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Dr. Celine E. (Sr. Vinitha)
Professor Emeritus and Manager
St. Teresa's College (Autonomous)

From The Manager's Desk

Research is significant for the sustainability and development of an educational institution. The quality of research work renders directly to the quality of teaching and learning, thus benefitting the students, community and country. Research publications give international recognition and add value to an institution. The research journal goes beyond providing a means of communication and is an intellectual platform for scholars of international/national repute.

I welcome all researchers, academicians and students to the world of a host of research journals from St. Teresa's College, of which ***Teresian International Journal of Chemical Sciences*** is one.

The Department of Chemistry and Center for Research of St. Teresa's College has been acknowledged as one of the best in the state and I am immensely pleased that the Department has decided to initiate the publication of this Journal. This is a double blind peer-reviewed quarterly international journal which aims to unveil the research talent and the works done by chemical science students and academia.

We hope that this will help research in this field to flourish and great researchers will find this as an avenue for disseminating research knowledge all over the globe. Our mission and vision, both will ultimately culminate in getting enlisted in the most relevant databases including SCOPUS.

It is commendable that the chemistry department has taken a new stride in its glorious path to enlightenment. I wish them good luck and all success in this noble venture.

Dr. Lizzy Mathew
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Principal's Message

It is indeed exhilarating to note that the Department of Chemistry and the Research Center is publishing the first issue of ***Teresian International Journal of Chemical Sciences.*** This exemplifies the culmination of perseverance, team-work and co-ordination among the faculty, researchers and the guiding spirit of the editorial board. The publication of the research journal will finesse an eco-system for dissemination and assimilation of knowledge and know-how on the emerging vistas of Chemical Sciences.

Research studies provide impetus towards critical, creative thinking and facilitate re-imagining of new dimensions and horizons. Also, research involves more of in-depth learning, as well as re-learning and un-learning so that it may result in innovative and inventive methodologies, processes, products, utilities and technologies that will be outcome-oriented and value-additive both from theoretical and pragmatic perspectives. Thus, the efforts will help in furtherance of industry-interface and societal orientation.

St. Teresa's College has been in the forefront in promotion of research activities and all the requisite infrastructure and organizational arrangements have been set up, which will be further enhanced. Even though the output of research papers has been on the increase, as regards publication of research journals, we have to still tread ahead. The commitment of the Department of Chemistry and the Center for Research is exemplary in this regard, which can be emulated by other Research Centers. May I compliment all of them and wish that their endeavors may fructify further and continue to succeed in future!

Best Wishes!!

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Editorial

Dr. Saritha Chandran A.

What Chemistry can, to fight Covid 19?

We are tense as the pandemic yonder in front. We are scared, as even the developed nations are not spared. We are concerned as the pandemic can at any moment pounce on us. The clouds of desolation, dejection, and depression have enveloped us.

Yet we are excited; yes we are elated, as we learn that MIT have taken to resolve the aporia to tame Covid 19 virus with their research, when all the academia, but a few over the globe have been in the corona slumber.

The MIT campus suffers a desperate silence. Academic scene all over has been in a sense of awe and wonder. It is then, that the members of the Hong, Kiessling, Pentelute, Shalek, and Swager labs continue their research to find a way out from the global pandemic.

Five small research bands in MIT, in a race to discover possible solutions to the world's viral crisis – sought special permission for their research on campus at a responsible

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social distance. Efforts from the labs of Professor Mei Hong, Professor Laura L. Kiessling, Professor Bradley L. Pentelute, Professor Alex K.Shalek, Professor, Timothey Manning Swager aim to contribute to resolving COVID-19.

Mei Hong's band has directed its membrane protein expertise to investigate the structure of an essential SARS-COV-2 protein, the envelope protein E.

Laura Kiessling's band are investigating whether human carbohydrate-binding proteins (lectins) limit viral infection. Human lectins are present at mucosal barriers, including in the lung. The levels of these proteins can differ between individuals in response to age or polymorphisms (changes in the genetic coding) that alter their production or stability.

The Kiessling Group anticipates that these lectins can function *in vitro* as tools to capture virus and *in vivo* as immunomodulators. Thus, understanding those lectins that can bind coronaviruses from human patients will lay the groundwork to elucidate fundamental aspects of human immune responses to the virus. Moreover, because the lectins the group proposes to examine are human proteins, they do not expect them to have problematic effects. If they block viral infectivity (or effectively modulate immune responses), they are unlikely to have major deleterious effects such as toxicity or immunogenicity. The group has made some models that suggest the lectins have the right alignment.

Researchers in Professor Brad Pentelute's lab are focused on delivering safe and effective peptides for prophylactic treatment and rapid early therapeutic intervention against COVID-19 infection. They approach this goal by design of peptide binders specific to the spike protein of the SARS-CoV-2 coronavirus. Disrupting the SARS-CoV-2 spike protein interaction with its human cell membrane receptor can prevent virus cell entry, offering a promising therapeutic modality.

We have every right to dream: Every Chemistry lab, emulating the penta bands of MIT, may use its research for the humanity!

Mechanical and Thermal Properties of Bio-based Rigid PU Foams: Effect of Aramid Fibre

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Abstract

This study investigates the effect of aramid fibre on the properties of rigid Polyurethane foams derived from modified castor oil. Aramid fibre has been used to enhance the mechanical and thermal properties of castor oil-based rigid PU foams. Foam samples have been subjected to flexural and compressive testing. Prepared foams are characterized by TGA for their thermal properties. It is observed that the addition of aramid fibre shows improved mechanical and thermal properties. Aramid fibre is proved to be good reinforcing filler, as the flexural strength increases upto 251% and compressive strength increases upto 115% on the incorporation of aramid fibre as reinforcing filler. So, aramid fibre has great potential as an additive to incorporate good mechanical and thermal properties in vegetable oil based rigid PU foams.

***Keywords**: Mechanical Strength, Filler, Aramid Fibre, PU Foams, Castor Oil, Thermal Stability, Weight Loss.*

To enhance the mechanical properties of various composites, different types of fibres have been incorporated. Fibres, which have been commonly used as reinforcement, may be categorized as synthetic or natural. Synthetic fibres are man-made fibres with some advantageous properties such as high tensile strength and stiffness, which validate them as an excellent reinforcement material in the production of fibre-reinforced composites (FRCs). Synthetic fibres are further classified as organic and inorganic fibres. Synthetic organic fibres such as aramid, nylon, PE, and carbon fibre, have been widely used as reinforcement in the FRCs. Of these, aramid fibres are high-performance man-made fibres with certain exclusive properties such as good chemical resistance, good abrasion resistance, heat resistance, no melting upto decomposition, electrical non-conductivity and low flammability. Aramid fibres may, therefore, incorporate excellent performance characteristics in the reinforced composites (Chawla 2012).

PU foams are a requirement of the modern world as they have a wide range of applications. Polyurethane foams are universally used materials with a wide range of applications from disposable packaging and cushioning to insulation and construction. Properties such as low density and low thermal conductivity establish them as a good insulation material while flexibility and softness make them a promising material to provide comfort (Sivertsen 2007).

Commercially available polyurethane (PU) foams are developed by using polyols and polyisocyanate as raw materials that are derived from petroleum. But the rising concern about varied factors such as global warming and depletion of petrochemical resources have put a spotlight to replace these polyols from renewable resources (Xue, Bai-liang, et al. 2014). Vegetable oils such as castor oil, canola oil, soybean oil, sunflower oil, palm oil, and rapeseed oil are found to be suitable for use in the production of PU foam enabling them as renewable alternative resources for foam production (Miao, Shida, et al. 2014, Zhang, Liqiang, et al. 2013 and Mosiewicki, et al. 2009).

Castor oil is the only vegetable oil containing hydroxyl groups naturally which is essential to react with isocyanate groups (NCO) to form PU networks. Fillers are the materials which are added with a polymer matrix to reduce the cost of the product without much compromising on the properties. By choosing the appropriate filler, mechanical, thermal and electrical properties and processability of Rigid Polyurethane Foams (RPUF) may be tailored to requisite requirements. Foam prices may be reduced by the incorporation of fillers to the reaction mixture; in addition, it may improve the mechanical properties of the resulting product. Commonly reported fillers, which have been used in different studies to enhance the properties and to reduce the cost, are calcium carbonate, aluminium trihydrate, talc, kaolin, mica, glass fibre, carbon fibre, and carbon black. From the last few decades, many studies have been conducted for the preparation of PU foam from the polyols derived from different vegetable oils and reinforced with different natural and synthetic fillers. Rigid Polyurethane Foam prepared from lignin extracted from corncob residue using dilute alkaline solution and reinforced with pulp fiber has shown enhanced mechanical and thermal properties (Xue, Bai-Liang, et al. 2014). In literature, studies have also been reported on palm oil-based polyol with cellulose nanocrystal as reinforcement (Zhou, Xiaojian, et al. 2015). Properties of tung oil-based PU foam reinforced with rice husk has been studied and reported to have improvement in

dimensional stability (Ribeiro Da Silva, Virginina, et al. 2013 and Ribeiro Da Silva, Virginia, et al. 2013). Pineapple-based RPUFs were prepared and reinforced with banana rachis fibre to enhance the thermal stability of the foam. It was observed that thermal as well as thermo-oxidative stability of the foam was enhanced on the incorporation of up to 40% concentration of fibres (Garcia, Andres, et al. 2008). In a study, nano-aramid fibre-reinforced PU foam was developed and exhibited enhanced mechanical properties without any deterioration in other properties such as density, thermal conductivity, and processibility. These foams were reported to have a potential application as thermal insulation in crew exploration vehicles, crew launch vehicles, and lunar building blocks (Semmes, Edmund B., and Arnold Frances 2008).

Recent studies have reported castor oil-based polyurethanes reinforced with glass fiber having enhanced tensile and compressive strength (Agrawal, Anuja, et al. 2017). But the literature is devoid of much data on castor oil-based RPUF reinforced with fibrous fillers. The present study has been conducted as an attempt to overcome such research gaps to produce low cost, environment-friendly rigid polyurethane foams with enhanced mechanical and structural properties, by the use of aramid fibre.

This study investigates the effects of aramid fibre on the thermal and mechanical performance of rigid polyurethane (PUR) foam prepared from polyols derived from vegetable oil.

2. Materials and Methods

2.1 Materials

Castor oil (99.9%) is purchased from Thomas Baker Chemicals (Pvt.) Ltd., Mumbai and 4, 4'-diphenylmethane diisocyanate (AR grade) is obtained from Krishna Enterprises, Delhi. n-Pentane (99.5%) and Silicon oil, are purchased from CDH. Glycerol (99%) is supplied by Sisco Industries Pvt. Ltd, Mumbai. Catalyst DABCO 33 LV is purchased from Sigma-Aldrich. Aramid fibre is purchased from Dhingra Plastic and Plasticizers Pvt. Ltd. All the reagents are of analytical grade and used as supplied.

Table 1- Foaming formulation of rigid castor oil-based polyurethane foams modified with aramid fibre

Material	Amount
Modified Polyol	20 gm
DABCO 33 LV	2 pbw
n-Pentane (blowing agent)	10-15 pbw
Silicone oil (surfactant)	3 pbw
Filler	1-5 pbw
MDI	25 gm

Pbw = parts by weight of Polyol

2.2 Methods

2.2.1 Foam Preparation

The rigid polyurethane foams are obtained by the same method as reported in the literature (Kaur, Raminder, and Mukesh Kumar 2013 and Agrawal, Anuja, et al. 2019). In brief, the procedure is as follows:

The modification of castor oil is carried out under inert atmosphere of nitrogen using a 1:2 ratio of castor oil to glycerol at 180-200°C for 4 hours. The predetermined quantity of the filler is added to the modified polyol taken in a beaker. Before the addition, the fillers have been dehydrated in a vacuum oven at 60°C for 4 hours. Then calculated amount of other ingredients such as catalyst (DABCO 33 LV), surfactant (Silicon Oil), blowing agent (*n*-Pentane) are added to the contents of the beaker and thoroughly mixed under controlled temperature conditions at 35±2°C to form polyol-premix. A calculated amount of MDI is then added to the beaker. The resulted reaction mixture is poured into a metal mould (100mm x 100mm x 10mm) coated with releasing agent i.e. silicon oil.

To ensure complete curing, the moulds are left to stand for 24 hours. After demoulding, the resulted RPUF is cut into desired dimensions and tested for its mechanical and thermal properties. Different concentrations of aramid fibre are used to carry out studies on the effect of aramid fibre on the properties of RPUFs. Table 1 shows the foaming formulation of rigid castor oil-based polyurethane foams modified with different concentrations of aramid fibre.

3. Characterization

The resulted castor oil-based rigid polyurethane foams incorporated with aramid fibre in varied concentrations, are subjected to the mechanical and thermal analysis to verify alterations in their properties induced by the incorporation of aramid fibre filler. Various characterization techniques used are as follows:

3.1 Mechanical Testing

The mechanical properties of the castor oil-based rigid polyurethane samples have been determined according to the standard procedures. Testing is conducted on three specimens of each concentration and the average value has been reported. Flexural and compressive properties of the resulted foams are measured at room temperature using Instron (model No. 3369) Universal Testing Machine (UTM). For mechanical testing, the samples are cut to the required dimensions. Flexural tests are performed according to the ASTM D-790 using a specimen with dimensions 80mm x 10mm x 4mm. The compression tests are performed according to the ASTM D-695. Specimens of dimensions 25mm x 25mm x 25mm are cut from foam in the in-plain direction and tested for 10% compression. The rate of crosshead movement is fixed at 2 mm/min for each sample.

3.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is performed utilizing a Thermogravimetric Analyzer (Perkin Elmer 4000) in a nitrogen atmosphere. The heating rate is 10°C/min, temperature ranging from 50 to 700°C.

4. Results and Discussion

Fillers are added to polyurethane foam to reduce cost and provide some desired structural and mechanical properties. The foam architecture depends on the particle size and the dispersion of filler in the reacting mixture (Zieleniewska,

Milena, et al. 2016). When a filler is added to a polymer, a conjugated biphasic material gets formed and the force applied to the polymeric matrix will partially transfer into the disperse filler phase, thus imparting properties better to that of the neat polymer (Fan, Hongyu, et al. 2012).

Table 2: Mechanical properties of Aramid fibre reinforced foams

Concentration of Aramid fibre	Compressive strength(MPa)	Flexural strength(MPa)	Density (kg/m^3)
0%	1.766	0.79	160
1%	2.53	0.99	288
2%	2.79	1.83	323
3%	3.27	1.98	349
4%	3.80	2.78	362
5%	1.36	1.83	364

4.1 Mechanical Testing

Upon reinforcing rigid polyurethane foam with aramid fibre, flexural strength reaches upto 2.78 MPa as compared to 0.79 MPa of unreinforced polyurethane foam. So the percentage increase in flexural strength is 251%. The compressive strength at 10% deformation is reported as the compressive strength of the prepared RPUFs. Aramid fibre reinforced PU foam shows an increase in compressive strength upto 3.80 MPa as compared to 1.766 MPa for unreinforced polyurethane foam before the failure occurs.

Table 3: Thermal characteristics of RPUF incorporated with Aramid fibre

Concentration of Aramid fibre	$T_{5\%}$ (°C)	T_{Max} (°C)	Residual mass (%)
0%	192±2	488±4	8.1±2.0
1% w/w	160±2	474±2	12.9±1.0
2% w/w	215±1	475±2	14.7±1.0
3% w/w	250±1	474±1	15.3±2.0
4% w/w	199±2	487±1	16.6±1.0
5% w/w	154±2	470±2	17.0±2.0

4.2 Thermogravimetric Analysis (TGA)

To evaluate the thermal stability of these foams, TGA is conducted under the flow of nitrogen. Thermal properties of aramid fibre reinforced RPUF have been investigated using a Thermo gravimetric Analyzer (Perkin Elmer 4000). Results show that thermal properties enhanced on the incorporation of aramid fibre, while an increase in the concentration of aramid fibre does not show much effect on the thermal properties. Maximum char residue is observed in the foam with a 6% alumina concentration. Figures 1 and 2 show the TGA and DTG curves

Figure 1: TGA curves of neat and Aramid fibre reinforced RPUF

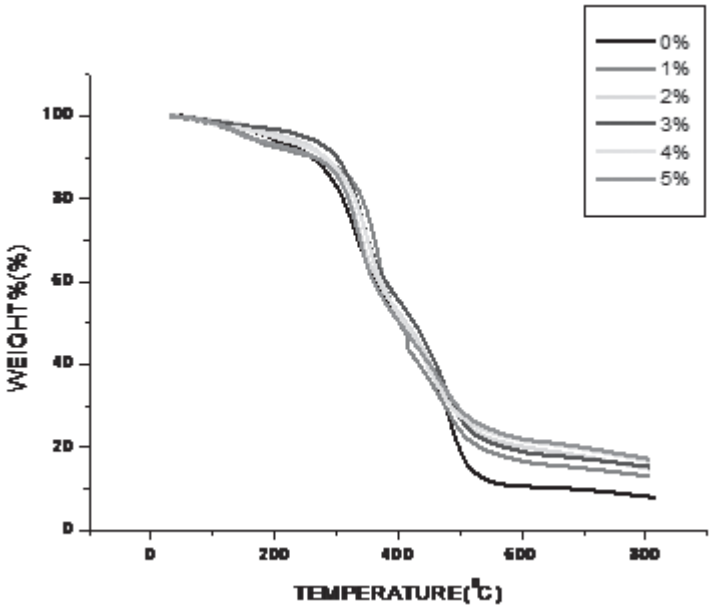
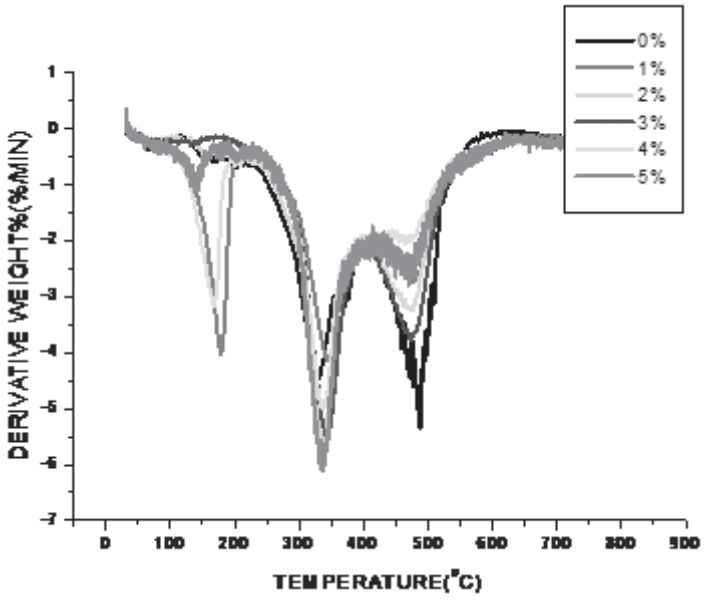


Figure 2: DTG curves of neat and Aramid fibre reinforced RPUF



of neat and aramid fibre reinforced RPUF and corresponding data are summarized in table 3. It shows that 5% weight loss temperature increases from 192°C to 249°C by the incorporation of 3% aramid fibre.

5. Conclusion

Rigid PU foams were prepared by incorporating aramid fibre to enhance the mechanical and thermal properties of foams. Compressive strength and flexural strength of aramid fibre reinforced PU foam increased upto 3.80 MPa and 2.78 MPa, respectively. TGA and DTG curves showed increase in thermal stability of resulted foams. 5% weight loss temperature increased up to 249°C by the incorporation of 3% aramid fibre. Char residue was also found to increase on the addition of aramid fibre. As the incorporation of aramid fibre improves the mechanical and thermal properties of vegetable oil-based rigid PU foams, it may prove a potential additive to improve the mechanical and thermal properties of rigid PU foam.

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Stability of Nanomesoporous Lanthanum Oxide Synthesized by Sol gel and Co-precipitation Methods

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Abstract

Nano crystalline lanthanum oxide (La_2O_3) was successfully synthesized by sol gel and co-precipitation methods. XRD, FT-IR analysis was done to confirm the formation of La_2O_3. TGA-DTG/DSC/DTA analysis of precursor was done to study the mechanism of formation of La_2O_3. Stability of synthesized nano La_2O_3 was tested with XRD and FT-IR. Nano La_2O_3 was found to be chemically unstable in ambient air and transformed into lanthanum hydroxide ($La(OH)_3$) within few hours. The method of synthesis does not have influence on its stability. Thus moisture absorption is an inherent property of La_2O_3.

Keywords: *La_2O_3, Sol Gel, Co-precipitation, $La(OH)_3$.*

Among the rare earths, La_2O_3 appears to be the most extensively investigated ones, because of its low price and good chemical and physical performances in applications. La_2O_3 has many industrial, biological and technological applications. La_2O_3 can act as quality promoter on cathode of molten carbonate fuel cells and as a scavenging agent for zirconia electrolyte in solid oxide fuel cells (Escudero et al 2002 and Carvalho et al. 2000). It is also used in optical coatings, nano scale self assemblies, piezoelectricity materials, galvano-thermy materials, thermoelectricity materials and superconductors (P. Allenspach 2000 and H. Arakawa, Bull 1994). La_2O_3 is widely used as a catalyst for various industrially important reactions. Quan Zhou et al. used nano La_2O_3 for biodiesel synthesis by transesterification of jatrophacurcas oil (Quan Zhou et al. 2015). Synthesis of compounds like phytosterol esters, glycerol carbonates and octahydroquinazolinone derivative were executed successfully using La_2O_3 as a catalyst (Valange et al. 20007, Liguo Wang 2011 and Kuaritheerthakumaran 2011). The catalytic activity of La_2O_3 in automobile exhaust gas convertors, NO_x decomposition and reduction of organic compounds like cyclohexanone were also confirmed (B. Klingenberg et al. 1999, Wang et al. 2006, and Sugunan et al. 1994). Generally, rare earth oxides have the tendency to absorb water and carbon dioxide from the environment (Baskys et al. 2014, Saravani et al. 2015, and Xie, J. et al. 2015). But the stability of La_2O_3 and the factors affecting its stability was not investigated much. In this paper $La_2O_3$was synthesized by different methods and its stability was checked.

2. Experimental

2.1 Catalyst preparation

All the chemicals were of analytical reagent grade and used without further purification. In this study, $La(NO_3)_3$ was taken as the starting material for the preparation of nano particles. In sol gel method, $La(NO_3)_3$ solution was mixed to 0.1 M citric acid solution in 1:1 molar ratio. The resultant solution was stirred for 30 minutes and was heated in a water bath until a viscous gel was obtained. The gel was dried at 100°C and calcined (Xue-Song Liu et al. 2009). La_2O_3 synthesized by sol gel method was noted as LaSOL.

In co-precipitation method 50 mL 25% aqueous NH_3 solution was added drop wise with stirring to 50 mL 0.1 M $La(NO_3)_3$ solution followed by addition of 10 mL 1 M NaOH solution. The resultant solution was stirred for 30 minutes. The resultant precipitate obtained was washed, dried in an air oven and calcined (Jun Wang et al. 2008). La_2O_3 synthesized by co-precipitation method was noted as LaCOPP.

