra of the Schiff bases were recorded using QP 2010 model Shimadzu GCMS at a source temperature of 300^0C [19-21]

Antibacterial studies

Preparation of the media

Nutrient agar (NA) was used as the media for the plate preparation and nutrient broth (NB) was used for culturing the bacterial strains.

Compositions of the medium

a) Nutrient Agar (NA):- Peptone(10g), Beef Extract(10g), NaCl(5g), Agar(20g), Distilled Water(1L)

Dissolved the ingredients in sufficient quantity of distilled water. Then it was sealed with a sterilized cotton plug and autoclaved at 100^0C for 15 minutes.

b) Nutrient Broth (NB):- Peptone(10g), Beef Extract(5g), NaCl(5g), Agar(20g), Distilled Water(1L)

Dissolved the ingredients by heating in distilled water. Distributed in 25ml quantities in 250ml conical flask, plugged with non absorbing cotton and autoclaved at 100^0C for 15 minutes.

Preparation of agar plates

1000ml of pH adjusted NA was prepared and autoclaved. After autoclaving it was allowed to cool for 10 minutes at 40-45^{0}C. Then it was poured into sterilized petri plates inside the Laminar flow hood chamber. The plates were allowed for solidification, dried and they were kept for sterility checkup for 24 hours.

Preparation of sample discs

Stock solutions of the synthesized ligands and complexes were prepared in DMSO. Then it was dissolved and further diluted to obtain different concentrations ranging from 100µgdisc^{-1} to 500µgdisc^{-1}. These samples were applied to paper disc with the help of a micro pipette. The discs were kept in an incubator for 24 hours at 37^0C

Antibacterial screening

Antibacterial activity of the transition metal complexes and ligands was determined by the micro dilution method according to the national committee for clinical laboratory standards (NCCLS) and paper disc diffusion method. Few

drops of sterilized water was taken in a test tube and with the help of inoculation loop, test organisms were taken off from the slant culture and diluted in the test tube. Using a sterile swab, the activated bacterial strains were spread over the entire surface of the nutrient agar plates in a uniform manner and allowed to dry for 15-20 minutes. The plates were incubated at 37^0C for 24 hours. The zone of inhibition was then measured around the disc using vernier caliper.

Results and Discussions

Characterization of ligand

Elemental analysis, Found C%(72.16), N%(10.35), H%(4.30); Calc: C%(72.72), N%(10.6), H%(4.54). In the HRMS of the ligand molecular weight is confirmed by molecular ion peak at m/z 264 and itself acted as a base peak. Other prominent peaks are M+1 peak at m/z 265,decarboxylation give peak at m/z at 219 and loss of acetylene moiety from the cation $[C_6H_5\text{-}COOH]^+$ give at m/z at 96. The ^{1}H NMR (DMSO-d_6) signal for proton of the carboxylic acid appeared as a singlet at δ 11.99. Also the azomethine proton, showed its own singlet signal at δ 9.79. The NH proton on indole ring exhibit a broad signal at δ 6.83. The aromatic protons of both indole and benzene rings resonated in the region δ7.14-8.19. The ^{13}C NMR spectrum in DMSO-d_6 showed the carboxylic acid carbon signal at 185.57ppm. Azomethine carbon resonate at 130.32. The IR spectrum showed the characteristic C=N and OH stretching vibration in the region of 1600cm^{-1} and 3000cm^{-1}.The olefinic and aromatic CH stretching bands appeared in the range 3100-2850cm^{-1}. The asymmetric and asymmetric stretching vibrations of the carboxylate group were observed at 1668cm^{-1} and 1498cm^{-1} respectively. In the electronic spectrum, the absorption bands because of the n→ σ*,π→π* and n→π* transitions, were observed at 38500,31300 and28900cm^{-1} respectively. On the basis of the above results, structure of the ligand IMABA was confirmed and shown in Fig.1

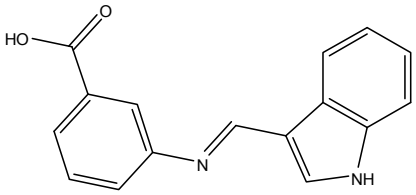

Figure1 Structure of IMABA

Characterization of complexes

All the complexes are found to be amorphous solids and stable to light and air.The analytical data and the physical characteristics of VO(II), Cr(III), Mn(II) and Fe(III) complexes are given in Table 1.

Molar conductance

Molar conductance values of the complexes in DMSO at a concentration of 10^{-3}M at room temperature were in the range of 7-16ohm^{-1}cm^{2}mol^{-1}, which establish the non electrolytic behaviour of the chelates.