2.2 Catalyst Characterization

In order to study the decomposition process of nano catalyst precursor, TG/DTG and DSC analysis was conducted at a heating rate of 10°C/min in air, using Perkin Elmer STA 6000 Thermo gravimetric apparatus. The phases of La_2O_3 and $La(OH)_3$ were identified by means of X-ray diffraction with a RIGAKU D/MAX-C diffractometer using Cu Kα radiation (λ = 1.5405 Å) at a scanning rate of 5° s^{-1}. The FT-IR studies were done in KBr medium using Thermo Nicolet Avatar 370 model FT-IR spectrophotometer.

3. Results and Discussion

3.1 Formation of La_2O_3

3.1.1 TG/DTG/DSC Analysis

TG/DTG curve of LaSOL precursor (Figure 1) contain three steps of thermal decomposition during the formation of La_2O_3. The initial step of degradation at 100.8°C may be due to the removal of adsorbed water. Small dip at 437.9°C with a

Figure 1 (a) TG/DTG (b) TG/DSC analysis of LaSOL precursor

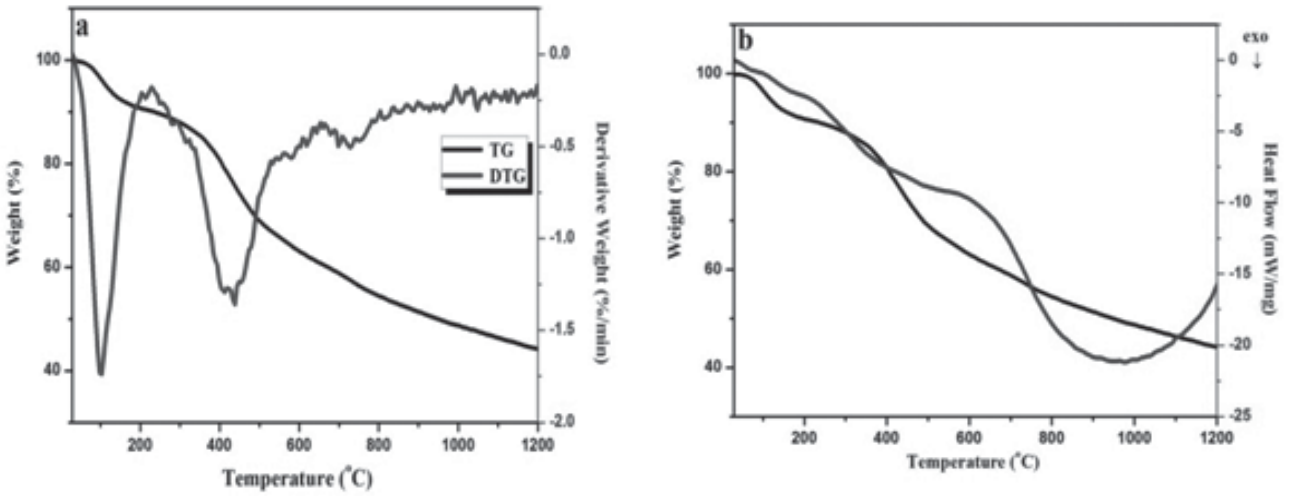
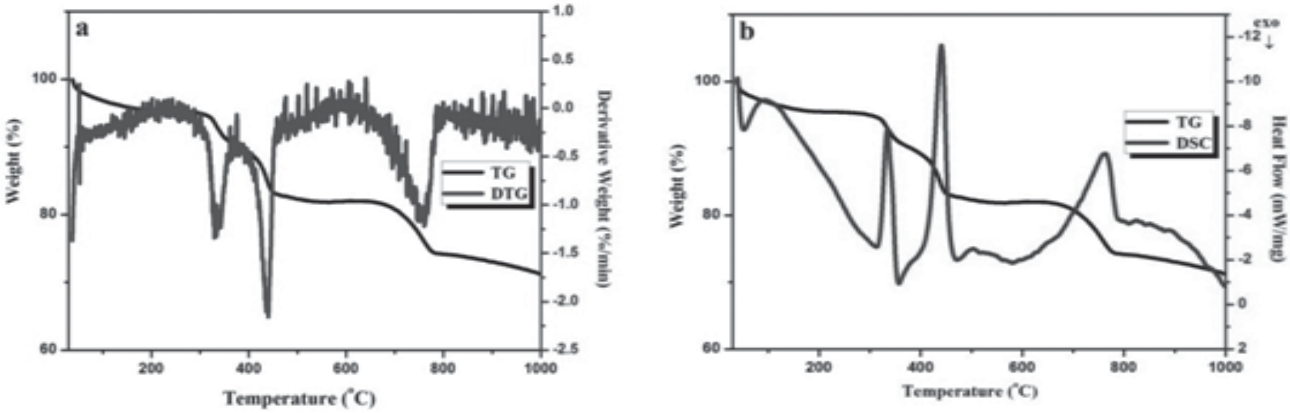


Figure 2 (a) TG/DTG (b) TG/DSC analysis of LaCOPP precursor



mass change of 29.4% may be attributed to the decomposition of lanthanum carbonate ($La_2(CO_3)_3$) to more stable polydentate lanthanum oxy carbonate ($La_2O_3CO_2$). The third step of weight loss of about 12% at 699°C can be assigned to the decomposition of polydentate oxy carbonate with the formation of La_2O_3.

TG/DTG curve of LaCOPP precursor (Figure 2) contain an extra peak at 328.2°C with a weight loss of about 5%, and is attributed to the decomposition of $La(OH)_3$ and volatilization of NH_4NO_3. Further decomposition of lanthanum carbonates at 440.3°C and 759.1°C can also be seen from the graph.

3.1.2 XRD

Figure 3 depicts the XRD patterns of LaSOL obtained after calcinations of La_2O_3 precursor at 400, 600 and 800°C for 2 h. An amorphous solid is formed upon calcination of lanthana precursor at 400°C. XRD pattern of sample after calcination at 600°C matches with monoclinic $La_2O_3CO_2$ (JCPDS 23-0435) and pure La_2O_3 is formed when temperature reaches to 800°C (JCPDS 73-2141).

Figure 3: XRD patterns of samples obtained after calcination of LaSOL precursor at 400, 600 and 800°C for 2 h

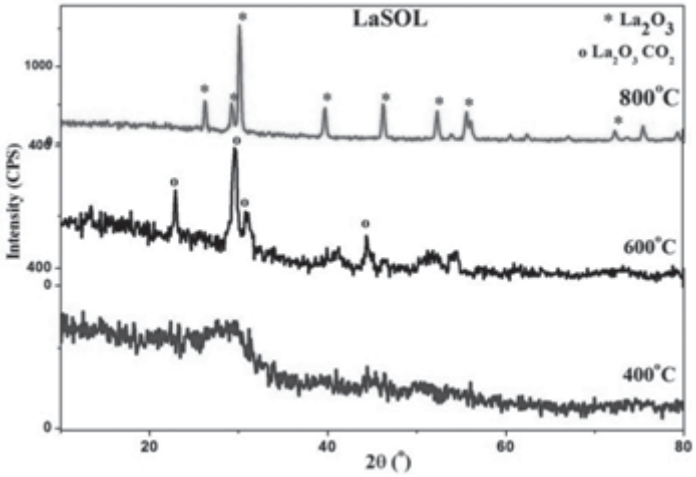


Figure 4: XRD patterns of samples obtained after calcination of LaCOPP precursor at 400, 600 and 800°C for 2 h

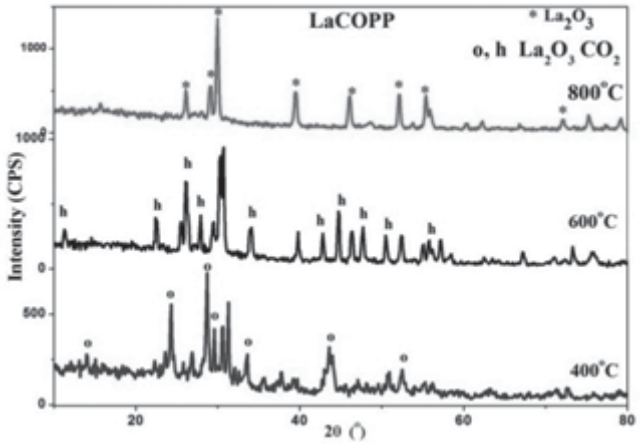


Table 1: XRD parameters of nanoLa_2O_3 synthesized by different methods

Catalyst	Williamson-Hall method	
	Av. Crystallite size (nm)	Lattice strain (10^{-4})
LaSOL	26.2	6.5
LaCOPP	24.4	3.0

Figure 4 depicts the XRD patterns of LaCOPP obtained after calcinations of La_2O_3 precursor at 400, 600 and 800°C for 2 h. The XRD pattern of the sample after calcination at 400°C contain peaks of monoclinic $La_2O_3CO_2$. The peaks of La_2O_3 and monoclinic, hexagonal phases of $La_2O_3CO_2$ are

$$La(NO_3)_2 + 3NH_4OH \rightarrow La(OH)_3 + 3\ NH_4NO_3 \quad \ldots\ldots 1$$

$$2La(OH_3)_2 \rightarrow La_2O_3 + 3\ H_2O \quad \ldots\ldots 2$$

$$La_2O_3 + 3\ CO_2 \rightarrow La_2(CO_3)_3 \quad \ldots\ldots 3$$

$$La_2(CO_3)_3 \rightarrow La_2O_3CO_2 + 2\ CO_2 \quad \ldots\ldots 4$$

$$La_2O_3CO_2 \rightarrow La_2O_3 + CO_2 \quad \ldots\ldots 5$$

present in the XRD pattern of the sample obtained after calcination at 600°C. When calcination temperature reached 800°C, XRD pattern contain peaks of hexagonal La_2O_3 only. Based on the TG/DTG/DSC and XRD results, pathway for the decomposition of lanthana precursor is proposed as follows (Xue-Song Liu et al. 2009).

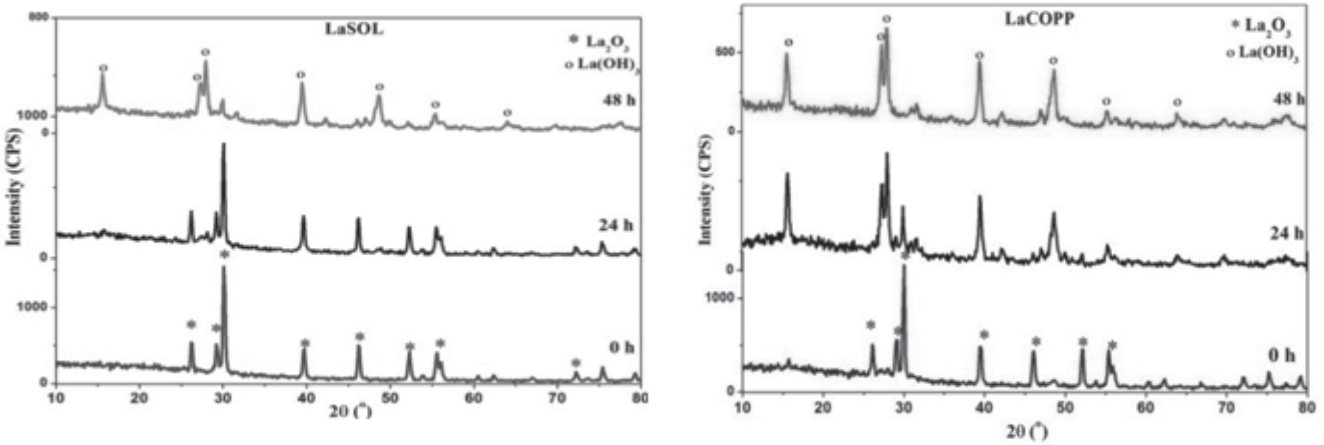
Crystallite size of La_2O_3 prepared by different methods was in the range of 26.2-24.4 nm and lower crystallite size was achieved for coprecipitation method. The difference in the particle size is due to difference in the methods of preparation.

3.2 Stability of Nano La_2O_3

3.2.1 XRD

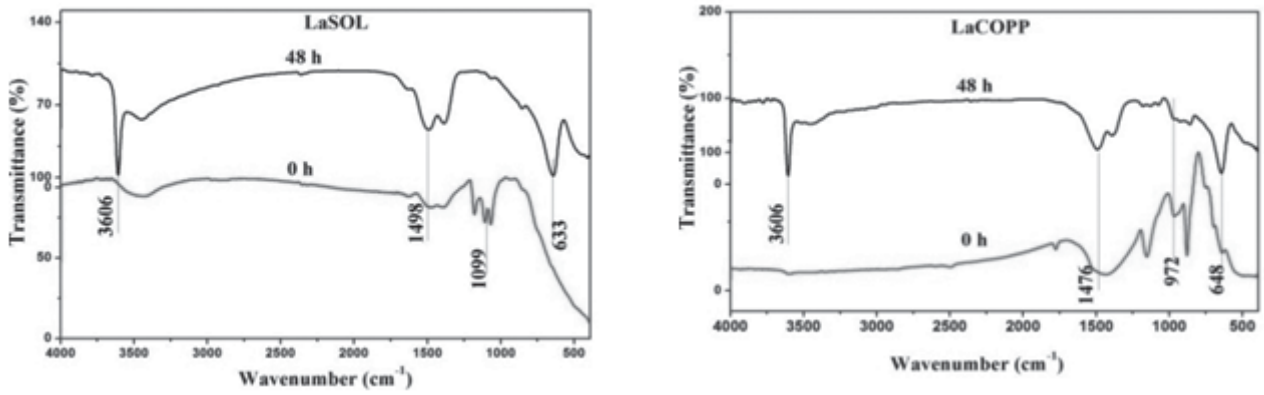
Figure 5 shows the XRD patterns of La_2O_3 exposed to air for different times. It can be clearly seen that synthesized La_2O_3 is chemically unstable in air and hydroxylated completely to form $La(OH)_3$.

Figure 5: XRD patterns of nano La_2O_3 after exposure to air for different time intervals



As the time exposed to air increases, a couple of peaks of $La(OH)_3$ appear, with decrease in the intensities of peaks of La_2O_3 and finally all peaks of La_2O_3 disappear completely. Oxygen vacancies created during calcination of La_2O_3 and its intrinsic small lattice energy may be the reasons for its high moisture absorption phenomena (Xingang et al. 2006 and Yi Zhao et

Figure 6: FTIR spectra of nano La_2O_3 after exposure to air for different time intervals



al. 2010). In the case of sol gel method, $La_2O_3$is stable upto 24h and complete hydroxylation takes place only after 48h of exposure and has greater stability compared to La_2O_3 prepared by co precipitation method. Higher crystallinity and small lattice strain of synthesized LaSOL may be the reasons for its greater stability (Yi Zhao 2012).

FTIR analysis of as synthesized La_2O_3 and La_2O_3 exposed to air for different times (Figure 6) confirms the instability of La_2O_3 in air at room temperature. FTIR analysis of La_2O_3 exposed to air shows that after exposure to air, peaks assigned to stretching and bending mode of tridentate hydroxyl group linked to La^{3+}cation (3590-3613 cm^{-1} and 633-652 cm^{-1}, respectively) appeared (Mekhemer 2002).

Moisture absorption of La_2O_3 is associated with lanthanide contraction (L.Calmels et al. 2011). Large quantity of the heat generated by the hydration of La_2O_3 also promotes further hydration reaction (Ding Jiawen 2006). The other reasons for high moisture absorption tendency of La_2O_3 are (a) the very similar structure of La_2O_3 to that of $La(OH)_3$; (b) large negative Gibbs free energy change for moisture absorption (G = -175 $kJmol^{-1}$); (c) small lattice energy and (d) high permittivity (Yi Zhao 2012 and Yi Zhao et al. 2010). Thus moisture absorption is an inherent property of La_2O_3, which cannot be avoided but can be decreased. It was shown that independent of synthesis methods and various treatments of the samples, the hydration of La_2O_3 takes place. The process is found to be reversible and form the oxide at around 300°C (Michael Denise T. 1977).

Based on the results, mechanism of moisture absorption by La_2O_3 can be expressed by the following equations.

$$La_2O_3 \rightarrow 2\ La^{+3} + 3\ O^{-2} \quad \text{.....6}$$

$$3\ O^{-2} + 3\ H_2O \rightarrow 6\ OH^- \quad \text{.....7}$$

$$2\ La^{+3} + 6\ OH^- \rightarrow 2\ La(OH)_3 \quad \text{.....8}$$

4. Conclusions

Sol gel and co-precipitation are found to be efficient methods for the synthesis of nano-crystalline La_2O_3. XRD and FT-IR analysis confirmed the formation of nanocrystalline La_2O_3 and thermal analysis of La_2O_3 precursor revealed the mechanism of its formation. Nano La_2O_3 is found to be chemically unstable in ambient air and transformed into $La(OH)_3$. XRD and FT-IR analysis proved this fact. La_2O_3 prepared by sol gel method is stable upto 24 h and has greater stability compared to La_2O_3 prepared by co precipitation method. Higher crystallinity and small lattice strain of synthesized LaSOL may be the reasons for its greater stability. The method of synthesis does not have profound influence on its stability.

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$PM_{2.5}$ and Its Remediation by Using Electrospun Nanofibrous Membranes

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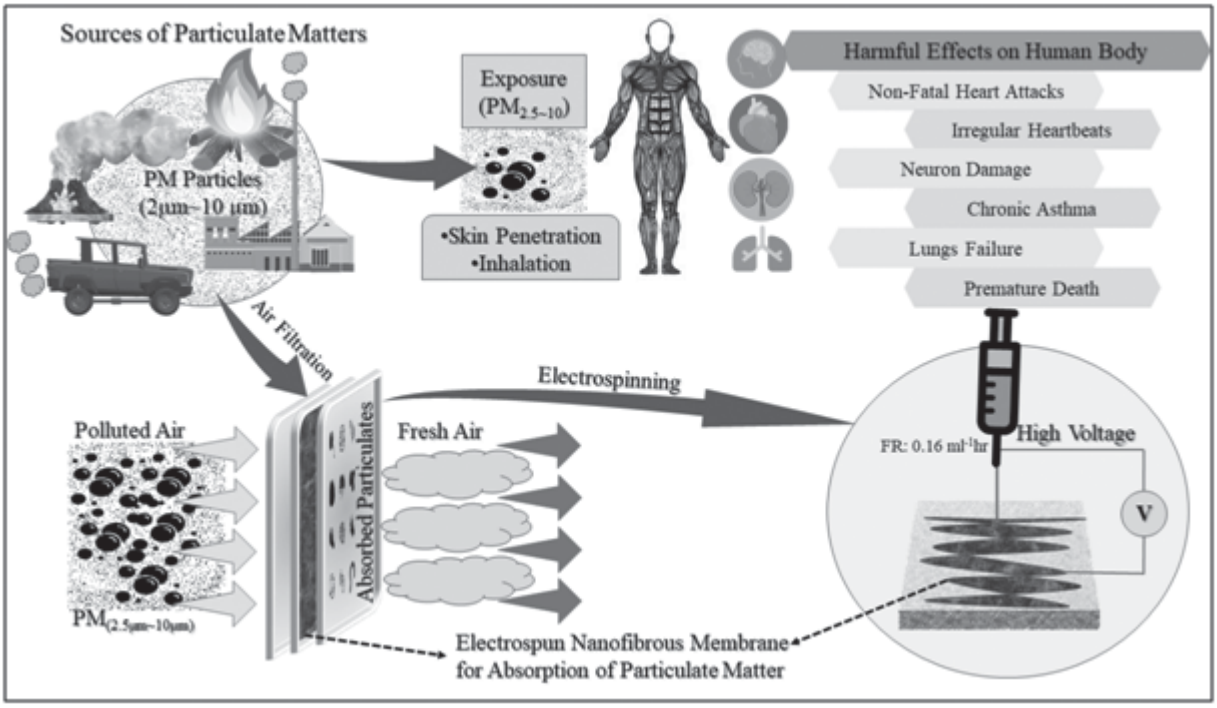
Abstract

Technological advancements led to various extraordinary developments, but on the contrary, it has also affected human civilization and ecology to a considerable extent. Among all the venoms of the environment, air pollution is becoming the throat-cutting object for living organisms where particulate particles suspended in air is a major cause of pervasive air pollution. The size of the particulates is much smaller than the human tissues, making it penetrable directly into the lungs and blood streams. The exposure to Particulate Matter (PM) is deleterious to humans as it can cause acute tissue damages that lead to premature death. As a redressal, Electrospun Nanofibrous Membranes (ENM) can be utilitarian to capture particulate matter of targeted shape and size, drawn by Electrospinning. The review aims to converse the accounts and detriments of PM as well as their filtration with the use of ENMs, competent to filter PM particles of selected size due to their small pore size and high specific surface area. The well-turned utility of these membranes can be lucrative for filtering and capturing the most noxious element of air and also holds a good promise of epochal use in various other applications that can be hale and hearty for the environment and humankind.

***Keywords**: Globalization, Air Pollution, Particulate Matter, Health Hazards, Electrospinning, Electrospun Nanofibrous Membranes.*

Graphical Abstract

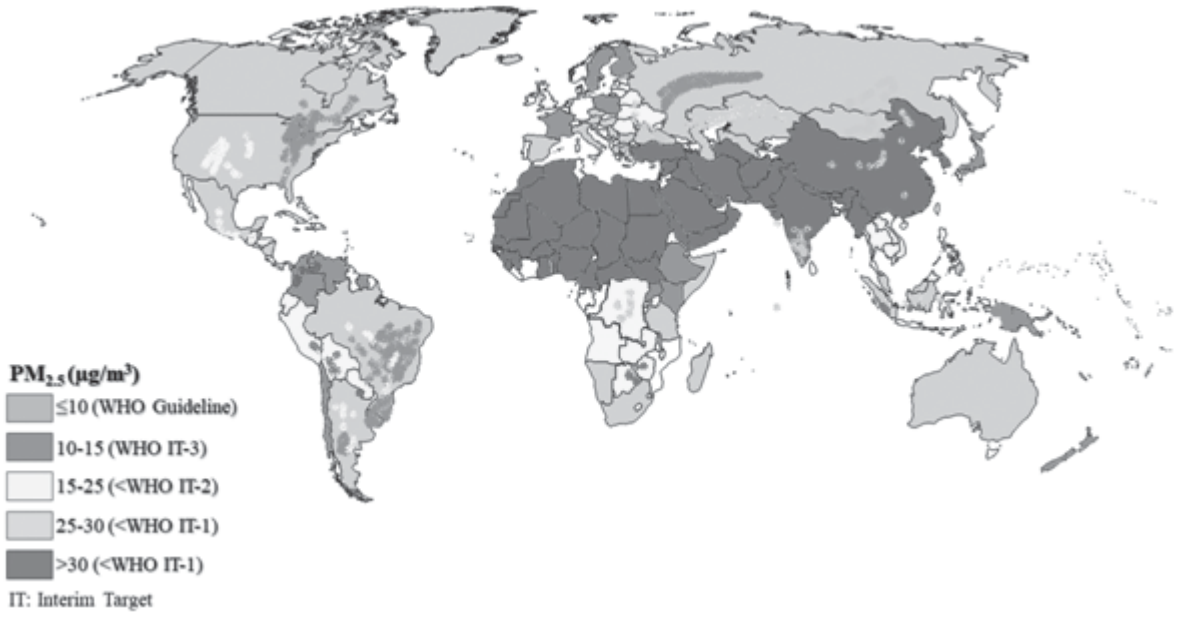


Particulate Matter' (PM) are condensed phases suspended in the air in the form of an aerosol (fine solid particles and liquid droplets). Particles having a diameter smaller than 50μm and higher than 10nm are said to be PM particles. PM is mainly present near the surface areas and often classified into two categories (i) Primary PM: which arises from the water sprays, pollens, and dust (ii) Secondary PM: which emerges from the fog, droplets, weather transformations, and industrial fumes. The process of PM formation is entirely different from gases (Dominici et al. 2014). PM shapes can be formed of thousands of chemicals, and their size distribution is very distinct, where most of the PMs are composed of Nitrogen Oxides and Sulphur Dioxides, emitted mainly from industrial fumes. The size of these particulates is so small that it requires an electron microscope to observe it. The standard studies of PM include two sets of size distribution, PM_{10} and $PM_{2.5}$. Of the two sets, $PM_{2.5}$ is much hazardous to human health as its diameter range is ~2.5μm, which can penetrate directly into the blood streams through inhalation and can be deadly to humans (the United States Environmental Protection Agency 2018). The release of heavy metal ions from factories, power plants, and vehicles is also a leading factor for the formation of PM, which causes the failure of body organs, leads to premature death (Fortoul et al. 2015). According to reported data of the World Health Organization, around 7 million people die annually due to Heart Attacks, Strokes, Pulmonary Diseases, Lung Cancer, and Respiratory Damages caused by ambient $PM_{2.5}$ pollution. In India, New Delhi loses 80 lives per day due to $PM_{2.5}$ pollution (Apte et al. 2015). As per a joint study of IIT Delhi and The Energy and Resources Institute (TERI), the levels of $PM_{2.5}$ were double than the safe limit in the city in the last three years. The city has also been marked as the most defiled city in the world by the World Health Organization (WHO) based on

Air Quality Data (AQD). The average levels of $PM_{2.5}$ were recorded to be 103.4μg/m^3 in May 2018. Data of concentrations of $PM_{2.5}$ in the world in the year 2016 are shown in Figure 1 (IHME 2019).

The rising levels of PM in the environment can be controlled by using Electrospun Nanofibrous Membranes (ENMs), a type of nanomaterial prepared by using the electrospinning technique of drawing fibers that are suitable for making

Figure 1: Concentrations of $PM_{2.5}$ in the world for the year 2016

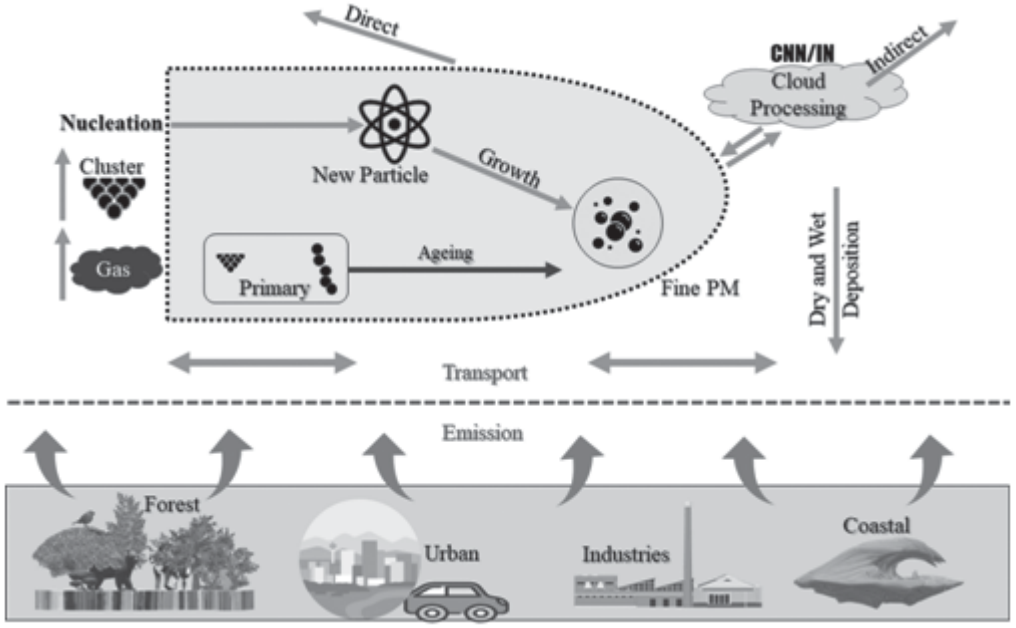


high-porous networks (Kenry and Lim 2017; Wohllebe et al. 2009). Electrospinning is a voltage-accelerated process which uses a syringe filled with a polymer solution of the desired material, to which a high voltage is applied to create an electrically charged jet of the polymer solution. The charged solution drop comes out of the needle in a spiral thinning motion due to mutual repulsive forces present in the solution. After that, the ENMs can be obtained on the collector in the form of a web of high porosity and high specific surface area (Homaeigohar and Elbahri 2014; Sawicka and Gouma 2006; Huang et al. 2003). Several ENMs can be drawn by using different substrates and polymer solutions. The most common ENMs include Polyvinylidene Fluoride (PVDF), Polyvinyl Alcohol (PVA), and Poly-acrylonitrile (PAN) membranes with solute NaCl, $MgSO_4$, and Oil/Water (Haider et al. 2018). The drawn ENMs are subjected to drying for around 12 hours at a temperature range of 90°C~110°C, and their characterization can be done by using SEM, TEM and FTIR spectro photometer (Zeytuncu et al. 2016).

2. Particulate Matter$_{2.5}$: A Case Study

The emissions of PM range widely from natural to anthropogenic sources like volcanic activities, agriculture, transport, urban activities, forests, and industrial smoke. They have direct impacts on climate, weather, and ecological balance that adversely affects environs (Mabahwi et al. 2014; Brown et al. 2013; Steinfeld 2012). Particulate Matters of larger sizes (greater than 10μm) tend

Figure 2: Emission Sources of PM and its Routes of Travel in the Environment



to deposit to the ground level under the effect of gravitational force, and Particulates of smaller sizes (less than 10μm) remain suspended in the atmosphere and are mostly deposited to ground by precipitation. Among all the sources of emission, particulates vehicular combustion is the most harmful and highly present in the environment (Goswami et al. 2013). A schematic diagram of emission sources of $PM_{2.5}$ and its mechanism of travel in the atmosphere is shown in Figure 2 (Zhang et al. 2015).

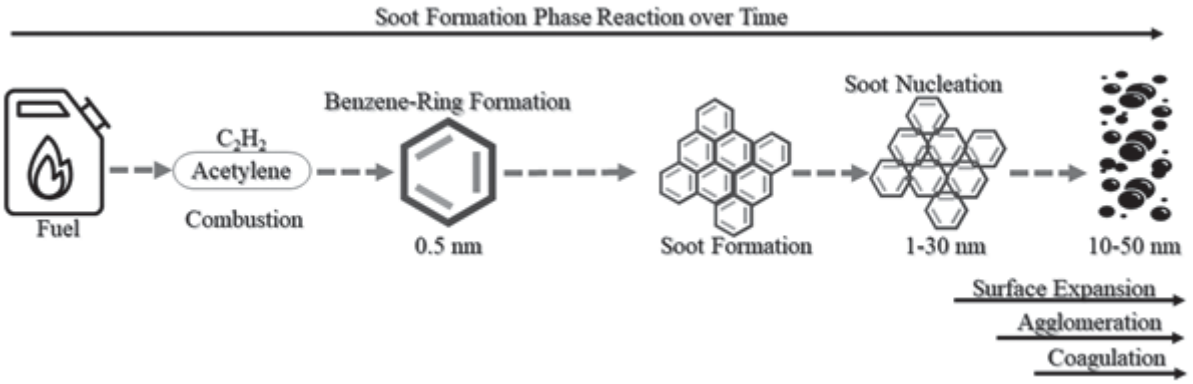
2.1. Formation of $PM_{2.5}$ by Vehicular Diesel/Petrol Combustion:

The Particulate Matter released by vehicles is much hazardous because it exerts a direct exposure to the human body just after its formation and releases to the environment. When the combustion takes place inside the engine, it produces PM particles as a result of various chemical and physical reactions over time of different shapes, sizes, and compositions. Within a few microseconds, the soot forms in the form of solid particles from fuel droplets. When compared to gasoline engines, soot formation rate is much higher in diesel engines. The process of soot formation occurs due to the oxidation and decomposition of hydrocarbons (thermally). The first recognizable soot particle forms at around 2nm called nuclei and take part in nucleation. Small particles having a diameter of ~2nm undergoes Brownian Motion and collides with each other to form larger particles of higher atoms, which leads to an increase in surface area and agglomeration. Both these processes continuously occur to produce small particles in large quantities, resulting in a condensed matter, i.e., Particulate Matter, which is also known as Particle Pollution (Sahoo and Kandasubramanian 2014; Hiroyasu et al. 2010; Xi and Zhong 2006). A chemical reaction for soot formation taking place during vehicular diesel combustion is shown in Figure 3 (Bockhorn 1994).

2.2. Exposure of $PM_{2.5}$ on Human Health:

Recently, the increasing studies of Toxicology and Epidemiology demonstrated that $PM_{2.5}$ is nearly

Figure 3: Process of Soot Formation in Vehicle Engines by Diesel Combustion



related to various chronic diseases in a human being. After examining 29 European Countries by researchers, it was reported that an increase in every 10μg/m^3 could escalate a mortality rate of 0.58% with a raised hospitality rate of 8%. Also, the inhalation of $PM_{2.5}$ polluted air could cause severe pulmonary diseases, lung cancer, strokes, heart attacks, kidney failure, and much more. $PM_{2.5}$ can cause oxidation of living cells, leading to bodily injury and internal bleeding. Various damaging mechanisms of $PM_{2.5}$ on the respiratory system have been studied which show how they can induce free radicals to promote oxidation of lung cells. The surface layers of $PM_{2.5}$ are rich in Iron (Fe), Copper (Cu), Zinc (Zn), and other transition metals, which can increase free radical production and cause oxidative stress (Xing et al. 2016). Some studies also showed that $PM_{2.5}$ could target cerebral/cortical matters and Basal ganglia, which leads to various cognitive and neural changes in the human body. Particles, less than 2 Microns can penetrate directly into the brain via olfactory bulb which can reduce cognitive functions (Ailshire and Crimmins 2014; Gatto et al. 2014) and reduce brain volume (Chen et al. 2015). A long term exposure to $PM_{2.5}$ can cause Autism Spectrum Disorder and can induce Alzheimer (Fu et al. 2019).

2.3. $PM_{2.5}$ Guidelines and Most Affected Countries:

The increasing concentrations of $PM_{2.5}$ brought various harmful effects to all the regions of the world like global warming, premature deaths, health hazards, and ecological disbalance. In 2005, World Health Organization (WHO) set guidelines for air pollutants concentrations annually and hourly to monitor the health-risk of different countries and areas most prone to particle pollution known as Air Quality Guideline (AQG). WHO stated that passing the admissible concentrations of PM would pose health risks. According to the AQG, the annual mean concentration of $PM_{2.5}$ should not exceed 10μg/m^3 and 25μg/m^3 24 hour mean (World Health Organization 2006). The guidelines were applied worldwide based on expert evaluation of scientific evidence of particulate matter, Ozone, Nitrogen Dioxide, and Sulphur Dioxide as Air Pollutants. In the world, the most affected countries by $PM_{2.5}$ lies in the Asia continent, where the PM due to vehicular combustion and Industrial smoke is extremely high than the guideline values. As a particular case to India, the capital city has been perceived as the most defiled and dirtiest city in the country. Its annual mean $PM_{2.5}$ concentrations were around 113μg/m^3 in 2017-2018, making it a

very unhealthy city (Rahim 2019; Gorai et al. 2018). Additionally, in the same year, particulate pollution was responsible for around 12 lakh deaths in India. Also, it was reported that one of the eight deaths was due to the particulates. The leading causes of particulate pollution in India is the vehicular combustion of petrol and diesel. The soot formation by combustion in vehicles increases the concentration of $PM_{2.5}$ due to the lower fuel standards (Xi and Zhong 2006; Bockhorn 1994). Heavy metal ions and fuel ions induce during the combustion of diesel and petrol, which then incorporates the process of soot formation and add more hazards to the living bodies (Spencer et al. 2006; Sharma et al. 2005). Direct exposure of metallic $PM_{2.5}$ can penetrate the bloodstreams, followed by inhalation and skin penetration, which can lead to long term health effects and can even cause unexpected deaths (Jin et al. 2018). A large number of people die every year due to the ambient air pollution promoted by particulate matter and other metallic particles induced by vehicular combustion.

2.4. Effects of $PM_{2.5}$ Pollution on Economy:

Increasing levels of pollutants in the air are causing severe health hazards that are indirectly connected to the economic factors of a country. In 2011, economic damage was around USD 131 billion, where most of the cost was due to the people who fell sick from particulate pollution. A study in the United States demonstrated that the efficiency of workers diminished due to PM pollution, and their sickness caused less work in industrial sectors, leading to severe economic damage (Chang et al. 2016). The US government implemented the Clean Air Act of 1970 to control vehicular pollution, which required people to follow or face penalties (Isen et al. 2013). A study by the Office of Tax Analysis, US, stated that those who were born after the Clean Air Act 1970 earned around USD 4300 extra than the others. There is also evidence from the Call Centre Industry of China that employees had to take more breaks than usual due to the health issues caused by PM pollution (Chang et al. 2019). A study by IIT Bombay found that India cost around USD 10.66 billion in 2015 only from Mumbai and New Delhi because of the air pollution, that was approximately 0.71% of the GDP of the country (Times 2018). India lost over USD 505 billion towards health welfare and over USD 55.4 billion due to a lack of labors caused by air pollution.

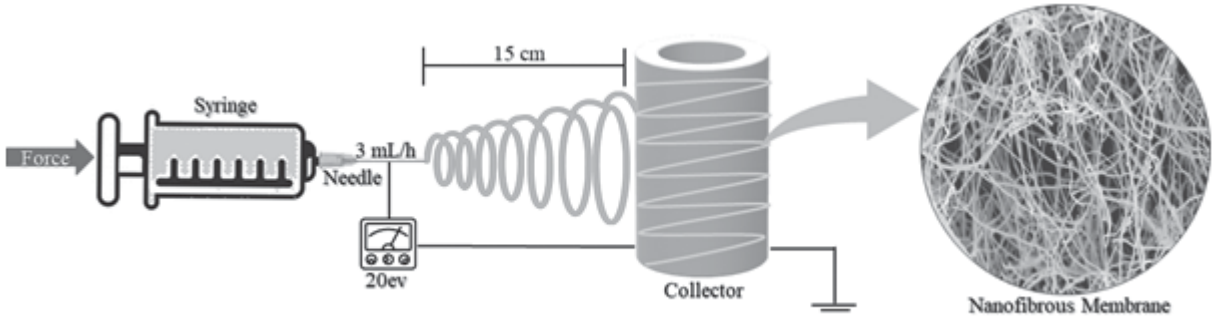
3. Remediation of Environmental $PM_{2.5}$ by using ENMs:

3.1. Formation of ENMs by Electrospinning Technique:

Electrospinning is an efficient technique to produce nanofibrous membranes posing industrial interest due to cost efficiency, high porosity, low basis weight, and much more (Karakaş, et al. 2016). Electrospinning is an extension to the electrospraying where electrospinning has an advantage of producing continuous (one-by-one) nanofibers. This technique gained much attention in the late 1980s due to the increasing interest in Nanotechnology by the use of fibers in nanometer and submicron scale (Gupta et al. 2017; Bahrami and Gholipour Kanani 2011; Bhardwaj and Kundu 2010; Huang et al. 2003). It uses mechanical and electrostatic force to draw fibers from the tip of the syringe. When the value of the electrostatic force becomes higher than the surface tension, an electrically charged jet ejects out from the syringe and gets elongated due to the electric field effect. Upon solvent evaporation, the jet spray solidifes and deposits on the collector plate to form a nanofiber.

A schematic view of the electrospinning technique for drawing Nanofibrous Membranes is displayed in Figure 4 (Zeytuncu et al. 2016).

Figure 4: A Schematic Diagram of Electrospinning Technique



The polymer solution is prepared in a specific weight ratio (~10 to 15% polymer) and filled in a syringe which pumps the solution out of the needle at a constant rate under the influence of high voltage, which makes the jet electrically charge and make polymer spray to eject out of the syringe. One connection of voltage is attached to the electrode placed in the polymer solution and the other to the collector plate for grounding. The electric charge is forwarded to the tip of the syringe needle, where the polymer solution is held by surface tension at the end of the tube. This electric field induces a significant charge on the polymer solution surface, and a force opposite to the surface tension is produced due to mutual charge repulsions. A conical shape is formed by the elongation of solution fluid at the tip of the syringe, known as Taylor Cone. Continuously increasing the electric field attains a threshold value where the electrostatic force overlaps the surface tension and a charged jet spray of polymer solution is ejected out of the capillary tube. After ejection, the polymer jet spray attains instability whereas the elongation process makes the jet spray long and fine. When the solution evaporates, it leaves a polymer fiber collected on the collector plate, which is an Electrospun Nanofibrous Membrane (Fong and Reneker 2018; Kim et al. 2018; Qin and Subianto 2016; Dua 2013; Hale Karakaº 2012). The formula gives a balanced relation between applied voltage and surface tension:

$$V_c^2 = 4\frac{H^2}{L^2}\left(\ln\frac{2L}{R} - \frac{3}{2}\right)(0.117\pi\gamma R) \quad (1)$$

where V_c is the critical voltage value, H is the distance between the ground and the capillary tube, L is the capillary length with the radius, R and γ is the surface tension of the liquid exerted on the capillary opening (Zhu et al. 2017; Zhou 2007).

A series of nanofibers can be produced by electrospinning with required pore sizes, density, and surface area. The electrospinning technique depends on various parameters, which also affect the shape, size, and distribution of nanofibrous membranes. The parameters affecting this technique can be altered to produce significant nanofibrous membranes of desired material and properties.

3.2. Effect of Various Parameters on the Properties of Nanofibers:

3.2.1. Applied Voltage:

Increasing the applied voltage above a particular value leads to the formation of beaded nanofibers. The nanofiber diameter was reported to increase with a gradual increase in applied voltage. Furthermore, the change in diameter of fiber by

modifying applied voltage also depends on the nature of polymer solution as the increased voltage value tends to decrease the size of Taylor Cone and increase the velocity of jet spray (Haider et al. 2018; Sill and von Recum 2008).

3.2.2. Solution Flow Rate:

Increasing the flow rate of the solution polymer jet above the threshold value leads to the formation of beads. When the flow rate is decreased to 0.07mL/min, bead-free nanofibers can be produced because increasing and decreasing the flow rate affects the formation and diameters of nanofibers. The rate of flow is directly connected to the applied electric field. Hence it is necessary to maintain a relation between the ejected polymer solution and the next solution for the jet formation for a nanofiber by the constant flow of solution jet (Haider et al. 2018; Megelski et al. 2002).

3.2.3. Needle-to-Collector Distance:

According to the studies of various research groups, it has been observed that it is indispensable to maintain a significant distance between needle tip and collector to produce a uniform and smooth fiber as non-calculated distance can produce defective nanofibers. When the distance is kept small, nanofibers of large diameters can be produced whereas large distance between needle and collector produce nanofibers of small diameters (Haider et al. 2018; Bhardwaj and Kundu 2010).

3.2.4. Polymer Concentration and Solution Viscosity:

The polymer solution concentration plays a vital role in determining the morphology of nanofibers. Making an increase in the concentration of polymer solution leads to an increase in viscosity of the solution, which can extend the chain entanglements that overlaps the surface tension and produces uniform bead-less nanofibers. Increasing the concentration over a critical value leads to the formation of deformed nanofibers (Haider et al. 2018; Pillay et al. 2013).

3.2.5. Humidity and Temperature:

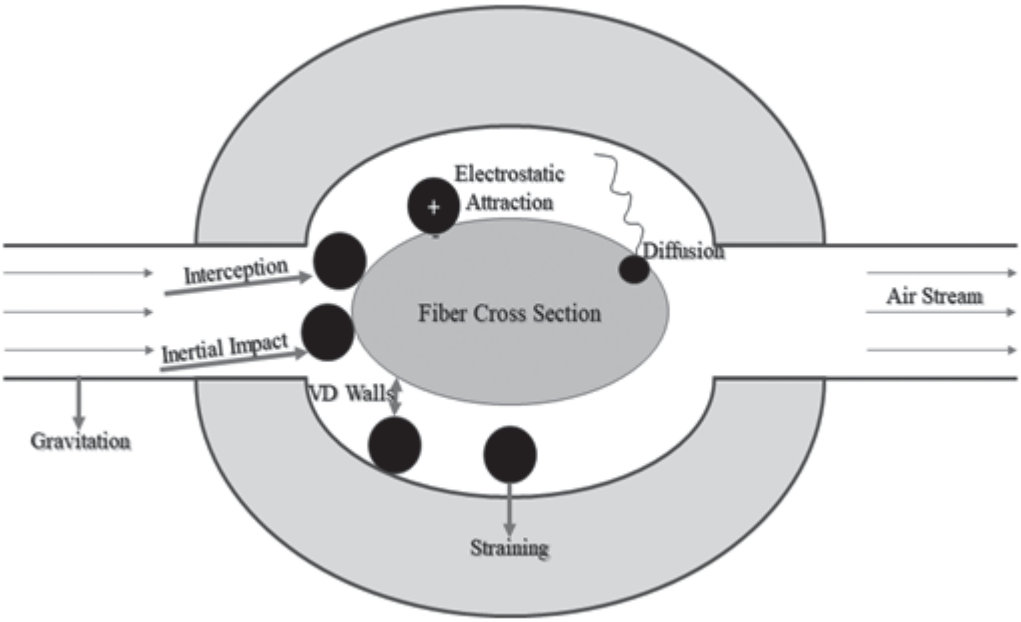
Humidity changes the diameter of nanofibers by dominating the solidification process of electrically charged jet spray. There occurs a decrease in the diameter of nanometers with an increase in humidity factor. Humidity is also very useful in making efficient porous nanofibers (Pelipenko et al. 2013; Rhee et al. 2010). The temperature factor can increase the evaporation process of the solution jet and decrease the viscosity of the solution leading to a decrease in mean fiber diameter (De Vrieze et al. 2009).

3.3. Particle Capture Mechanism of ENMs and its Filtration Efficiency:

ENMs are prepared efficiently by using electrospinning techniques of drawing nanofibers. ENMs can easily capture particulates as these membranes are usually made up of fibrous materials depending on the size of particulates. Based on inhalation, particulates are generally of two types (i) Fine (~2.5-10μm) and (ii) Ultrafine (<0.1μm). Particulate air filters are characterized by the Minimum Efficiency Reporting Value (MERV) and Most Penetrating Particle Size (MPPS). The typical value of MPPS is between 0.1μm and 0.3μm, where MPPS is the size of the particle at which no filter mechanism can capture it (Kadam et al. 2018; Hutten 2015). The filter mechanism of PM includes inertial impact, gravitation, diffusion, interception, straining, and coulombic attraction on the filter surfaces. The initial particle capture uses the diffusion and

interception in nanofibrous membranes. The diffusion process can capture the particle size (<0.5μm), moving due to Brownian Motion. A PM particle can intercept with the nanofiber when the distance between nanofiber and particle center is less than the particle radius (Kadam et al. 2018; Mukhopadhyay 2010; Maze et al. 2007). A particle capture mechanism is shown in Figure 5.