Magnetic moment measurements

The μ_{eff} shown by VO(II) complex is 1.26BM, which is slightly less than the expected value (1.7-2.0BM) for one unpaired electron. This

suggested a distorted square pyramidal geometry to the chelate. The Fe(III) complex showed low magnetic moment of 2.79BM than the value expected for the high spin Fe^{3+} complexes, a strong antiferromagnetic exchange in the complex can be assumed. Magnetic moment value of Mn(II) complex (5.59BM) clearly confirms that this chelate possess a high spin octahedral stereochemistry. Octahedral structure is ascertained for the Cr(III) complex of IMABA which is evident from the observed magnetic moment value of 3.10BM.

Infrared spectra

A characteristic band observed at 1600cm^{-1} is due to the stretching frequency of C=N group, which was shifted to lower frequencies in all the complexes, is a clear indication of the formation of a coordination bond through the azomethine linkage [22]. The asymmetric and symmetric carbonyl stretching frequencies of the carboxylate group of the ligand appeared at 1668cm^{-1} and 1498 cm^{-1} respectively. A considerable shift of these bands to lower frequencies in the case of chelates, indicate the binding of the ligand through carboxylate group. In all the complexes, the symmetric and asymmetric stretching vibrations of the carboxylate group occur near 1400 and 1650cm^{-1} respectively, showing a difference of about 250cm^{-1}. This elucidates that in all the present chelates, the carboxylate group exists as a monodentate moiety. Broad bands appeared in the IR spectrum of the complexes between 3350-3400cm^{-1} is a strong indication of the presence of coordinated water molecules. Additional significant bands correspond to γ_{M-O} and γ_{M-N} stretching frequencies appeared near 520cm^{-1} and 670cm^{-1} respectively in the IR spectra of the complexes.

Electronic spectra

Electronic spectra of all complexes exhibited considerable difference from the absorption of ligand 3FI3ABA. The ligand showed its characteristic absorption peaks at 28900, 31300 and 38500cm^{-1} which can be assigned due to $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$, $n\rightarrow\sigma^*$ respectively. All the complexes exhibited red shift of these frequencies compared to that of the ligand, which can be considered as due to chelation of the ligand to the central metal atom. In the VO(II) complex, a weak charge transfer band was observed at 12800 cm^{-1} and confirmed its square pyramidal geometry. In the case of Cr(III) complex also, a weak charge transfer band was observed to confirm the octahedral geometry. Mn(II) complex of IMABA exhibited three bands at 12600, 13200, 20100cm^{-1} in its electronic spectrum. These bands can be assigned to $^6A_{1g}\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}\rightarrow{}^4E_g(G)$ transitions respectively, which is in accordance with Mn(II) high spin octahedral geometry[23]. The Fe(III) complex exhibited one extra band at 29100cm^{-1} in the electronic spectrum. This can be assigned as the charge transfer band. A shoulder at 18900cm^{-1} was also observed. Since the ground state Fe(III) ion form high spin complex, all the d-d transitions are weak and obscured with charge transfer band. Therefore Fe(III) complex is proposed to possess octahedral geometry[24].

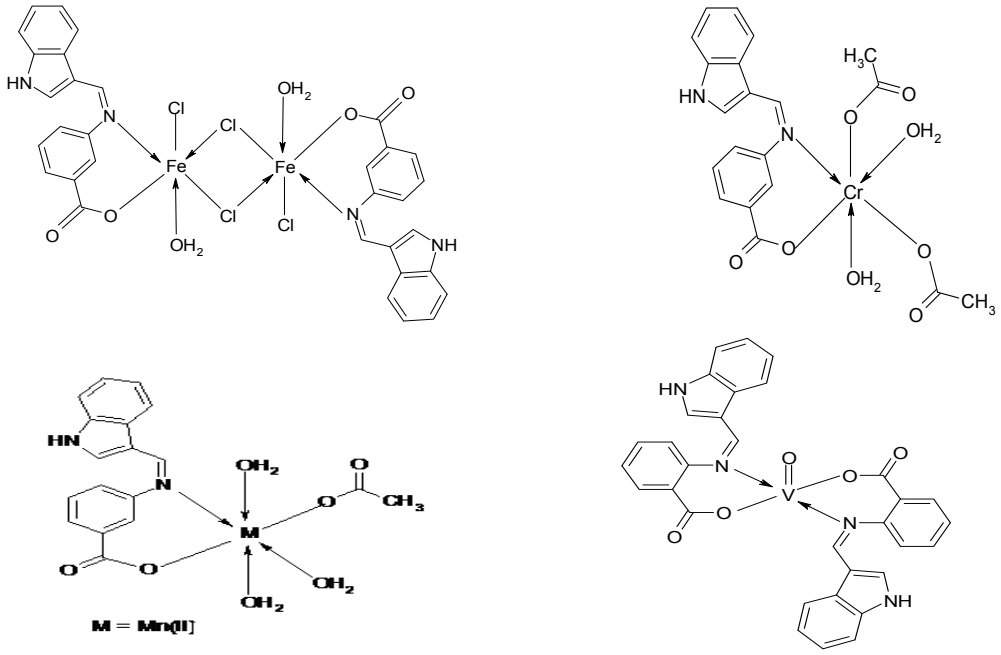

Fig. 2 Structures of metal complexes of IMABA

Table 1 Microanalytical, magnetic and conductance data of IMABA and its complexes