Figure 5: Particle Capture Mechanism of an Electropsun Nanofiber

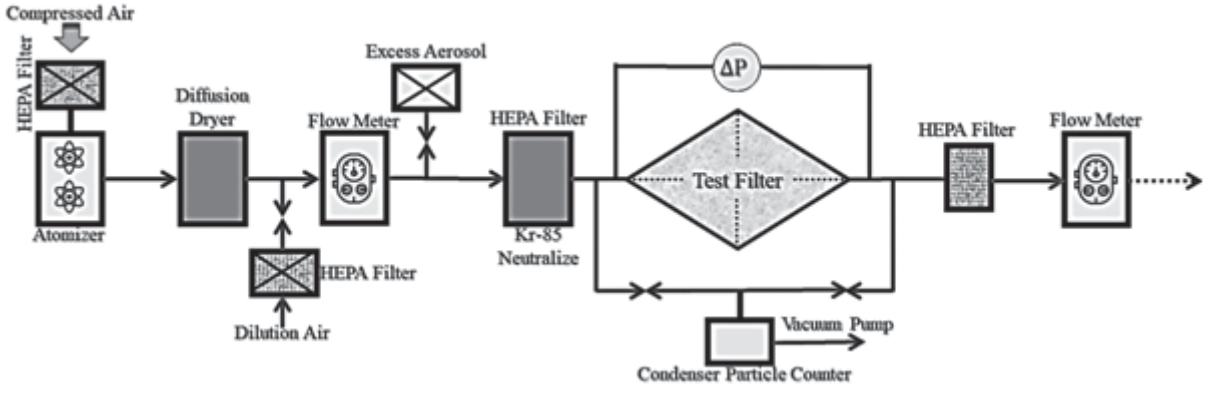


Inertial Impact and Interception are the main mechanisms of particle capture higher than 200nm, where diffusion is for particles having sizes less than 200nm.

3.4. Test Methods of Electrospun Air Filter:

Traditionally, the oil mist methods and flame methods were used to test High-Efficiency Particulate Air (HEPA) filters, but due to advancements in the technology of micro and nanoelectronics, these methods are going outdated (Zhu et al. 2017). A schematic diagram of the current testing mechanism used for HEPA filters is shown in Figure 6 (Zhu et al. 2017; Kim et al. 2008). The test structure is constituted mainly of an atomizer, diffusion dryer box, flow meters, and

Figure 6: A Structural Diagram of HEPA Filter Testing Mechanism



test filter screening (Vanangamudi et al. 2015). In this mechanism, when aerosol particles pass through the HEPA filter, the airflow is kept constant by a computer command. The amount of filtered and unfiltered aerosol particles is observed optically, resulting in the filtration performance of the membrane (Zhu et al. 2017; Wake and Brown 1991). Individual filtration mechanisms make the total efficiency of the fiber filter.

The total fiber filter efficiency for single fiber can be defined as (Al-Attabi et al. 2018; Yang 2012; Podgórski et al. 2006):

$$Ns = \frac{Particulates\ Captured\ by\ Nanofiber\ Membrane}{Particulates\ in\ Air\ Volume\ Swept\ out\ by\ Fiber} \quad (1)$$

where N is the efficiency of a single fiber to capture particulates, and s is the filter area factor.

The filtering efficiency of the tested nanofiber filters can be calculated by (Zhu et al. 2017):

$$N = (1 - P) \times 100 \rightarrow 1 - \left(\frac{C_{Downstream}}{C_{Upstream}}\right)(\times 100) \quad (2)$$

where N is the efficiency of the tested fiber and $P = \left(\frac{C_{Downstream}}{C_{Upstream}}\right)$; $C_{Downstream}$ is the concentration of particulates in the air after passing the filter and $C_{Upstream}$ is the concentration of particulates in the air before passing the filter (Zhu et al. 2017).

4. Polymeric ENMs for $PM_{2.5}$ Filtration: A Case Study

4.1. Overview of Polymers and its Uses in ENMs:

A polymer is a long-chained substance made up of large molecules (macromolecules) in multiples of simple chemical units called monomers. The monomer units form together in repetition to form a polymer chain (The Editors of Encyclopaedia Britannica 1998). For Example, Nylon 6 is a polymer made up of repeating monomer units of Caprolactam (Mathias et al. 2009). Polymers are classified into two categories based on origin (i) Synthetic polymers (ii) Bio Polymers (Tomar et al. 2016). Both types of polymers have their significance in producing ENMs with different properties and filter efficiency. The parameters and properties of electrospun fibers vary from polymer-to-polymer (Kadam et al. 2018).

Synthetic Polymers for ENMs: Synthetic polymers are preferred to produce electrospun membranes due to their ease of spinning, well-disciplined fluid characteristics, exceptional thermal, and chemical stability. Most of the nanofibrous membranes are prepared by Polyimide and Polyacrylonitrile polymers due to their narrow diameter distribution and high porosity factors. They can capture Particulate Matter even in critical pollutant concentrations (Kadam et al. 2018; C. Liu et al. 2015).

Natural Polymers for ENMs: Natural polymers are also being used to prepare electrospun membranes as they are more blended than that of the synthetics. They are also preferred for the fibers due to their antibacterial properties, e.g., Keratin biopolymer can capture particulates with an additional advantage of removing air bacteria, formaldehyde, and other Volatile Organic Compounds (Kadam et al. 2018; Govindaraj et al. 2014; Yadav and Kandasubramanian 2013; Tonin et al. 2012; Huang et al. 2007).

4.2. Polymeric ENMs for $PM_{2.5}$ Filtration: Recent Innovations

Nanotechnology innovations led to the development of various technologies (New and Existing) that proved life-saving agents for human civilization and much more for the environmental remediation (Malik et al. 2019; Porter and Youtie 2009). In the last 10 years, the ENMs became the right choice for Air Filtration due to their exceptional properties, stability, and reliability (Magisetty et al. 2019; Deoray and Kandasubramanian 2018; Huang et al. 2003). The highest number of studies and innovations were produced in the year 2018 because the PM concentration of the year 2016 and 2017 were very drastic and possessed a high number of deaths around the world (Balakrishnan et al. 2019). These factors led to the motivation of improving air quality to save lives, economy, and ecological balance between all the environs. A series of doping agents and polymer solutions were being used to modify the existing properties and efficiency of ENMs to make them more efficient and commercially viable. As an example, Wrinkled Silica was used as a doping agent into PAN nanomembranes for better filtration efficiency, combine the properties of high porosity and lower pressure drop (Al-Attabi et al. 2019; Balasubramanian and Tirumalai 2013). Some of the examples are given below, which proved as an excellent innovation and contributed to the cleaning of the environment.

4.2.1. PVDF and SiO_2 Incorporated ENMs:

Recently, a team of researchers from Donghua University produced highly efficient electrospun membranes by using a polyvinylidene fluoride (PVDF) as a matrix polymer SiO_2 nanoparticles modified by γ-glycidoxypropyltrimethoxysilane (GPS) as charge enhancers. They used SiO_2 NPs to generate interfacial charges between SiO_2 particles and PVDF. The PVDF solution was prepared by mixing SiO_2 Nanoparticles with N,N-Dimethylacetamide, further, by adding PVDF powders to the mixture at a continuous stirring for 8 hours. The electrospinning feed rate was taken to be 0.5mL/h with a high voltage supply of 30kV, and the syringe whose moving speed was taken to be 100 cm/min. It was observed that after a jet spray flight distance of 20 cm, the nanofibers were collected on a roller coated with nonwoven material (rotating velocity: 50 RPM). The produced ENMs exhibited electrets having the surface potential of 12.4kV, and the quality factor for filter performance was measured to be 0.14 (Ding et al. 2019; Li et al. 2015).

4.2.2. Polyvinyl Alcohol/Cellulose Nanocrystals Composite ENM:

Another scientific approach to ENM was the production of electrospun Poly {(Vinyl Alcohol)/ Cellulose Nanocrystals Composite (PVA/CNC)} membranes. The PVA/CNC suspension was prepared by dispersing PVA in deionized water and continuously stirring at a constant temperature of 80° C until its full dissolution. After cooling, the CNCs were added to the solution in particular amounts for different concentrations. The electrospinning feed rate was taken to be 0.5mL/h with a high voltage supply of 22kV, where the

needle-collector distance was set to 10cm at room temperature and ~50% relative humidity. This research holds great significance as its filter efficiency was observed to be 99.1% even in the extremely polluted conditions (~500 μg m^{-3}), where the permissible limit by WHO is only 30 μg m^{-3}. The materials (PVA and CNC) used in this work were also environment-friendly as both are biodegradable and non-toxic. The research was targeted to decrease the fiber diameter of membranes by increasing the surface charge density factor of the solution used in the electrospinning process. The small diameter sizes reduced the significant pressure drop and enhanced the efficiency of particulate removal from the air (Zhang et al. 2019; Joshi et al. 2013; Garg and Bowlin 2011).

4.2.3. Polyimide/Metal-Organic-Framework ENM:

A group of researchers from Beihang University and the China University of Geosciences established a new footprint in the evolution of ENMs. They produced an ENM composed of Zeolitic Imidazolate Framework-8, which is Metal-Organic Framework (MOF). They used ZIF-8 powder dispersed in N,N-dimethylformamide (DMF) with 0.4 gm of soluble polyimide. Then the mixture was subjected to continuous stirring for homogeneity purpose with different ZIF-8 contents. For electrospinning parameters, the feed rate was taken to be 0.5 mL/h with a voltage supply of 15 kV, putting the needle 15cm away from a collector at room temperature under ~<40% humidity. As a result of this procedure, ENMs of high filtration efficiency and higher-ranking thermal stability with outstanding mechanical properties were obtained. The filtering efficiency of these ENMs was observed to be around 96.6% with thermal stability up to 300° C, which provides a nice choice of ENMs for particulate filtration even in brutal conditions (Hao et al. 2019; Gonte et al. 2013; Huang et al. 2006).

4.2.4. Polyacrylonitrile/poly (acrylic acid) ENMs:

Another significant approach for the formation of high-efficiency ENMs is by using Polyacrylonitrile and Polyacrylic Acid for making High-Efficiency Particle Air (HEPA) filter. PAA is used in this membrane to increase the tensile strength of the membrane medium (Yadav and Balasubramanian 2015). Most of the active sites of PAN/PAA are negatively charged, making it more suitable for filtration membranes to establish an interaction between PM pollutants and capturing fiber. For the formation, PAA and PAN solutions were prepared by dissolving them in N,N-dimethyl-formamide (DMF) for 24 hours in (10%wt), and PAA (8%wt) contents, respectively. Then, the two solutions are well mixed with different weight ratios to use them in electrospinning techniques. The parameters used in this process includes a high voltage supply of 15 kV with a needle-collector distance of 14cm at room temperature with a relative humidity of around 45%. The filtration efficiency observed for this ENM is 99.99% with a lower pressure drop, which shows that the produced ENM is a good choice for particular filtration (Y. Liu et al. 2015).

4.2.5. Poly (lactic-co-glycolic acid)/Poly-caprolactone ENMs:

In a recent study, Poly(lactic-co-glycolic acid) and Polycaprolactone were used to produce electrospun nanofibrous membranes with a very nice filter efficiency, especially for the particle size of diameter 2.5μm and less (~up to 0.5μm). The PLGA and PCL exhibit properties by combining small pore sizes and high specific surface area, making them suitable for electrospun membranes. In the study, seven types of PLGA/PCL

nanomembranes were prepared with different content ratios. Then, the polymer solution forwarded to the electrospinning for drawing nanofiber membranes with was controlled affecting parameters where the needle-to-collector distance was taken to be 20 cm, having a voltage supply of 25kV. The nanofiber were collected on an aluminum foil directly and directed to cool down at room temperature. On test, the membranes were found to be very efficient for particulates capturing even in Hazy-Fog conditions with a filter efficiency of 97.81% and low-pressure drop of 181 Pa (Xu et al. 2018).

4.2.6. Silk Fibroin/PVA ENMs:

Another significant research to filter $PM_{2.5}$ by using ENMs includes filtration by using Silk Fibroin, a type of protein fiber with good environmental sustainability obtained from silkworm cocoons (Gore et al. 2019; Gao et al. 2018). In this technique, the Silk Fibroin (SF) solution was prepared by boiling 0.02 mol/L aqueous Sodium Carbonate solution to remove the sericin proteins of silk fibers and then washed with deionized water to remove the residues of sericin proteins. To remove the minute residues of silk aggregates, the solution was subjected to centrifugation at a speed of 9500 RPM for 20 minutes at 4°C for three cycles. Then for the fabrication of SF/PVA solution, SF solution was added slowly into the PVA solution with the contents of 18% and then stirred for 3 hours gently. The produced solution was then filled in the electrospinning syringe to produce nanofiber membranes under the affecting parameters of applied voltage at 20 kV with a needle-collector distance of 20 cm having a flow rate of 0.2 mL/h. The filtration efficiency of the filter membrane was observed to be 98.97% after an electrospinning process of 2 hours (Bian et al. 2018; Yang et al. 2015).

4.2.7. Polytetrafluoroethylene (PTFE) ENMs:

PTFE ENMs are used for filtration techniques at high-temperature factors. PTFE is well-known for its excellent properties like thermal stability, chemical resistance, and electrical insulations; that is why the hot air filters are mostly made by using PTFE (Brown and Dattelbaum 2005). Its nanofibrous membranes are very efficient in filtering $PM_{2.5}$ from the air due to its superior solvent resistance (Takagi et al. 2011). Recent research by the Chinese scientists produced PTFE incorporated nanofiber membranes by using emulsion electrospinning in which the PTFE emulsion and BA solution was added to PVA solution to form an electrospinning solution by continuously stirring it for 10 hours at room temperature. The applied voltage to the needle tip was set to 15 kV, having a needle-collector distance of 15cm with a flow rate of 0.5 mL/h. The membranes prepared by this technique were then dried for six hours at 70°C, and when tested, the filtration efficiency was measured to 98% effectively (Xu et al. 2019).

A variety of synthetic and biopolymers is used in the electrospinning technique as a solution material for producing Electrospun Nanofibrous Membranes of the desired diameter and pore size. A series of such polymers provide uniform and beadless electrospun membranes with a required diametric size-range processed by electrospinning parameters. A list of some different polymers is shown in Table 1.

The essential central aspect of an electrospun nanofibrous membrane is its filtration efficiency when it comes to testing or observational studies. The filtering efficiency of polymeric ENMs is much better than other materials due to their exceptional porosity factors, surface areas, pressure drop counts, flexibility to build, desired

Table 1: Various Polymers used for Making ENMs with their Parameters:

Name of Polymer	Type of Polymer	Name of Solvent	Voltage (kV)	Flow Rate	Collector Distance	Diameter of ENMs	Reference
PAN	Synthetic	DMF	13-20	2	10-16	200	(Barhate et al. 2006)
Chitosan/ PEO	Bio	AA	30	4.8	10	90-130	(Chuang et al. 2014)
PLA/PHB	Bio	$CHCl_3$	17	1.8	15	500	(Nicosia et al. 2015)
PET/CD	Synthetic	TFA/DCM	15	1	10	360-790	(Kayaci and Uyar 2014)
PAN/SiO_2	Synthetic	DMF	30	1.5	15	600-700	(Wang et al. 2014b)
Keratin/PA	Bio	FA	25	0.6	10	150	(Aluigi et al. 2009)
PEO	Synthetic	IPA	20	0.36	14	200-300	(Leung et al. 2010)
PA6/PA66	Synthetic	FA	70-80	~0.5	25-40	90-180	(Heikkilä et al. 2008)
BTEAC	Bio	$CHCl_3$	20	2	10	1500	(Cho et al. 2014)
PVA	Synthetic	DMF; AA	24	0.5	16	300-390	(Matulevicius et al. 2016)

Abbreviations: **PAN**: Polyacrylonitrile; **DMF**: N,N-dimethylformamide; **AA:** Acetic Acid; **PLA:** Polylactic Acid; **PHB**:Polyhydroxybutyrate; **$CHCl_3$**: Chloroform; **SiO_2:** Silicon Dioxide; **PET:** Polyethylene Terephthalate; **CD:** Cyclodextrin; **TFA:** Trifluoroacetic Acid; **FA:** Formic Acid; **PEO:** Polyethylene Oxide; **IPA:** Isopropyl Alcohol; **PVA:** Polyvinyl Alcohol; **BTEAC:** Benzyl Triethylammonium Chloride.

Table 2: Filter Performance of Most-Usable Polymeric ENMs

Name of Polymer	Fiber Diameter (μm)	PM Size (μm)	Filtration Efficiency (%)	Pressure Drop (Pa)	Quality Factor (Pa^{-})	Reference
PSU/TiO_2	1.59 to 0.76	0.3 to 0.5	99.99	45.3	0.07 to 0.1	(Wan et al. 2014)
PVC/PU	0.96	0.3 to 0.5	99.5	144	0.036	(Wang et al. 2013)
$PAN/SiO-_2$	0.6 to 0.7	0.3 to 0.5	99.98	117	0.02 to 0.14	(Wang et al. 2014b)
PAN/PU-FPU	0.17	0.3 to 0.5	99.98	120	0.07	(Wang et al. 2014a)
PAN	0.2	<0.1	96.12	133	0.024	(C. Liu et al. 2015)

solution viscosity, and conductivity. Filter performance of the five most available electrospun nanofibrous membranes with their calculated parameters for different values are shown in Table 2.

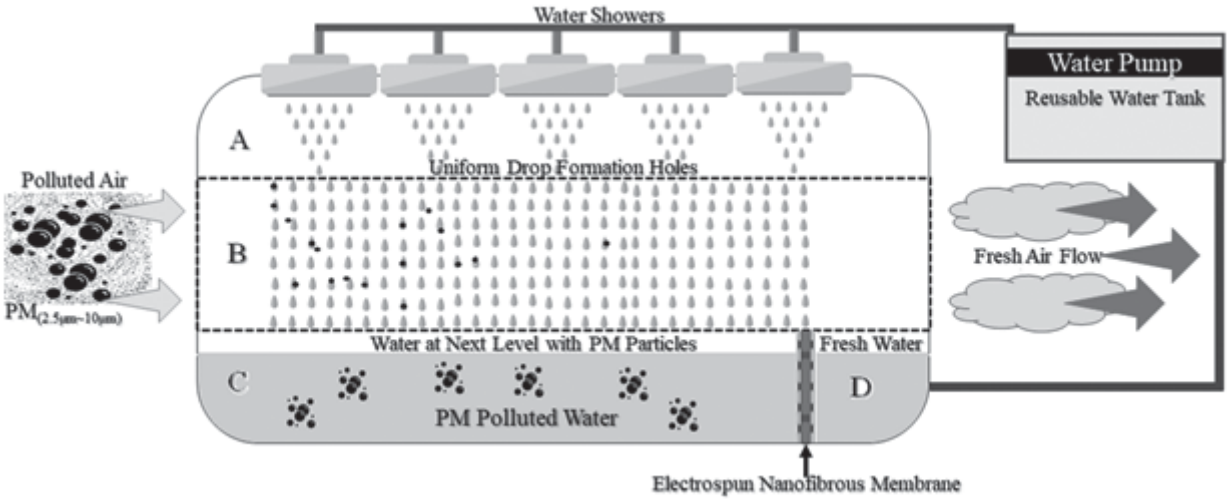
5. Future Scope of ENMs in Particulate Filtration

Nanoengineering is the leading interdisciplinary branch of research that covers almost all the fields of science and technology. ENM is also a product of nanotechnology innovations and came into an interest in the late 1980s by the increased studies of electrospinning (Barhoum et al. 2018; Roco 2003). Nanofibers exhibit extraordinary and novel physical, biological, and chemical properties due to their high specific surface area, tunable pore factors, and super mechanical properties.

An Example for Future Scope: In the context of Air Filtration, a recent study in China by a team of scientists showed the washout effects of rain on environmental particulates in which a scientific fact is associated with Particulate Matter that it can be captured within the water droplets of rain (Guo et al. 2016). Naturally, when rain occurs, the raindrops trap these PM particles and move them to the ground level where they get absorbed by the soil, but there is also a risk of polluting ground level water by this process. As an extension to this fact, ENMs can be very promising here for the sake of their properties. An efficient ENM device can be used here to capture environmental PM. A systematic representation of the device is shown in Figure 7.

In section A of Figure 7, water showers are fitted on the top of the structure from where water drops can flow continuously. When the polluted air would enter the device, the PM particles get trapped inside the water droplets distributed uniformly by a membrane placed over the section B structure for efficient capture. Then, the particles

Figure 7: A Schematic Diagram of Idea-Based PM Filter for Future Applications



of the particulate are moved to section C, where a continuous flow of water is present towards the Electrospun Nanofibrous Membranes placed in between the flow channel. At the ENM, the PM particles will get absorbed by the membrane, and the water will become fresh to use again in the showers with the help of a storage pump tank, and this cycle repeats. This innovation can change the future of ENMs in the field of filtration as both Water and Air can be filtered using this technique.

Currently, ENMs are at an early stage of evolution; hence, many aspects of it need to be studied further. The ENMs show the potential to be used as a substitute for glass-based air filters. ENMs can also be induced to purify air along with the filtration as various biopolymers like Chitosan and Keratin can capture microorganisms and VOCs. Thus, incorporating these polymers with electrospinning can have positive aspects of Filtration-Purification ENMs in the future with better filtration efficiency. There is a need to rectify nanoscale selectivity and mechanical weakness of ENMs to move it towards the commercialization and its production on a large industrial scale. The ENMs can also have a significant role in producing PM Filter face masks by incorporating nanofibrous membranes in face masks with activated materials to capture PM and other harmful pollutants on a single substrate.

6. Conclusion

Technological enhancements in the field of Electrospun Nanofibrous Membranes can be the medium for advanced filtration of Air and Water for the coming generation. This review was intended to study the Particulate Matter deeply, its concentration, effects on humans, and remediation by using different types of polymeric ENMs with a significant filter efficiency, including the formation of $PM_{2.5}$ by vehicular combustion which is the main pollution problem for today's world. The review also comprises the production of various ENMs by modifying the affecting parameters of electrospinning for efficient capture of $PM_{2.5}$ with a unique idea of a futuristic development of ENM device with their capture mechanisms. The capabilities of ENMs can be used in securing a pollution-free environment for all the environs of the ecological system. The final target of all the technological advancements

related to ENMs is to move this technology from drawbacks to success, ideas to researches and laboratories to industries that would lead to commercialization for a clean, safe, and risk-free environment.

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Biomimetic Bone Grafts for Bone Tissue Engineering: Concept to Design

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Abstract

Bone is a complex dynamic connective tissue with significant remodelling potential. Even though the regeneration capacity of bone declines with age in the later adult phase, its inherent self-healing capacity is well appreciated and presents valuable opportunities for better regenerative approaches. However, when the defect dimension arising due to trauma/degenerative diseases exceeds critical size; systemic augmentation cannot be anticipated and therapeutic strategies are inevitable to invoke new bone formation/regeneration primarily by modulating the microcellular environment and elicit active host tissue-graft interactions. The unique structure of bone accounts for its specialized properties and functions; simultaneously presenting challenges while designing ideal synthetic bone-graft with appreciable osseointegration/osseinduction. This scenario leads to prevailing need for novel approaches to meet the colossal demand for successful bone-grafts. Designing clinically successful bone-grafts with active host-bone-graft interaction is both exciting and challenging task. This review presents an understanding of the requirement, design considerations to be followed and various advanced approaches towards the development of biomimetic bone grafts for bone tissue engineering applications.

***Keywords**: Biomaterials, Biomimetics, Biomineralization, Bone Graft, Osseointegration, Tissue Engineering Scaffolds.*

The human skeleton not only provides shape and physical support to our body but also protects the vital organs. Together with the muscular system, bones enable us to move. The high strength and elasticity of the skeleton is attributed to 'Bone' the organic-inorganic hybrid connective tissue with a highly mineralized extracellular matrix and intrinsic regenerative potential (Paul Ducheyne et al. 2015). The organic component of bone mainly consists of type 1 collagen (95%) and minor amount of proteoglycans, non-collagenous proteins like osteocalcin, osteopontin, osteonectin, and bone sialoprotein (Paul Ducheyne et al. 2015) while the inorganic part is calcium phosphate in the stable form of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] (Joon Park and R. S. Lakes 2007). The remarkable strength complemented by the light-weight of bone originates from its unique intriguing geometry. Based on its structure, bone tissue is classified into two major types: cortical (compact) and cancellous (spongy). The dense and tough arrangement of collagen fibrils in the cortical bone accounts for its superior mechanical characteristics to withstand high loads, enable protection and facilitate movements of human body. It is noteworthy to mention that bone also function as a calcium repository (Buddy D. Ratner et al. 2012). The cancellous bone is a spongy inner layer, also known as trabecular bone which is a loosely organized porous matrix that furnish metabolic functions of bone (Buddy D. Ratner et al. 2012 and Mc. Connel D et al. 1971).

The concept of bone tissue engineering has been steeply growing upwards ever since it has been first proposed in 1987 (Huawei Qu et al. 2019). Bone tissue engineering has become a clinically significant topic of research because of the increasing demand of the problems associated with orthopaedic traumatology and degenerative diseases including osteomyelitis and bone cancer (Rozalia Dimitriou et al. 2011). Bone is a dynamic remodelling tissue in which the regeneration is achieved by the synchronised activities of bone cells (Rozalia Dimitriou et al. 2011). When a bone defect is occurred due to trauma, injury or any other orthopaedic malfunctions, bone itself augment the defect; but when the defect dimension exceeds the critical size, self-healing capacity cannot be anticipated and such kind of injuries present a huge demand for bone-grafting materials. Clinically significant bone grafting materials are auto graft, allograft and synthetic grafts. The autogenously bone graft is still considered as the gold standard because the origin is patients' own body, which when implanted certainly leads to osseointegration at a faster rate without any immunological response (Elena Garcia-Gareta et al. 2015). Never-theless, harvesting of autologous tissue presents severe discomfort to the patients together with the need for another surgical procedure and induces donor-site morbidity. These are the major challenges which diminishes the escalating demand of auto-grafts in the clinical level (Elena Garcia-Gareta et al. 2015). Even though clinical acceptance is high, allograft has obstacles due to poor donor availability, tissue rejection, infection and cost which make them unacceptable bone-grafts for the orthopaedic damages. Hence the present research is focused on synthetic bone grafts with osteoconducting/ osteoinducting characteristics with combinatorial approaches intended for improved clinical performance (Elena Garcia-Gareta et al. 2015).

2 Biomaterials for Bone grafting

According to the American National Institute of Health, Biomaterial is "any substance or combination of substances, other than drugs,

synthetic or natural in origin, which can be used for any period of time, which augments or replaces partially or totally any tissue, organ or function of the body, in order to maintain or improve the quality of life of the individual"(Clinical Applications of Biomaterials 1982). Biomaterial based orthopaedic treatments are growing at a faster rate. An ideal biomaterial intended for bone grafting should be bioactive and osteoinductive in nature with a controlled biodegradation. In addition, it should also offer ossintegration to induce ectopic bone formation without causing any adverse reaction to the host tissue (Huawei Qu et al. 2019). The performance of a biomaterial after implantation is normally validated by the ability of the material to support cellular infiltration with minimum inflammation and immune response to the host tissue (S.K. Nandi et al 2010).

The bioinert materials such as metals, bio ceramics (Alumina and Zirconia) and biocompatible polymers are generally considered as the first generation biomaterials (Chengyun Ning et al. 2015 and T. Kurien et al. 2013). Whereas the bioactive materials such as bioactive glass, glass–ceramics, calcium phosphates and natural polymers are considered as the second generation bio-materials (T. Kurien et al. 2013). These bioactive materials interact with the biological environment and enhance cell- material interaction, and thereby invoke cell proliferation, differentiation and gradually undergo degradation when new tissue regenerates and heal (T. Kurien et al. 2013). The bioactivity of these biomaterials can be increased either by surface coating or by chemical modifications to improve cell-material interactions. The concept of bioactive and biodegradable materials is the basic characteristic of third generation biomaterials. These biomaterials can effectively act as a temporary favourable environment to induce cellular proliferation and thereby activate the regeneration of bone tissue (Joon Park and R.S. Lakes 2007 and Amogh Tathe et al. 2010).

2.1 Biocompatible metallic Bone grafts

Biocompatible metals based on stainless steel 316 L, Co based alloys and titanium based alloys, Ti-6Al-4V, are used as implanting materials in orthopaedic and dental surgery for the replacement of damaged bone or to assist in bone healing process (S. Weiner and H.D. Wagner 1998). Metals are suitable for load bearing applications because of their high mechanical strength, biocompatibility, high corrosion resistance and exceptional durability. However their relatively high stiffness and modulus mismatch with host bone lead to poor bonding with host tissue eliminating the possibility of osseointegration rather cause chronic inflammatory response if the toxic ions are released after corrosion or isolate them from host tissue by the formation of a fibrous tissue wall. The lack of biodegradability and bio-inert nature further makes metals irrelevant to be used for soft tissue engineering (J.R. Lieberman et al. 2007 and Wolfgang Schilickewei and Carsten Schilickewei 2007).

2.2 Bioceramic Bone grafts

Bioceramics are the class of biomaterials which impart new insights in the field of efficacious bone tissue engineering. Bioceramics are highly crystalline materials synthesized from non-metallic mineral salts and processed at relatively high temperature by a technique known as 'sintering' which offer them very high mechanical properties. Plenty of methods are available to fabricate porous bioceramic network structure to mimic bone tissue and serve as a platform for cellular invasion by providing appropriate growth

factors and osteoproginetor cells. These osteoproginetor cells further differentiate into osteoblast cells (Michael R. Whitehouse and Ashley W. Blom 2009 and S. Weiner and H.D.Wagner 1998). The most widely used bioceramic based bone grafts are β-tricalcium phosphate (β-TCP), hydroxyapatite etc., (Fabrizio Matassi et al. 2011). These materials are highly biocompatible and osteoconductive in nature. The mechanical and biological properties of bioceramic implants depend upon the micro-structure and eventually the manufacturing process. Even though these bioceramics possesses high compressive strength with favourable clinical functionalities, their inherent brittle nature diminishes their use for large size orthopaedic damages (Petra Chocholata et al. 2019). In this context, synthetic as well as natural polymers become promising candidates for bone-grafting due to their excellent biocompatibility, biodegradability, feasibility to surface modification, easy processability and ease of availability.

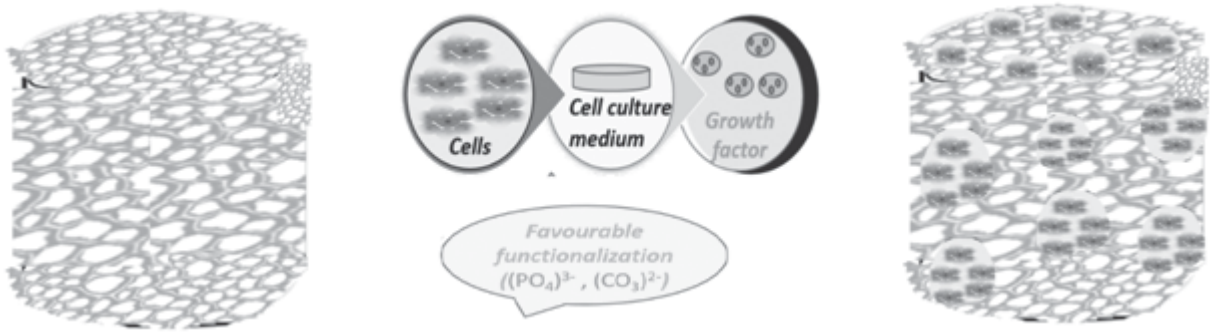
2.3 Bioactive Polymeric Bone grafts

Bioactive polymeric graft materials are another class of materials which play a vital role in the field of bone tissue engineering. Poly Lactic acid (PLA) based bone screws and Poly Ether Ether Ketone (PEEK) based bone substitutes are promising candidates for bone tissue engineering due to their high strength, modulus and biocomptibilty (Toktam Ghassemi et al. 2018). Synthetic biodegradable polymers such as polyanhydrides, polyglycolide, polycaprolactones, polyphosphazenes etc., have also been widely used as platforms for tissue engineering. The mechanical properties, degradation behaviour, porosity, hydrophobicity/hydrophilicity etc can be customized according to the intended application. Nevertheless these polymers lack osteogenic, osteoconductive or osteoinductive properties (Toktam Ghassemi et al. 2018). A wide variety of polymeric materials and inorganic materials are available but only very few polymeric bio-materials are explored today because they fail to address critical issues such as mis-match of compressive strength for load-bearing bone grafts (Toktam Ghassemi et al. 2018 and Ahmad Oryan et al. 2014).

2.4 Bioactive Polymeric scaffolds as Bone grafts

Scaffolds are the materials which provide basic structural support to the tissue and serves as a template for preferred cellular interactions. (Ahmad Oryan et al. 2014). The natural extracellular matrix (ECM) should be mimicked to fabricate the tissue engineering scaffolds so that the material itself invoke early mineralization and enhances the osteogenic differentiation at a faster rate (Ahmad Oryan et al. 2014). The rational strategy of the development of an ideal tissue engineering scaffold, basically depends upon the interconnected pores of the material to allow cellular attachment, differentiation and proliferation. Physicochemical characteristics and controlled degradation kinetics of the material allow the scaffold as a promising tool employed for bone regeneration pathway. Mechanical properties should resemble to that of bone repair site. However the higher porosity and pore size affects the strength of the scaffold (Ahmad Oryan et al. 2014 and C.M. Murphy et al. 2013). Therefore proper choice and optimization of scaffold properties are essential to act as a successful graft. The controlled degradation profile of the scaffold generate structural integrity and eventually break down as the newly formed tissue takes part in load bearing process and the degradation by-products should be non-cytotoxic and non-inflammatory (Jiang S.P. Nukavarapu et al. 2010).

Figure 1: Schematic illustration of design of a typical polymeric scaffold with enhanced bone tissue regeneration



In addition, the scaffolds should be highly bioactive and osteoconductive in nature so that proper interactions occur with the surrounding tissue and enhances the regeneration process of damaged bones. One of the biggest challenges in scaffold designing is the fabrication of scaffolds with appropriate mechanical and physical properties suitable for bone tissue regeneration (Jiang S.P. Nukavarapu et al. 2010). Natural as well as synthetic polymers have been widely used for the fabrication of scaffolds. The key factors that determine the functionality of a material to be used as a scaffold are molecular weight, solubility, hydrophobicity/hydrophilicity, erosion rate and mechanical properties (N.G Johnathan et al. 2017). In parallel, they should also provide versatile characteristic properties such as sufficient porosity, high surface to volume ratio and good biodegradation profile. The natural polymers which are used for the fabrication of scaffolds are chitosan, collagen, silk, fibrinogen, actin, myocin, gelatin, dextran, cellulose etc (N.G Johnathan et al. 2017).

2.5 Biomimetic Scaffolds for Bone Tissue Regeneration

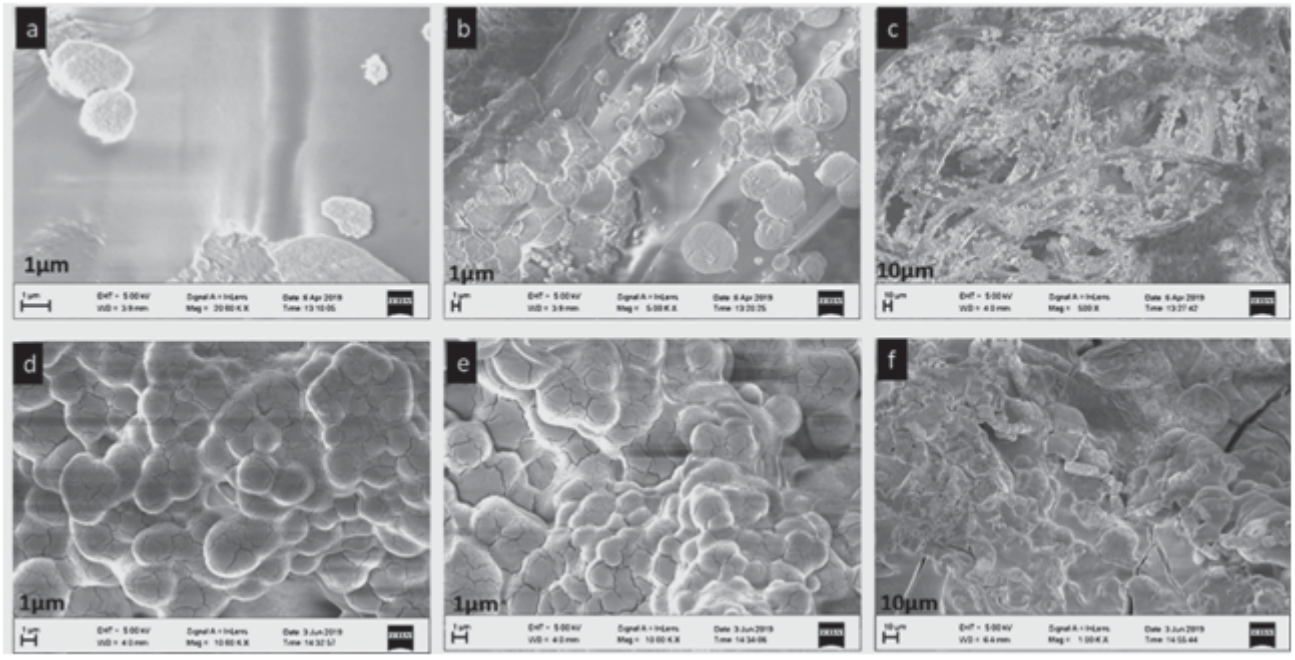
Biomimetics, presents exciting innovative platform for bone tissue regeneration as researchers present inspired ways that invokes bone tissue regeneration and has been adopted as a contemporary sight for mending new bone formation utilizing both natural and synthetic resources as scaffolds (H.D. Kim et al. 2017). The biomimetic scaffolds provide a suitable atmosphere for bone cells to adhere, proliferate and thereby offer an osteofriendly environment to generate the extracellular matrix conditions leading to osseointegration (A.H. Barber et al. 2015). Pre-requisites for a biomimetic scaffold essentially entails hierarchical porous structure resembling the native tissue to provide adequate mechanical strength, higher rate of biocompatibility, biodegradability and bio-mineralization potential (A.H. Barber et al. 2015).

Limpet teeth, calcified corals, magnetic bacteria, coccolith, trumpet spines and cocosphere are typical examples of naturally biomineralized structures (Yuanyuan Chen et al. 2019). Like biomineralized structures, the biomimetically mineralized scaffolds facilitate the cellular interactions in the molecular level and also trigger the organic matrix to perform its functionality in a better way. Significant quantum of research is still continuing in this field to accomplish an ideal choice with a superior regeneration index.

2.6 Biomineralized Scaffolds for Bone Tissue Regeneration

Biomimetic mineralization is a biologically induced natural process which utilizes natural resources/mimicking from nature to achieve the mineralization under laboratory conditions (G.S. Sailaja et al. 2016). Biominerals such as calcium phosphate, calcium carbonate, hydroxyapatite loaded biomimimetic scaffolds are widely investigated in biomedical field especially as bone tissue engineering scaffolds (A. H. Barber et al. 2015). The hydroxyapatite coated and β-TCP porous materials acquired considerable attention towards tissue engineering scaffolds because of the material specificity to invoke ostoconductivity/ osteoinductivity, and the ability to promote positive influence on the cell-matrix interaction (Yuanyuan Chen et al. 2019). This concept of bio-inspired approach utilizes the early mineralization potential of the material to increase the growth of

Figure 2: SEM images of biomineralized scaffolds. (a-c) represent in vitro mineralization on surface functionalized Poly ethylene terephthalate (PET) at day 14 and (d-f) represent SEM micrograph of biomineralized surface functionalized Poly (2-hydroxy ethyl methacrylate - co - methyl methacrylate) at day 14.



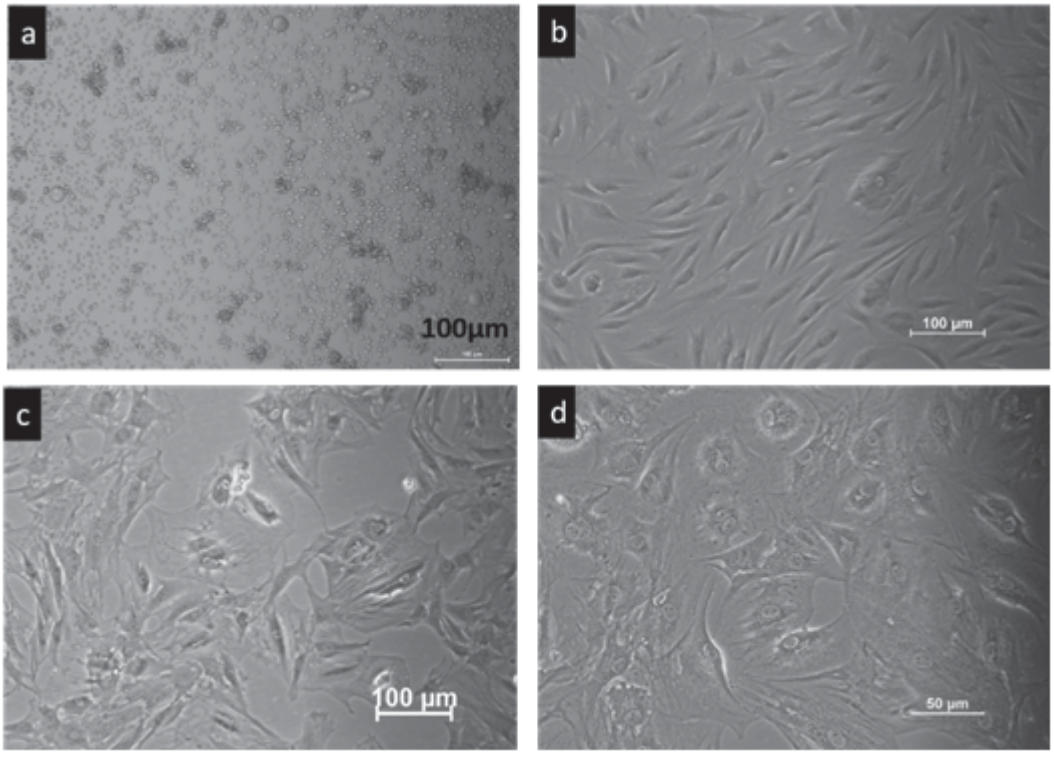
new bone at a faster rate with gradual degradation kinetics. Modification with surface functional groups such as –COOH, -PO_4, -NH_2, -OH are capable of activating the nucleation level of hydroxyapatite (G.S. Sailaja et al. 2016). In addition, the surface functionalization also impart early osteogenic responses, cellular invasion, and systemic bone regeneration pathways.

Varma et al. reported that the direct phosphorylation of chitosan and surface functionalization of Poly (methyl methacrylate) (PMMA) with

coupling of adenosine triphosphate (ATP) molecules elicit early mineralization of hydroxyapatite coating (G.S. Sailaja et al. 2016, H. K. Varma et al. 1999, and H. K. Varma et al. 2003). Sailaja et al. developed a biomineralized surface from phosphorylated Poly (vinyl alcohol) (PVA) and it has been found to be effective in the nucleation of hydroxyapatite within 10 days (G.S. Sailaja et al. 2016 and 2009). The material also promoted better cell adhesion when seeded with human osteosarcoma cells. In another study, Sailaja et al. investigated the nucleation effect of calcium phosphate on phosphorylated poly (2-hydroxy ethyl methacrylate-co-methyl methacrylate) up on immersing in simulated body fluid (SBF) and found that the material could induce hydroxyapapite formation and offer better cell attachment and proliferation in presence of human osteosarcoma cells (G.S. Sailaja et al. 2016 and 2006).

Figure *3:* Microscopic images of the BMCs isolated from the femur bone of an eight week old male *Sprague dawley* rat.(a) and (b) represent images of isolated and adhered BMCs respectively whereas (c) and (d) represents images of BMCs at eighth day of passage at different magnification

*All animal care has been taken in accordance with the Institutional Ethical Committee (363/GO/Re/S/01/CPCSEA, 28/12/2017/10) and CPCSEA guidelines.



2.7 Bone Morphogenic Proteins

Bone morphogenic proteins (BMPs) are a group of TGF–family which has been considered as the most effective osteoinductive molecule to induce bone formation via endochondral ossification (Elena Garcia-Gareta et al. 2015). There are 30

different BMPs recognised with promising efficacy of bone formation capability whilst BMP-2 and BMP-7 have obtained clinical licence (Elena Garcia-Gareta et al. 2015 and Food and Drug Administration). A wealth of research are ongoing to analyse the combinatorial approach of BMPs loaded biomaterial scaffolds. Stenfelt et al. investigated efficacy of chemically cross-linked hyaluronan hydrogel loaded with hydroxyapatite and BMP-2. After five week of implantation an ectopic cancellous bone formation was observed (S. Stenfelt et al. 2014). This result predicts efficacy of BMP loaded scaffold as a promising material for bone tissue engineering (S. Stenfelt et al. 2014).

2.8 Stem Cell based approaches

The most promising option among the ongoing approaches of bone tissue engineering is stem cell based therapeutic strategies. The self-renewing ability and the differentiation capacity of mesenchymal stem cells trigger faster new bone formation. The combinatorial approach of stem cells embedded biodegradable scaffold serves as an effective tissue engineering construct. Jozafina et al. studied the expansibility of mesenchymal stemcells - by embedding in polycaprolactone-hydroxyapatite hybrid scaffold in bone regeneration. The result has demonstrated the potential applicability of this hybrid scaffold towards osteogenic differentiation and boosts the rapid growth of bone formation (Jozafina Haj et al. 2017).