Complex	Yield (%)	Metal % Found (Cald.)	C % Found (Cald.)	H % Found (Cald.)	N % Found (Cald.)	μ_{eff} (BM)	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)
IMABA (LH)	79	-	72.16 (72.72)	4.30 (4.54)	10.35 (10.60)	-	-
$[(VO)L_2]$	74	12.16 (12.53)	53.76 (53.07)	3.45 (3.93)	6.22 (6.88)	1.26	14
$[Cr\ L_2Ac(H_2O)]$	67	11.56 (11.09)	51.93 (51.17)	4.42 (4.47)	5.12 (5.97)	3.10	7
$[MnLAc(H_2O)_3]$	73	12.51 (12.76)	50.57 (50.10)	4.68 (4.64)	6.20 (6.49)	5.59	12
$[FeLCl_2(H_2O)]_2$	75	13.48 (13.72)	47.78 (47.05)	3.89 (3.19)	6.26 (6.86)	2.79	16

**Calculated values*

Table 2. Characteristic infrared absorption frequencies of 3FI3ABA and its transition metal complexes

Complex	γ_{H_2O}	γ_{COO} (asym)	$\gamma_{C=N}$	γ_{COO} (sym)	γ_{C-O}	In plane bending	Out of plane bending	γ_{M-O}	γ_{M-N}
IMABA (LH)	-	1668	1600	1498	1222	1157	941, 754	-	-
$[(VO)LAc(H_2O)]$	3410	1649	1593	1438	1226	1145	977, 754	678	542
$[Cr\ LAc_2(H_2O)_2]$	3373	1635	1573	1448	1240	1128	790, 759	677	533
$[MnLAc(H_2O)_3]$	3354	1573	1544	1452	1242	1124	900, 777	680	525
$[FeLCl_2(H_2O)]_2$	3356	1647	1575	1404	1230	1145	754	682	513

Table 3. Antibacterial activity of the Schiff base IMABA and its transition metal complexes

Compound	Diameter of zone of inhibition (mm) at different concentrations (µgdisc^{-1})																	
	S. aureus			*B. subtilis*			*B. thuringiensis*			*E. aerogenes*			*E. coli*			*P. vulgaris*		
	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
IMABA	4	3	6	2	4	5	2	2	5	3	2	5	1	3	5	2	3	7
VO(II) complex	11	13	20	9	15	17	6	11	17	8	12	16	7	11	17	6	11	15
Cr(III) complex	12	13	17	10	14	18	7	10	16	5	10	14	11	12	16	8	10	13
Mn(II) complex	4	5	6	3	3	3	2	7	9	3	7	9	3	6	8	2	6	9
Fe(III) complex	1	6	10	7	8	11	6	8	10	7	7	11	9	10	15	6	11	11

*C_1=100 µgdisc^{-1}, C_2=200 µgdisc^{-1}, C_3=500 µgdisc^{-1}

Antibacterial Studies

The studies shows that the metal chelates have higher antibacterial activity than the corresponding free ligand. The growth inhibition power of complex of the ligand IMABA is as that of standard antibiotics and sometimes its activity is more than that of the standards, especially in the bacterial growths of *E. coli, E. aerogens* etc. The increased activity of the metal chelates is due to the increased cell permeability. On chelation, the charge density of the metal ion will reduce considerably due to the partial sharing of the metal ion with the donor moiety. Because of the increased delocalization of the π electrons, lipophilicity of the complexes will be enhanced. This will cause the complex to penetrate into the lipid layer of the bacterial cells. The complex will bind certain enzyme sites of bacterial cells and thus prevent the growth of micro organisms.

Conclusion

1) Novel heterocyclic Schiff base IMABA its transition metal complexes were synthesized and characterized.
2) Octahedral geometry was exhibited by Cr (III), Mn(II), Fe(III) complexes.Square pyramidal geometry was assigned to VO(II) chelate.
3) The ligand and the complexes were screened for their antibacterial activities.
4) The metal chelates have higher antibacterial activity than the corresponding free ligand.
5) The increased activity of the metal chelates is due to the increased cell permeability.

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