3. Conclusion

Contemporary investigations present several highly favourable performances for diverse bone-graft materials in the *in vitro* and *in vivo* level. Unfortunately, many of the aforementioned strategies could not transform to a complete clinically successful bone graft with desired level of bone tissue regeneration, mechanical property matching and a predictable pathway of self-degradation, which is the ideal scenario. Continuous efforts are actively ongoing to fabricate bone graft materials which support to achieve proper vascularization, host-tissue integration, suitable mechanical properties, porosity, biodegradability, biocompatibility, regenerated bone quality and functionality. It is anticipated that these strenuous efforts will be successful in the near future to address the pivotal need of an ideal bone-graft.

Acknowledgements

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In Situ Precipitation and Characterization of Nano Zinc Oxide: Different Polymeric Media

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Abstract

In the present study, Zinc oxide (ZnO) nanoparticles were prepared using Zinc chloride and Ammonium hydroxide with proper concentration in different polymeric media by in-situ precipitation method. Here, we have tried three different polymeric mediums, like chitosan, starch and polyvinyl alcohol (PVA). The structural properties of the synthesized ZnO nanoparticles have been confirmed using the Scanning Electron Micrographs. The crystallinity and particle size of the nano particles were also determined. From the surface morphology, it is clear that the prepared ZnO is nano in nature and the shape of ZnO changes with respect to the medium of precipitation. The ZnO particles obtained from chitosan medium exhibit cuboidal shape, while those obtained from starch have cylindrical shape and coral shape from PVA medium.

***Keywords**: Nano ZnO, Chitosan, Starch, PVA.*

Nanoparticles of metal oxides have attracted increasing technological and industrial interest because of interesting changes in their optical, magnetic, electrical and catalytic properties accompanied with improved physical properties like mechanical hardness, thermal stability or chemical passivity (Look D.C. et al. 1998 and 1999 and Reynolds D.C. et al. 1996). Many physical properties of nanoparticles often differ drastically from those of single crystals with the same chemical composition. At nanometer size, crystallites are influenced by the presence of significant number of surface atoms and by the quantum confinement effect of the electronics states and this influences the property of nano materials as compared to their bulk phases.

Nano crystalline oxide particles have technological applications; they are used as catalysts (Zou C.W et al. 2009, Han J. et al. 2009, and Han J. and W. Gao 2009) passive electronic components and high performance ceramics. The potential applications of nano structured materials include paint pigments, cosmetics, pharmaceuticals, medical diagnostics, catalysts and supports, membranes and filters, batteries and fuel cells, electronics, magnetic and optical devices, flat panel displays, biomaterials, structured materials, and protective coatings (Y. Sasaki et al. 2005, M. Azharuddin et al. 2008, Surabhi Sivakumar et al. 2013, and N. H. Nickel and E. Terukov 2005).

Zinc oxide is a material, which combines semiconductivity, piezoelectric and electromechanical properties. It is an important functional oxide, exhibiting near fluorescent emission. Because of its nano-central symmetry, ZnO is piezoelectric, which is the key factor in building sensors and transducers. ZnO nano materials are promising candidates for nanoelectronics and photonics. A great variety of nano structures like nano belts, nano rods, nano rings etc. can be made of ZnO. Due to these factors it was cited as the material of the 21st century in Materials Today (Zhong Lin Wang 2004). Semi-conductor zinc oxide (ZnO) nanoparticles have attracted much attention because of their interest in fundamental study and also their applied aspects such as in solar energy conversion, varistors, luminescence, photocatalysis, electro-static dissipative coating, transparent UV protection films, and chemical sensors (J. W. Park et al. 2006).

Different techniques for preparing ZnO nanoparticles have been reported such as, sol– gel technique, (Mondelers D. et al. 2002) microemulsion synthesis (Singhal M. et al. 1997) mechano-chemical processing (Zhong Lin Wang 2004) spray pyrolysis, thermal decomposition of organic precursor, RF plasma synthesis, supercritical-water processing, (Viswanathan R. et al. 2003) self-assembling, vapour transport process, sonochemical or microwave-assisted synthesis, direct precipitation,(Wang J.M. and Gao L. 2003) homogeneous precipitation, (Kim J.H. et al. 2005) chemical co-precipitation, (Wang L.N. and Muhammed M. 1999) chemical vapour deposition, thermal decomposition, (Audebrand N. et al. 1998) hydro-thermal synthesis, Liu B. and Zeng H.C. 2003) solid-state reaction, spray pyrolysis, (Tani T. et al. 2002) and microemulsion precipitation. Among these synthetic routes, precipitation approach compared with other traditional methods provides a facile way for low cost and large-scale production, which does not need expensive raw materials and complicated equipments.

With the unique characteristics, zinc oxide is one of the most important nano materials in future research and applications. The diversity of nano structures of ZnO will open up many new fields

of research in nanotechnology as the properties strongly depend on the dimensions and morphologies (Heo Y.W. et al. 2004 and Wang X et al. 2007). In our present investigation, an in situ preparation of nano ZnO was carried out in different polymeric media like Chitosan, Starch and Polyvinylalcohol (PVA). A comparitive study of ZnO obtained from various media were done by scanning electron microscopy (SEM), X-ray diffraction studies (XRD) and particle size analysis.

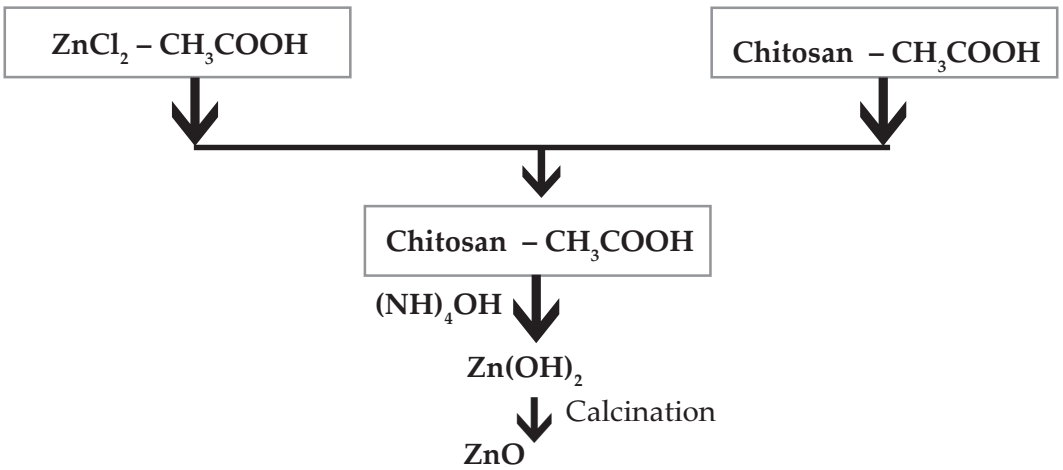
2. Materials and Methods

Analytical grade solvents and chemicals were used throughout. $ZnCl_2$, commercial nano zinc oxide, NH_4OH, starch and polyvinyl alcohol were all products of Merck. Chitosan was obtained from India Sea Foods. Kannammali, Kochi. The XRD data were recorded on Xpert PRO MPD. The Scanning electron microscope studies were performed on equipment with model number JSM-7600 F. Analysis of particle size was performed on a Microtrac.

2.1 Preparation of ZnO

Zinc Oxide was prepared using in-situ precipitation method. The medium for precipitation was prepared using 2% polymer solution. The schematic overview of the preparation of zinc oxide is shown in a flow chart. 2gm chitosan is dissolved in 100 ml of 2% acetic acid and stirred for 1-2 hr. 5gm of $ZnCl_2$ is added slowly by stirring

Figure 1: Schematic representation of in situ preparation of ZnO in chitosan medium



and stirring is continued for 1 hr. It is followed by the addition of 12 ml of NH_4OH dropwise with stirring. After half an hour stirring, the solution is kept undisturbed for 12 hrs. The precipitate obtained was filtered, washed several times with distilled water and the precipitated $Zn(OH)_2$ was dried and calcined at 400°C.

The same procedure is followed in the preparation of ZnO by using Starch and Polyvinyl alcohol medium.

3. Results and Discussion

Nano-sized metal oxide with uniform shape and narrow size distribution are shown to possess

many interesting properties not shown by their bulk counterparts. They have larger surface area and wider band gap between valence and conduction bands. Nano ZnO exhibit excellent physical and chemical properties. In the present work, we have prepared nano ZnO using different polymeric media like chitosan, starch and poly vinyl alcohol.

Zinc Oxide has been prepared using insitu precipitation method. Different polymeric media like chitosan, starch and PVA were used for precipitation. The precipitated $Zn(OH)_2$ was dried and calcined at 400°C. Prepared samples were characterized using XRD, SEM and particle size analyzer.

Figure 2: XRD pattern of ZnO in chitosan medium

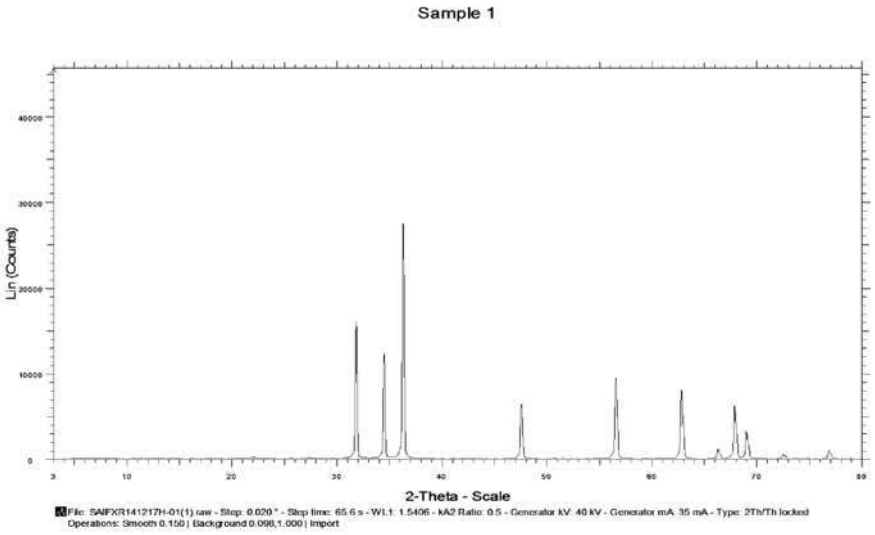
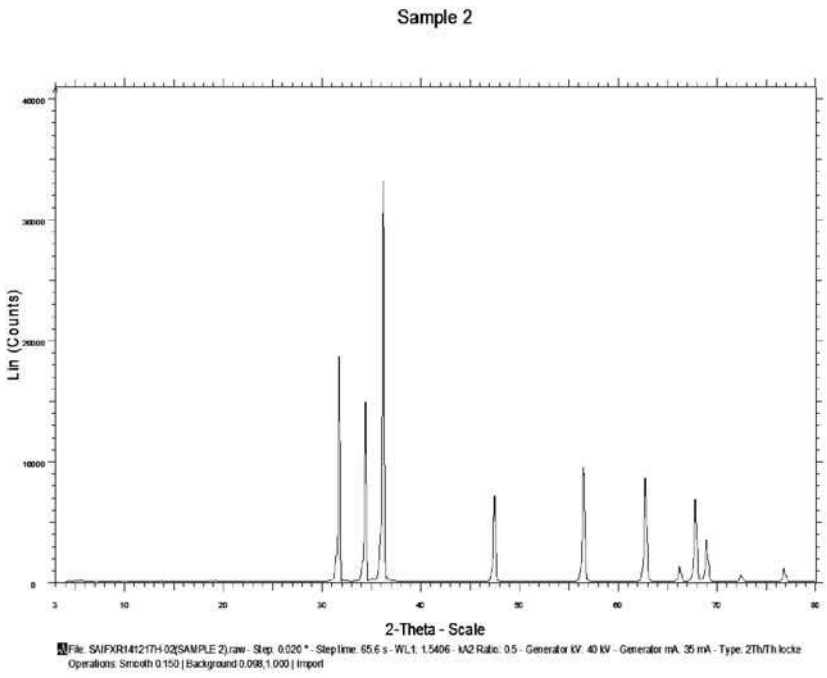


Figure 3: The XRD pattern of ZnO in starch medium



3.1 X-Ray Diffraction Studies (XRD)

The zinc oxide prepared from chitosan medium shows that the highest peak is observed at 36.278° with full width half maximum (FWHM) value as ".202." Figure 2 shows the XRD pattern of ZnO in chitosan medium.

Figure 3 shows the XRD pattern of ZnO prepared using starch medium. The XRD pattern of zinc oxide in starch shows a similar pattern as that of zinc oxide in chitosan. Chitosan and starch are natural biopolymers and they will give XRD patterns similar to that of metal oxides. The highest peak is observed at 36.186° and with FWHM value as ".203." There is a difference between the metal oxides prepared from these two polymeric media.

Figure 4: The XRD pattern of ZnO in PVA

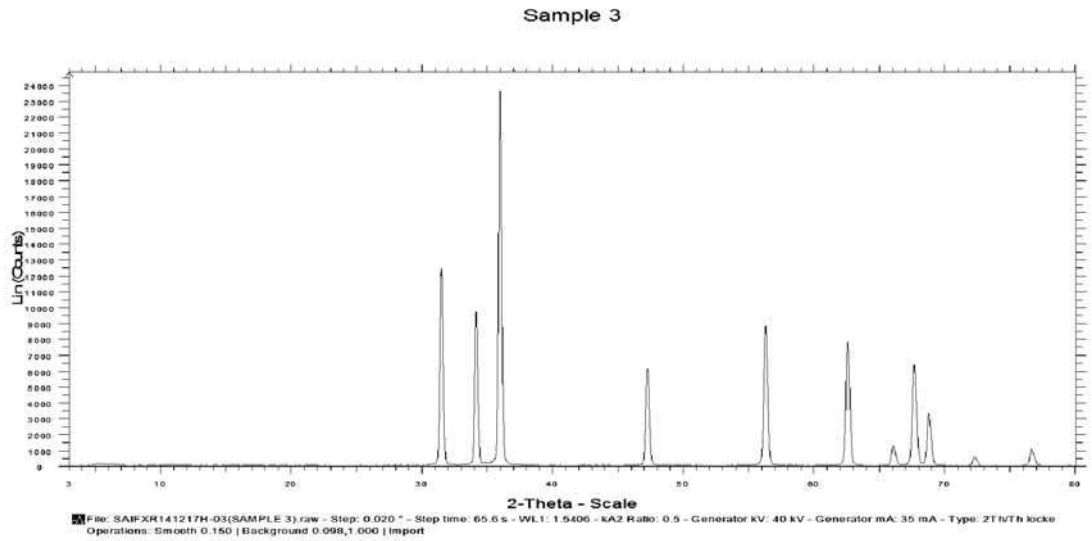
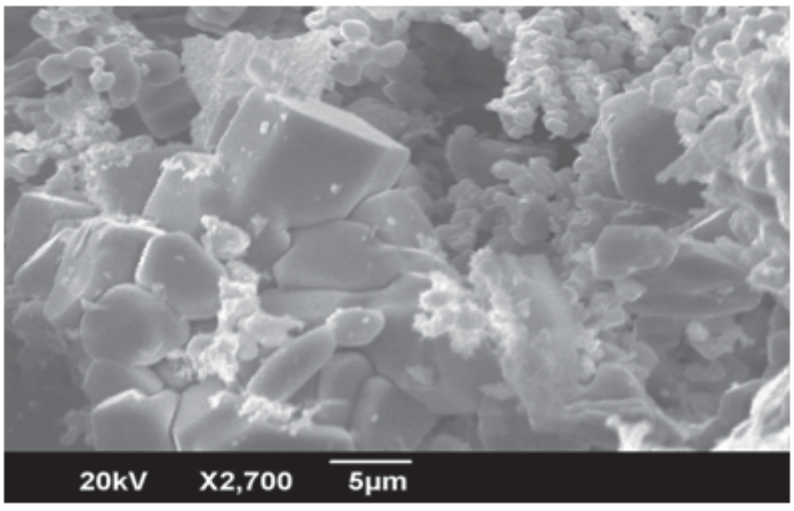
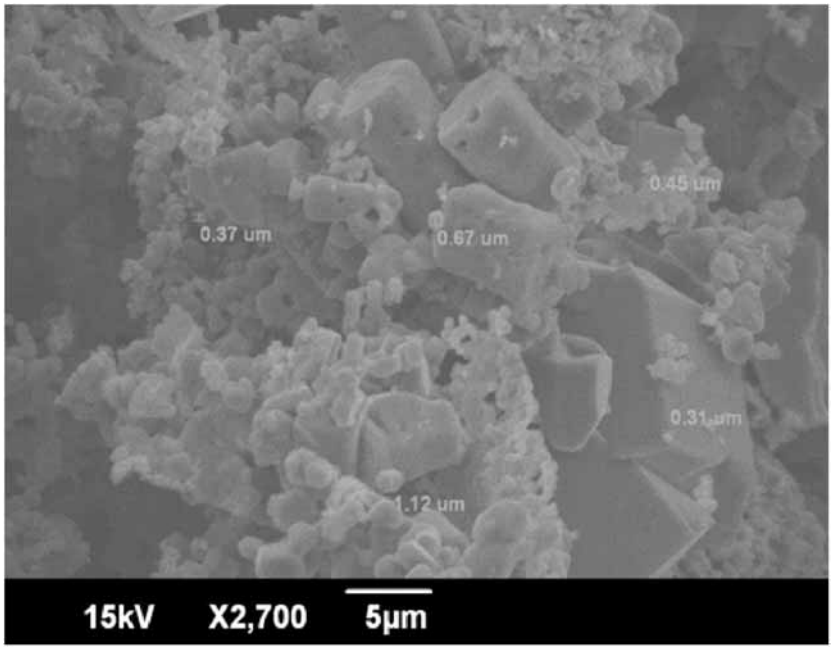


Figure 5: SEM Micrograph of nano ZnO in Chitosan



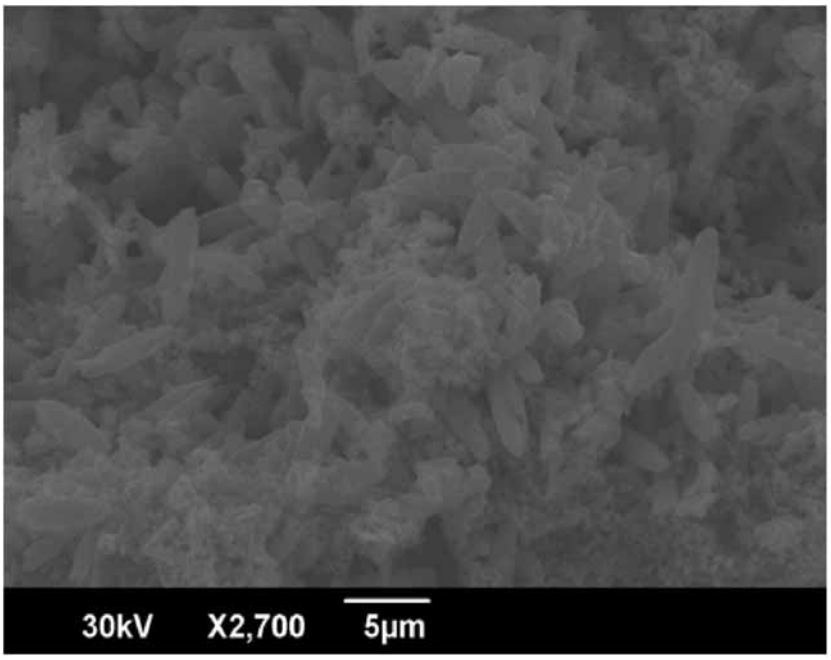
ZnO is also prepared by using synthetic polymer PVA. Figure 4 shows the XRD pattern of ZnO precipitated in PVA. The XRD pattern of ZnO in PVA shows maximum peak at 35.939° and the

Figure 6: SEM Micrograph of nano ZnO in Starch



FWHM value as ".260." The full width half maximum value of ZnO from this medium is slightly greater than that of ZnO obtained from other two media.

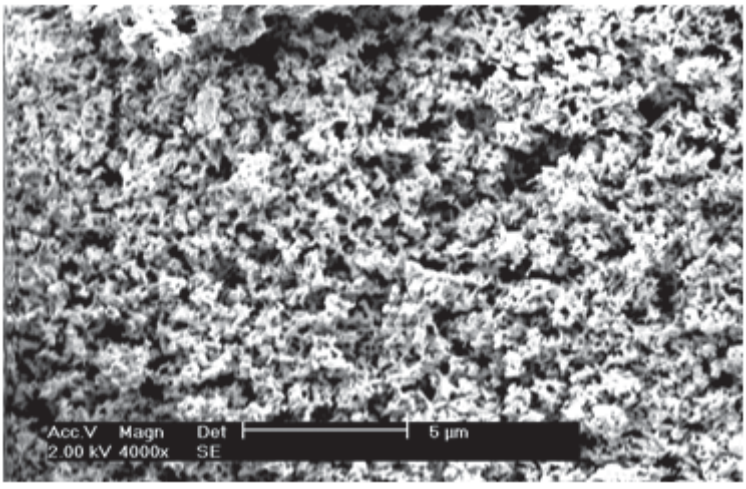
Figure 7: SEM Micrograph of nano ZnO in PVA



3.2 Scanning Electron Microscope (SEM) Studies

Surface morphology of the prepared ZnO was characterized using SEM. The scanning electron micrographs of ZnO prepared in chitosan medium (Figure 5) shows that the particles have a cylindrical cuboidal structure, and with non uniform crystallites.

Figure 8: SEM Photograph of amorphous commercial zinc oxide



The scanning electron micrographs of ZnO prepared from starch medium is shown below (Figure 6). It is clear from the figure that zinc oxide formed is crystalline and its structure is cylindrical in nature.

The scanning electron micrographs of ZnO prepared from PVA is shown below (Figure 7). It is clear from the figure that zinc oxide formed has a coral shape and the crystals formed shows uniformity.

For comparative study we have also taken the SEM photograph of commercial nano ZnO (Figure 8). It was observed that commercial nano ZnO shows a honey comb structure. Thus it is clear that there is variation in shape as well as size with respect to the medium of preparation. The difference in shape of crystals may be due to the difference in the formation of metal-polymer complex. The structure of the

Table 1: Comparison of Particle size

ZnO SAMPLE	FWHM VALUE	CRYSTALLITE SIZE (nm)
ZnO/CHITOSAN	0.202	5.7724
ZnO/STARCH	0.203	5.7372
ZnO/PVA	0.260	4.4654

complex change with polymer medium and that results in the difference in morphology of ZnO crystals.

3.3 Particle Size Analysis

Comparison of Particle Size

The grain size of zinc oxide prepared from Zinc chloride in different media like chitosan, starch, PVA were determined and compared (Table 1). The full width at half maximum of an hkl peak at theta value and crystal size of all the zinc oxide samples shows that zinc oxide prepared from PVA has smaller crystal size compared to the zinc oxide prepared from other media. It is also observed that the zinc oxide prepared from chitosan shows the high particle size but lower FWHM value.

Natural polymer media like chitosan and starch gave almost same crystallite shape and size. But low molecular weight PVA gave smaller particle size and coral shape. All these depend on the structure of metal-polymer complex. Compared to Chitosan and starch, PVA has low molecular weight and good water solubility; these two parameters enhance the stability of the complex formed. The formation of smaller crystallites of ZnO depends on the stability of the complex and diffusion of the reacting species.

4. Conclusion

Nano zinc oxide has a wide range of applications in various fields due to its unique and superior physical and chemical properties compared with bulk zinc oxide. The large specific surface area, high pore volume, low toxicity, nano structured properties and low cost of nano zinc oxide, make it a promising candidate particularly in catalyst, chemical absorbents as polymer additives and advanced ceramics. Nano zinc oxide with higher crystallinity is successfully prepared by the in situ precipitation of ZnO in different polymeric media like chitosan, starch and PVA. The characterization studies were done using XRD, SEM and particle size analyser. It was found that nano ZnO prepared from the bio polymer media like chitosan and starch have almost similar crystalline shape and size. Whereas, nano ZnO prepared from synthetic polymer media, PVA has slightly different structure and smaller particle size. The difference in structure and crystalline size may be due to the difference in structure of polymer-metal complex. Compared to Chitosan and Starch, PVA has low molecular weight and good water solubility, these two parameters enhance the stability of the complex formed.

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Molecular Imprinted Myoglobin Sensor using Polyphenol - Barium Ferrite Nanocomposites

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Abstract

An electrochemical myoglobin sensor based on molecularly imprinted polyphenol- barium ferrite (MI-MG-PP-BF ITO) was fabricated. The Polyphenol- Barium ferrite composite has been prepared using an electrolyte comprised of 20 mM phenol and 1mg hydrolyzed barium ferrite particles. Myoglobin was incorporated in Polyphenol-barium ferrite composites film. In order to fabricate myoglobin imprinted cavities inside polyphenol-barium ferrite films, the films have been washed several times with sodium dodecyl sulphate, followed by washing with water. A non-imprinted electrode (PP-BF/ITO) has been prepared by resorting to the same conditions without template myoglobin (MG). The prepared electrodes have been characterized using Ultra Violet (UV) spectroscopy, Scanning Electron Microscopy (SEM), Contact Angle (CA) measurements etc. The response study of the MIP-MG-PP-BF/ITO electrode has been investigated by electrochemical impedance spectroscopy (EIS). These electrodes show the linearity of the sensing response in the range of 80 μL to 100 μL with regression coefficient and standard deviation as 0.999 and 1.02, respectively. These electrodes exhibit a high sensitivity of 2.5 $Hz\mu g^{-1}L$ and very low detection limit of 1.26 μL. These studies reveal that the myoglobin imprinted electrode act as a highly efficient and competent sensor.

***Keywords**: Myoglobin, Barium Ferrite, Electrolyte, Ultra Violet, Spectroscopy.*

Molecular imprinting has recently attracted worldwide attention in the field of material science and technology. It is known to be an elegant technique for creation of desired template-shaped cavities in doped matrix with the memory of the template molecules to be used in rebinding and subsequent molecular recognition (Cameron A. et al. 2003). In this context, molecular imprinting polymers (MIP) have been prepared using a template molecule and functional monomers that assemble around the template and are subsequently cross-linked to each other (Chandrakanth N. and Careem M.A. 2000). These functional monomers that are self-assembled around a template molecule by interactions between functional groups, on both the template and monomer, are polymerized to form an imprinted matrix. The template molecule is then removed from the matrix, leaving behind a cavity complementary in size and shape of the template. These cavities can work as selective binding sites for specific template recognition. Both covalent and non-covalent imprinting methods are useful in MIP fabrication.

Conducting polymer (CP) based imprinting materials are promising systems for development of synthetic recognition sites that are considered important in the field of sensors Haupt K. and Mosbach K. 2000). Electro-polymerization is one of the most widely used method for fabrication of the conducting polymer based MIP, particularly for those target analytes that can act as templates as well as dopant during polymerization. Among various conducting polymers, PANI has been found to be a good matrix due to its unique, controllable chemical and electrical properties, (Kang Y. et al 1992) environmental and thermal stability, (Chandrakanth N. and Careem M.A. 2000) and interesting electrochemical, optical and electro-optical properties (Heeger A. 2001). Various PANI based MIP have already been fabricated and characterized to explore their role in the field of molecularly imprinted technology. Adsorption studies have been performed on molecularly imprinted PANI matrix for different nucleic acid bases and their extent of adsorption investigated using FT-IR technique (Shreenivasan K. 2007). MIP with multi-affinity sites have been prepared for multi-component (ATP, ADP and AMP) detection using PANI matrix. Efforts have also been made to explore polystyrene as coating material on molecularly imprinted PANI for creatinine detection (Shreenivasan K. 2006). All the aforementioned reports pertain to the preparation and characterization of molecularly imprinted PANI. But considerable efforts are required to explore these imprinted matrices for sensor applications.

Myoglobin is a protein that appears in the human body when muscular necrosis occurs. It is a small globular monomeric heme protein having a single polypeptide chain of 17 kDa and its crucial function is the uptake of oxygen from oxy-hemoglobin in the bloodstream. Moreover, it can bind with ligands such as CO and NO reversibly at the heme iron and is a well known vital biological index for the diagnosis of various diseases (Y. Haik et al. 2002). Myoglobin holds oxygen inside heart and skeletal muscle. It is continually released into the blood in small amounts due to normal turnover of muscle cells. Kidneys discard the myoglobin into urine. Myoglobin is one of several cardiac markers used to make diagnosis. Cardiac markers are substances in blood whose levels rise in the hours following a heart attack. Increased levels help diagnose a heart attack; persistent normal levels rule it out.

Each cardiac marker raises, peaks, and returns to a normal level according to its own timeline, or diagnostic window. Myoglobin is useful because it has the earliest diagnostic window. It is the first marker to rise after chest pain begins. These factors signify that the fabrication of precise and sensitive myoglobin detection biosensor is very important for myocardial infarction recognition. Myoglobin is one of the primitive studied protein structure whose crystal was characterized by XRD and the magnetic property had been characterized. Electrochemical sensors for hemoglobin and myoglobin detection based on methylene blue-multiwalled carbon nanotubes nanohybrid-modified glassy carbon electrode was also fabricated (Hsin-Yi Lin et al 2007 and Saithip Pakapongpan et al. 2011).

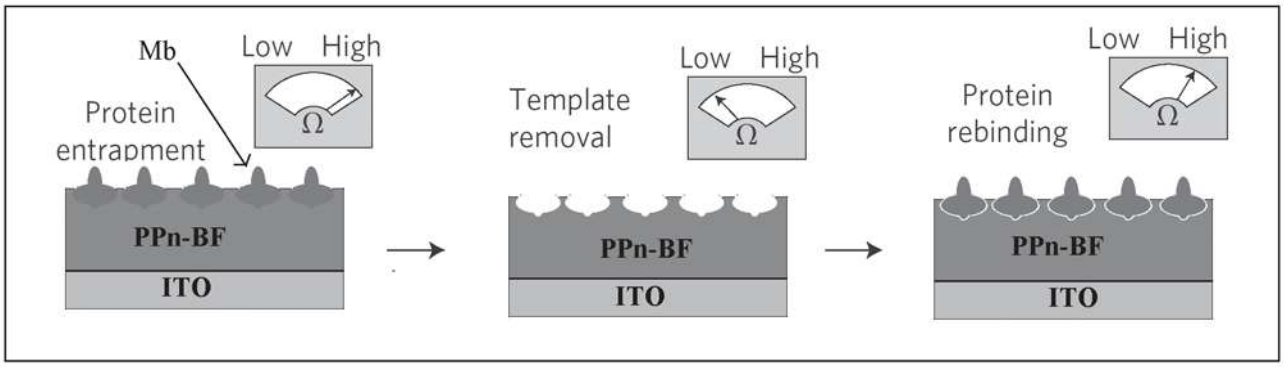
Herein, we report results of the preliminary studies related to the fabrication of molecularly imprinted Polyphenol-barium ferrite composites for selective recognition of myoglobin. The molecularly imprinted electrode has been prepared with potentiodynamic polymerization method.

2. Experimental

2.1 Preparation of Molecularly Imprinted Polyphenol-barium ferrite composites

The Polyphenol nanostructured barium ferrite (PPn-BF) composite film was prepared with potentiodynamic polymerization method using an electrochemical cell containing Ag/AgCl as reference, platinum wire as counter and ITO as working electrode (Area 0.03 cm^2). The monomer solution comprising of 20 mM phenol and 1mg hydrolyzed barium ferrite particles in 10 ml buffer 7.4 solution was subjected to potentiodynamic polymerization in the voltage range from -1.5V to 0.7 V having scan rate 0.01V/Sec and step potential 0.0025 V having number of scan 10.

For the formation of the myoglobin imprinted polyphenol barium ferrite (MbI-PPn-BF) composite film, we have followed the procedure as mentioned above but the deposition was conducted in presence of myoglobin (Mb). Moreover, to entrap template proteins in the polymer, 5 μL (5 mg Mb in 20 ml) of Mb solution was added into the deposition buffer. A 300 mV



Scheme 1: Schematic representation of various steps and the interactions concerning to the fabrication of Mb selective molecularly imprinted polyphenol-barium ferrite composites.

D.C. voltage (30 s) was first used to attract proteins onto the ITO plates, and then similar potentiodynamic polymerization was performed as described above.

Protein Imprint Development

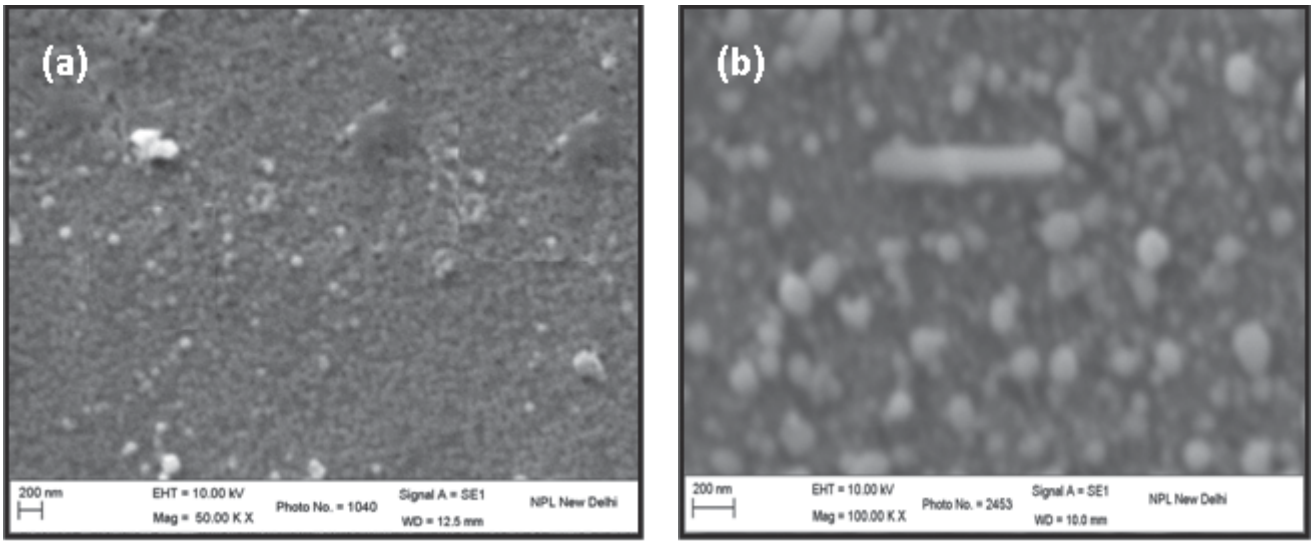
The embedded myoglobin from the polymer composite has been removed by incubating overnight in deionized water at room temperature and washing with buffer containing 5% acetic acid and 10% sodium dodecyl sulphate. A non-imprinted electrode (PPn-BF/ITO) has been prepared by resorting to the same conditions without template (Mb) for carrying out the comparative studies with the molecularly imprinted electrode. Scheme 1 shows the various steps and the interactions concerning to the fabrication of Mb selective molecularly imprinted polyphenol-barium ferrite composites.

2.2. Characterization

The structural and morphological analysis of M*I*-MG-PP-BF *ITO* electrode non-imprinted electrode and (PP-BF/ITO) has been carried out using UV-Vis spectroscopy (Perkin-Elmer) and scanning electron microscopy (JEOL, JSM-35), respectively. Contact angle studies (Data physics Instrument, Model No. OCA 15EC) have been done using sessile drop method to reveal the surface modification of PP-BF. Autolab Potentiostat/ Galvanostat (Eco Chemie, Netherlands) with a conventional three-electrode electrochemical cell consisting of Ag/AgCl as reference electrode and platinum foil as the counter electrode has been used for electrochemical studies of fabricated electrodes. Cyclic voltammetry and differential pulse voltammetry studies have been carried out in phosphate buffer saline (PBS, 50 mM, pH 7) containing 0.9% NaCl.

For the formation of the myoglobin imprinted polyphenol barium ferrite (MbI-PPn-BF) composite film, we have followed procedure as mentioned above but the deposition is conducted in the presence of myoglobin (Mb). Moreover, to entrap template proteins in the polymer, 5 μL (5 mg Mb in 20 ml) of Mb solution was added in to the deposition buffer. A 300 mV D.C. voltage (30 s) was first used to attract proteins onto the ITO plates, and then similar potentiodynamic polymerization was performed as described above.

Figure 1: SEM studies of (a) PPn/ *ITO, (b)* Mb-PPn-BF *ITO* electrodes



3. Results and Discussion

3.1 SEM Studies

In order to investigate the surface morphology changes of the different electrodes, the SEM studies of PPn/ ITO, and Mb-PPn-BF ITO (c) electrodes (Figure 1) have been conducted. The Scanning Electron Micrograph of PPn/ ITO surface (Figure 1 (a) reveals the flattened and smooth surface morphology of the polymer. The PPn-BF ITO /ITO Nano composite film shows the formation of well-dispersed, globular nano-structure of barium ferrite with porous topology and also confirm the presence of the nano-structured particles on the surface of the

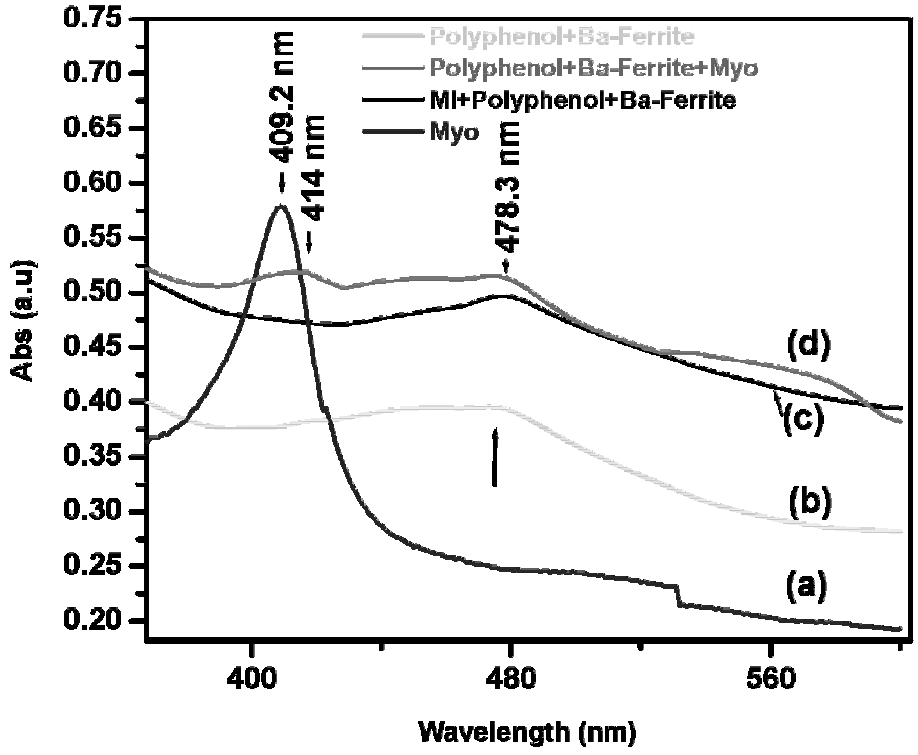


Figure 2: The UV visible spectra of the electrochemically deposited films of myoglobin solution, Mb (in buffer solution), PPn-BF/ITO and Mb-PPn-BF/ITO Mb*I*-PPn-BF *ITO* electrodes.

composite film. The observed regularity in PPn-BF/ITO nanocomposite reveals uniform dispersion of BF nanoparticles in the polyphenol matrix. This may be attributed to electrostatic interactions between the polyphenol and the hydrolysed nanoparticles.

3.2 UV-Visible Spectroscopy

The UV-Visible spectrum of various electrodes like pure myoglobin, M*I*-MG-PP-BF *ITO* electrode non-imprinted and (PP-BF/ITO) were taken. The incorporation and removal of myoglobin is clearly visible from UV-Visible spectroscopy. The spectra of various electrodes are shown in Figure 2.

Figure 2 shows the UV visible spectra of the electrochemically deposited films of myoglobin solution, PPn/ITO, PPn-BF/ITO and Mb-PPn-BF/ITO electrodes. In figure 2, curve (a) represent the UV visible spectrum of myoglobin in water. It shows a sharp absorption peak at 409 nm. The

409 nm absorption band intensity depends on the folding and unfolding of myoglobin (Saithip 2011). By comparing the absorption spectra of PPn-BF(b) and Mb-PPn-BF(d), the absorption spectrum observed at 414 nm in (d) is responsible for the Mb present inside the composite matrix. In curve MbI-PPn-BF (c), the peak around 414 nm is absent, which confirms the complete removal of template and hence the formation of myoglobin cavities inside composite. A difference in wavelength of myoglobin is observed in curve (a) and curve (d). This may be attributed to the fact that the UV visible spectra of Mb (a) has been recorded in the aqueous media in the first case, but in curve (c) Mb is set inside the composite network.

After the incorporation of Mb, the peak intensity at 414 nm increases and the broadening of the peak also occurs. The increase in the peak intensity and broadening of peak observed is due to the interaction of Mb in the polymer composite matrix.

3.3 Contact Angle (CA) Measurement Studies

To study the surface hydrophilicity of different electrodes, the contact angle measurements using the sessile drop method have been carried out on PPn-BF/*ITO* (b) Mb-PPn-BF *ITO* (c) Mb*I*-PPn-BF/*ITO* electrodes and Mb rebounded Mb*I*- PPn-BF/*ITO* electrodes, respectively (Figure 3). The change in the value of CA reveals the hydrophobic/hydrophilic character of the surface that in turn can be related to the modification of the surface in presence of template. The PPn-BF/*ITO* film shows a contact angle of 40.9° and after the addition of Mb, the contact angle decreases from 40.9° to 18.1°. The decrease in contact angle is due to increase in hydrophilicity of the polymer surface which is caused by the incorporation of Mb in the polymer matrix. Washing of Mb-PPn-BF/ITO electrodes with sodium dodecyl sulphate followed by rinsing with deionized water shows an increase in contact angle of 38.7°. This result proves the removal of template from the polymer

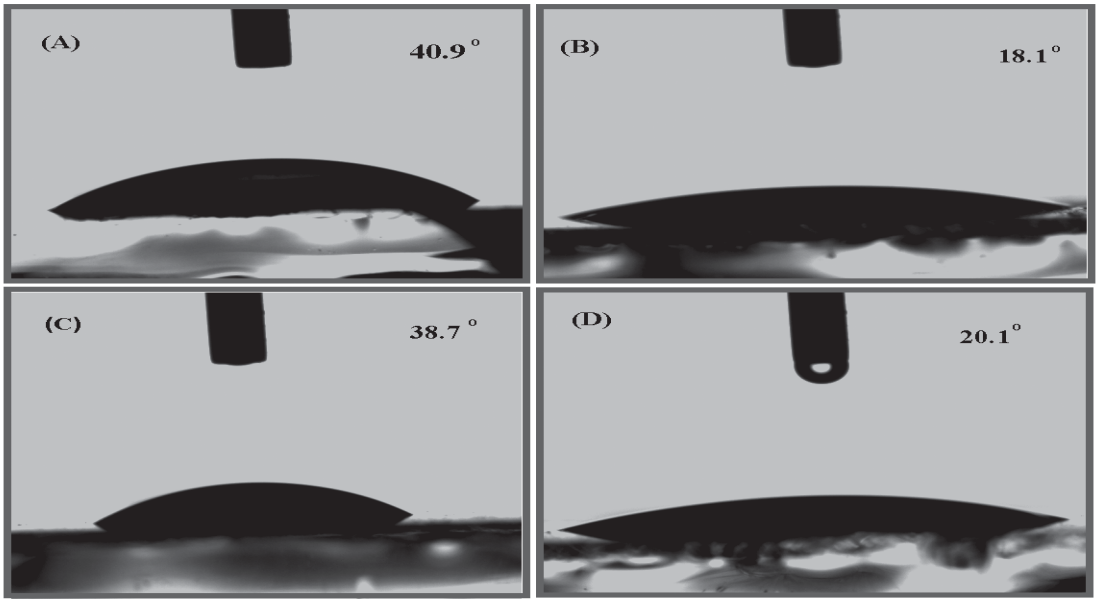
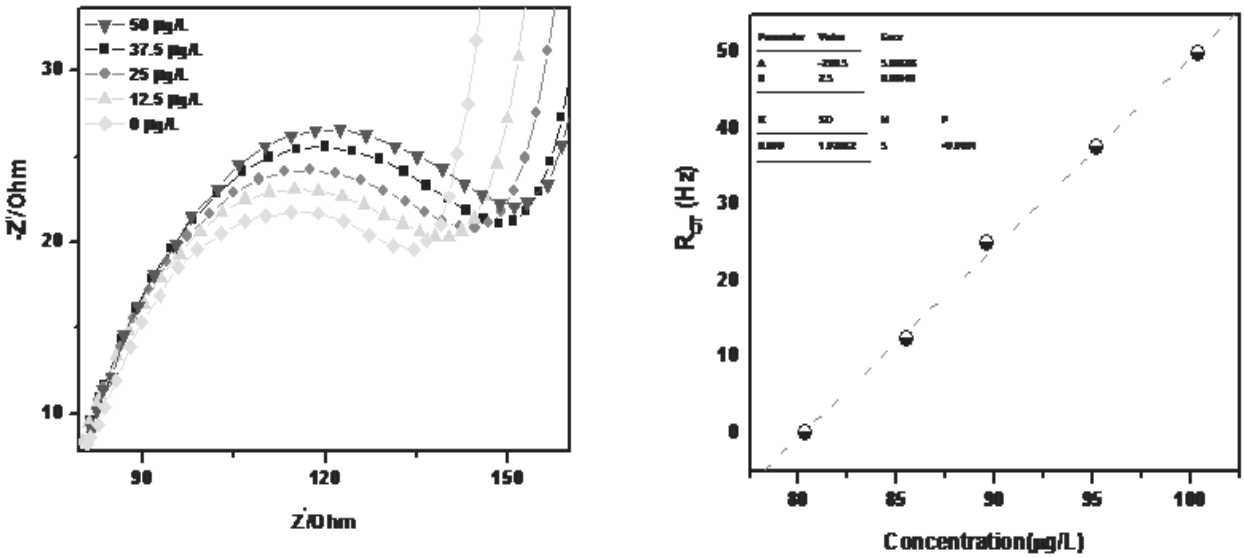


Figure 3: Contact angle images of different electrode (A) PPn-BF/ITO (*B)* Mb PPn-BF /ITO (C) MbI-PPn-BF /ITO (D) Rebinding of Mb

composite matrix and leads to the formation of Mb imprinted PPn-BF/*ITO* electrodes. Theoretically, the value of the contact angle of Mb imprinted PPn-BF/*ITO* and PPn-BF/*ITO* should be same but it is observed that the two values differ by 2.2°. The reasons for this CA difference can be two: (i) remains of unremoved Mb in the polymer matrix (ii) removal of Mb increases molecular level roughness in the electrode surface. It is not clear from our study which factor contribute more for this decrease in contact angle. To investigate the binding ability of the molecularly imprinted electrodes, the contact angle measurements have been carried out after the incorporation of Mb molecule in these electrodes. The change in contact angle from 38.7° to 20.1° clearly reveals the presence of Mb selective cavities in the molecularly imprinted electrodes.

3.4 Response Studies

Electrochemical impedance spectroscopy (EIS) provides an effective method to probe electronic features of surface-modified electrodes. Figure 4 (i) shows the Nyquist plots obtained for myoglobin imprinted MbI-PPn-BF/ITO electrode with varying myoglobin concentration in the frequency range of 10–10^5 Hz. The Nyquist diameter i.e. the real axis value at lower frequency intercept gives us the value of charge transfer resistance (R_{CT}) i.e. hindrance provided by the electrode material to transfer of charge from solution to the electrode that can be correlated with the modification of surface. The response study of the MbI-PPn-BF/ITO electrode has been investigated by EIS spectroscopy after its incubation with different myoglobin concen-



(i) **(ii)**

Figure 4: Response studies of myoglobin imprinted polyphenol-barium ferrite composites

trations for 60 seconds. As clear from Figure 4 (i), there is a continuous increase in the R_{CT} value with increased myoglobin concentration. This can be assigned to the hindrance provided by the macromolecular insulating structure of myoglobin. So, more will be the concentration of myoglobin, more cavities of MIP matrix will be occupied with these molecules, leading to an

increase in R_{CT} value. The calibration plot (Figure 4 (ii) shows that the linearity of the sensing response is in the range of 80 μL to 100 μL with regression coefficient and standard deviation as 0.999 and 1.02, respectively. Further, the high sensitivity of 2.5 Hzμg $^{-1}$L and very low detection limit of 1.26 μL reveals the implication of this molecularly imprinted PPn-$Ba_2Fe_2O_3$/ITO electrode as highly efficient and competent sensing platform.

4. Conclusions

Nanostructured polyphenol-barium ferrite composite film onto indium-tin-oxide (ITO)-coated glass plate for the detection of myoglobin is fabricated electrochemically. This nanocomposite film has been explored as molecularly imprinted platform to observe myoglobin and its sensing characteristics. The SEM, UV, and CA measurements techniques have been employed for the structural and morphological analysis of the fabricated electrodes. The morphological studies clearly reveal uniform dispersion of nanoparticles of barium ferrite into the polymer matrix, resulting in homogeneous nanocomposite formation. Electrochemical response measurements of this electrode were carried out using impedance studies. Electrochemical impedance spectroscopy (EIS) provides an effective method to probe electronic features of surface-modified electrodes. It is clear that there is a continuous increase in the R_{CT} value of myoglobin imprinted electrode with increased myoglobin concentration. This can be assigned to the hindrance provided by the macromolecular insulating structure of myoglobin. So, more will be the concentration of myoglobin, more cavities of MIP matrix will be occupied with these molecules, leading to increase in R_{CT} value. The calibration plot also shows that the linearity of the sensing response is in the range of 80 μL to 100 μL with regression coefficient and standard deviation as 0.999 and 1.02, respectively. Further, the high sensitivity of 2.5 Hzμg^{-1}L and very low detection limit of 1.26μL reveal the implication of this myoglobin imprinted PP-BaF/ITO electrode as highly efficient and competent sensing platform.

References

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Seasonal Dynamics of Nutrients and Chlorophyll *a* Concentrations: Cochin Estuary

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Abstract

The present study focuses on the environmental assessment of the central part of the Cochin estuary, where severe industrial and anthropogenic perturbations imposed by the developmental, shipping, fishing and constructional activities occur. The physico-chemical characteristics and the chlorophyll *a* concentrations of the study region were analysed. The fluctuating saline conditions and nutrient concentrations observed during the study period characterize the study region as an extremely sensitive zone. In post and premonsoon seasons, the months of maximum seawater intrusion, comparatively high salinity values ranging between 20-35.65 psu was observed except at up stream stations, where the salinity values fluctuated between 0-20 psu. In pre-monsoon, the oxygen concentrations in the surface and bottom waters showed little vertical water column variation. But in summer monsoon, dissolved oxygen concentration in the surface and bottom waters varied marginally, indicating the existence of a highly stratified water column. During pre-monsoon, an exceptionally high peaking of nitrite was also observed at the southern end of the study region; prominently in the deeper waters (1.53 μmol L-1). The bottom waters showed fluctuating nitrite concentrations during all the seasons. Fresh water influxes due to pre-monsoon showers play an important role for the observed variability in the nutrient concentrations. Throughout the study period, estuarine waters showed high chlorophyll concentration except the northern and bar mouth stations. Chlorophyll concentrations were reduced considerably during summer monsoon throughout the study area. Post-monsoon observations recorded fluctuating chlorophyll *a* concentrations in the surface waters.

***Keywords**: Cochin Estuary, Salinity, Chlorophyll.*

Nutrient dynamics in most of the estuaries have been strongly influenced by Nutrient loading, prompting expensive control measures aimed at point sources. Management of nutrient levels is complicated by uncertainties regarding the importance of nutrient ratios vs. nutrient levels, and by the translocation of nutrients by fishes, including upstream migrations of certain fishes influencing productivity in upper watersheds. An increased appreciation of human modification of regional and global cycling of carbon and other materials, with potentially disastrous impacts, has led to increased emphasis on large-scale input-output budgets. Quantifying the link between land use and eutrophication can best be appreciated within the larger context of a full input-output accounting.

The Cochin backwaters (also called Vembanad Lake) constitute the second largest estuarine system in India. The estuary is undergoing drastic modifications due to human intervention. In its pristine condition, the Cochin backwaters sustained rich bio-resources. The anthropogenic influence in the Cochin backwaters increased in the second part of 19th century and remains high to the present day (Menon et al., 2000). Cochin Port Trust has recently embarked on many major constructional activities, like Vallarpadam Container Transshipment Terminal, Marina and Building Roads along the banks and bridges across the backwater for container traffic etc. With the onset of these developmental activities within the backwater system, it has become more important to monitor the water quality and the biodiversity of the backwater periodically, to prevent environmental degradation. Lack of awareness, inadequate technology and high cost involved for waste water treatment have also resulted in a progressive environmental degradation of the backwaters.

Many destructive changes occurred in the Cochin backwaters during the past few decades, due to the industrial and anthropogenic loadings (Central Pollution Control Board, 1996). Cochin estuary is strongly influenced by the tidal inflections and flushing characteristics which govern the biogeochemical processes of the estuary.

1.1 Turbulence

An upholding sediment contribution to the Cochin backwaters is from the rivers Muvattupuzha and Periyar compared to other four rivers. The Cochin estuary being a platform for the mixing of fresh water and sea water, appears to be turbulent especially during summer monsoon season. A continuous supply of fresh water keep the region turbid for a longer time duration than in the saline conditions (Balachandran et al., 1996). When the saline intrusion become weak in summer monsoon, heavy sediment loading occurs which causes metal accumulation in the region (Balachandran et al., 1996). In the shipping channels where the dredging operations are carried out, the suspended load in the water column vary drastically with values varying between 10 to 1150 mg L^{-1} (Sheeba, 2000). The rate of deposition and resuspension processes of sediments play an important role in the nutrient budgeting (Martin et al., 2011).

1.2 Currents

Cochin backwater is characterized by inconsistent current patterns due to heavy waterline traffic i.e. movement of ships and barges, passage of ferry and tourist boats etc. The speed and direction of currents varied considerably with the tidal phase, with a maximum velocity of 50 cm/sec and 77 cm/sec at the surface during flood and ebb tides, respectively (Martin et al., 2010). There is high flood velocity (90 cm/sec) in the Ernakulam

channel compared to that in the Mattancherry channel (70 cm/sec) during monsoon. During monsoon season, the large fresh water influx has a significant grip over the tidal influence in determining the flow pattern. The system becomes more complex as the existence of number of islands and the prevailing river discharges play crucial role in determining the estuarine flows (Srinivas et al., 2003; 2006).

1.3 Salinity

Salinity values interpret the mixing processes and demarcate the extent of intrusion of saline waters into estuaries. The longitudinal extent of saline water intrusion into the backwater system varies considerably with the seasons, which has a significant role in flushing out the pollutants introduced by the industries (Sankaranarayanan et al., 1984). Cochin backwaters undergo a characteristic transformation from a river dominated system during summer monsoon to tide dominant system during pre-monsoon season (Martin et al., 2008). Studies on estuarine characteristics of Cochin backwaters by Sankaranarayanan et al., (1984) revealed a major intrusion of saline waters during pre-monsoon (January to May) with a value > 30 psu even at a distance of about 18 km from the bar mouth. With the onset of monsoon, the near shore waters (off Cochin) depicted salinity values ranging between 3 to 19 psu. The brackish waters lying in a stretch of 5 km near the bar mouth traced a salinity < 1 psu and it vanished in the upper reaches.

Martin et al. (2008) has reported a salinity maximum of 34 psu near the Vallarpadam container transshipment terminal with a steady decreasing gradient towards north during pre-monsoon. During summer monsoon the salinity reduced below 4 psu.

1.4 Temperature

During pre-monsoon season the Cochin bar mouth region was characterized by comparatively warm waters with an average temperature of 32.6^{o}C and during monsoon season the surface water temperature was dropped by 2 – 4°C because of the fresh water influx (Madhu et al., 2007). Seasonal changes in temperature are more prominent along the northern part of the estuary (25 – 33°C) than the southern parts (29 – 33°C) (Lakshmanan et al., 1982). An elevation in water temperature was identified by Saraladevi et al. (1979) in the upper reaches (north) of Cochin backwaters where the industrial effluents are discharged. A tongue of cold saline waters, intruded from the Arabian Sea, was identified in the deeper layers of Cochin bar mouth by Ramamirtham and Jayaraman (1963).

1.5 p^{H}

The hydrogen ion concentration of an estuarine medium depends on many factors like fresh water input, nature of dissolved materials, discharge of effluences etc. Earlier studies (Paul and Pillai, 1976; Saraladevi et al., 1979) revealed that frequently occurring large scale fish transience, especially along the estuarine waters near the industrial region, can be attributed to the fluctuating p^{H} values (9-5.1). Backwater remains acidic during monsoon season (Martin et al., 2008).

1.6 Water Quality

Being the industrial capital of Kerala, coastal waters off Cochin and the backwaters are the prime location for ecological deterioration. Increasing population, agriculture and establishment of new industries along the banks of the backwater made it a dumping site of many organic and inorganic pollutants. The waste materials include fertilizers, pesticides, radioactive

materials, petroleum and heavy metals. Pioneering studies were carried out (Paul and Pillai, 1976; Jayapalan et al., 1976) to assess the effluent concentration and its dilution due to fresh water discharge, distribution of radioactivity in sediment-water-biota and heavy metal concentration of Periyar river water.

1.7 Dissolved Oxygen

A rapid decrease in dissolved oxygen content is reported in the bottom waters with values 1-2 ml L^{-1} during post monsoon season while the surface waters are subjected to little fluctuation (Sankaranarayanan and Qasim, 1969). Higher monsoonal values (7.07-8.50 ml L^{-1}) and pre monsoonal values (6.98-7.73 ml L^{-1}) were observed along the southern part of the estuary (Anirudhan, 1988). Dissolved oxygen concentrations were relatively higher during peak summer with average value 6.4 mgL^{-1} compared to pre-monsoon with average value 5.7 mg L^{-1} (Jyothibabu et al., 2006 and Madhu et al., 2007).

1.8 Nutrients

The significance of nutrients in the Cochin estuary and the adjoining sea is well recognized for the past few decades. Many attempts were made to understand the distribution and behavior of nutrients (especially Nitrogen and Phosphorous) in different geographical locations and seasons in the Cochin estuarine waters and the adjacent coastal environments in order to correlate with the potential fertility of the region. Silicate concentration also has significant characteristic features due to the seasonal influx of fresh water. Because of the overwhelming land drainage and pollution, the estuaries are generally enriched in nutrients (Anirudhan, 1988).

Observations made before and after dredging operations in the shipping channel of Cochin backwater showed drastic changes in the nutrient concentrations of the deeper waters (Thresiamma Joseph et al., 1998). The nutrient distribution in the shelf waters has a significant role in characterizing the water masses and their movements in conjunction with other physical oceanographic parameters. The distribution and variation of nutrients in estuarine waters are controlled by the physical, chemical and biological processes occurring in the allied environment (Aston, 1980).

1.9 Ammonia - Nitrogen

The maximum value range for ammonia (0.05-24.46 μ mol L^{-1}) was observed in the bottom waters along the northern part of the estuary during summer monsoon which decreased to a minimum value range (0.05-12.54 μ mol L^{-1}) as the season progressed to post monsoon (Anirudhan,1988). Ammonia represents 80% of the dissolved inorganic nitrogen and its highest values are always associated with fresh water inflow (Martin et al. 2007).

1.10 Nitrate - Nitrogen

Earlier studies reveal that the amount of nitrate in the Cochin backwaters was low (1.5-5.5 μ mol L^{-1}) except the monsoonal months when the nitrate concentration showed a sharp increase (25-30 μ mol L^{-1}) [Sreedharan Manikoth and Mohammed Salih, 1974]. The highest values for nitrate were observed during the fresh water dominated period (Sankaranarayanan and Qasim, 1969). The observation made by Anirudhan (1988), showed a gradual decrease in nitrate concentration from the bar mouth region to the upstream region. However nitrate showed an inverse relation with salinity during March and October (Martin et al., 2007).

1.11 Nitrite – Nitrogen

Sankaranarayanan and Qasim (1969) suggest that nitrite may be formed as a result of decomposition of organic nitrogen. According to their observations, the pre-monsoon season recorded low value of nitrite (0.2-0.8 μ mol L^{-1}) and the concentration gradually increased through summer monsoon to post-monsoon recording maximum values (surface – 5.58 and bottom 6.68 μ mol L^{-1}) in post monsoon along the northern part of the estuary (Joseph, 1974 and Anirudhan, 1988). The northern part of the Cochin backwater and the area around Willington Island were reported to be relatively elevated in nitrite concentration throughout the year (Sreedharan Manikoth and Mohammed Salhi, 1974).

1.12 Silicate - Silicon

Silicate concentration gradually increases from the mouth of the estuary to the upstream. Sankaranarayanan et al., (1984) observed this trend in almost all seasons with values ranging from 0.03 to 5.96 μ mol L^{-1}. The highest values recorded were in the monsoon season (0.37-5.96 μ mol L^{-1}) when the river discharge is maximum and the lowest values (0.03-2.66 μ mol L^{-1}) in the pre-monsoon season when the river discharge is minimum. The development of water mass with high residence time during pre-monsoon influences the loss of silicate in the Cochin estuary along with the biological conditions (Balachandran et al., 1996).

1.13 Phosphate - Phosphorus

The phosphate concentration in the estuary is largely dependent on the external sources such as fresh water discharge and land drainage. Earlier observations reveal that phosphate concentrations were high during monsoon season with values ranging between 1.8-2.7 μ mol L^{-1} especially along the southern parts of the estuary and with values ranging between 2-5.4 μ mol L^{-1} at the northern side of the estuary (Sreedharan Manikoth and Mohammed Salih, 1974). Anirudhan (1988) has reported high values for phosphate; 4.41 μmol L^{-1} at surface waters and 6.09 μ mol L^{-1} at the bottom waters in the northern region of Cochin estuary during post-monsoon.

1.14 Estuarine Sediments

The nature and distribution of sedimentary matter in an estuary are controlled by interaction between the kinds and quality of available sedimentary components (such as shells, organic matter, quartz, sand grains, fecal pellets and clay minerals), hydrodynamic processes and bottom morphology. Sediments plays an important role in biological and geochemical processes, and also serves as a good source for adsorption processes and bacterial activity. Estuaries have complex sedimentary environment and they may originate from a number of upstream and marine sources. The seaward and landward transport of sediments in the estuary impose several limitations in the geochemical interpretations of estuarine sedimentary processes.

2.Materials and Methods

2.1. Description of the study Area

The Cochin estuarine system (Vembanad Lake and surrounding islands), occupies nearly 256 km^2 of area with six rivers flowing into it viz. Periyar, Muvattupuzha, Pampa, Manimala, Meenachil and Achankovil. Seasonally fluctuating river discharge and tidal influx play a very important role in determining the biogeochemistry of the estuary. Vembanad Lake stretches about 80 km between Azheekode in the north and Thanneermukhum in the south which extends between $9^o40'$ and 10°

12′ N and 76° 10′ and 76° 30′ E. The coastline openings at Cochin Harbour and Azheekode facilitate the backwater system to have a permanent connection to the Arabian Sea. The depth of the estuary varies from 2 to 7 meters except the shipping channel where a depth of 10 to 14 m is maintained. The hydrography of the system is controlled by seasonally changing climatic conditions regulating the biogeochemical processes in the system (Menon et al., 2000).

Being a bar built estuary with coastline opening to the Arabian Sea at Cochin harbor and Azheekode, it has a heavy tidal influence especially in the regions of close proximity to the sea. The six rivers flowing into the estuary and heavy rainfall over the region bring in large amount of fresh water (20000 Mm^3) into the estuary (Balachandran et al., 2008). The Cochin Port Trust maintains three shipping channels viz. Approach channel (9 km), Ernakulam channel (5 km) and Mattancherry channel (3 km) with frequent dredging at around 10-12 m. Topographic disturbances due to continuous dredging facilitate variations in salinity intrusion and sedimentation.

2.2. Sampling Locations

The estuary, including southern and northern regions was sampled for different chemical oceanographic and ecological parameters to understand the possible impacts on the estuary due to anthropogenic activities. The observations carried out in the entire Cochin backwaters were mainly targeted to identify the sources and sinks of the nutrients and its variability during lean river discharge period. The large quantities of these nutrients, accumulated in this estuary are not only of ecological interest, but are also relevant to further water quality management.

The dependence of the hydrographic features of the estuarine system on the fresh water influx and on the availability of rain fall, induce a division of the observation period into three viz. pre-monsoon (Jan-May), summer monsoon (June-Oct), and post monsoon (Nov-Dec). The study area includes 10 pre planned stations (1. Bolghaty, 2. Mulavukadu north 3. Edavanakkadu 4. Ochanthuruthu 5. Mattanchery channel 6. Ernakulam Channel 7. Thevara 8. Vallarpadam 9. Vypin 10. Bar mouth) in the backwaters (Figure 1).

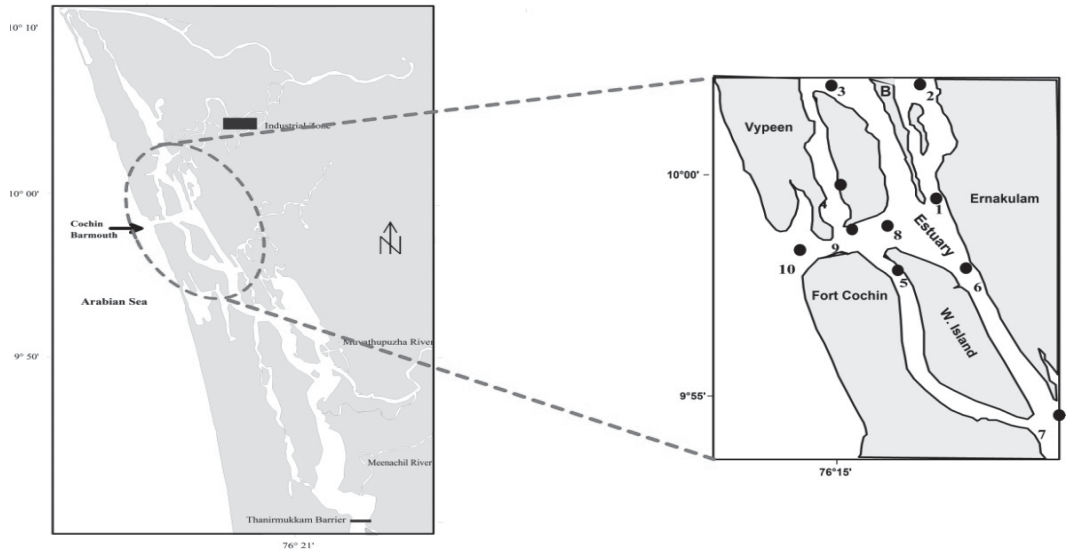

Figure 1: Sampling Locations

2.3. Analytcal Methods

The surface temperature was measured using a centigrade thermometer. pH measurements were made using a portable pH meter (Perkin Elmer, accuracy ± 0. 01) after calibrating with NBS standards. Salinity of the surface samples were measured using a calibrated (using standard sea water) salinometer (Digi Auto 3G, Tsurumi Seiki, Japan, accuracy ± 0.001psu).

Water samples were collected from the depths using Niskin samplers. Samples for dissolved oxygen (DO) were analysed by Winkler's method. Samples for nutrients (NO_3-N, PO_4-P, SiO_4-Si, and NH_4-N) were filtered through Whatman No.1 filter paper and analysed using a spectrophotometer (Shimazdu, Japan) following the standard procedures (Grasshoff et al., 1983). Water samples (500ml) were filtered through GF/F filter papers and the chlorophyll *a* was extracted using 90% acetone. The measurements were carried out using a spectrophotometer following the procedure of Strickland and Parsons (1972).

3. Results and Discussion

3.1 Water temperature

In general, the water column temperature in the study region ranged between 25-32°C (Figure 2 and 3). During post monsoon relatively high temperature values (27.5-32°C) in the surface waters were recorded along the entire study region concomitant with the high atmospheric temperatures (Maximum atmospheric temperature 33°C). In summer and pre-monsoon season, relatively cooler conditions prevailed along the river end of the estuary (northern part). A lower temperature (25°C) was recorded during summer monsoon for the bottom samples of station 5 and 6. In pre-monsoon, the bottom waters of station 2 showed lower temperature (28.5°C). During pre-monsoon at the bar mouth station (Station 10) the surface and bottom waters showed almost same temperature, probably being an interactive region of saline and fresh water with severe water column disturbances.

3.2 Salinity

Figure 2 and 3 shows spatial variation in salinity along the study region. In post and pre-monsoon seasons, the months of maximum seawater intrusion, comparatively high salinity values ranging between 20-35.65 psu was observed except up stream stations, where the salinity values fluctuated between 0-20 psu. Due to the monsoon showers over the study region, the salinity values at stations were considerably dropped with the lowest value in the surface waters of station 2. Except in monsoon, the coastal waters maintained an average salinity of 34.03 psu. Obviously station 2 appeared fresh water dominant during the study period.

3.3 pH

In general, the pH profile in the water column showed a slight increase towards the coastal region from the estuarine waters (Figure 2 and 3). The estuarine region recorded an average pH of 7.85 and in the coastal stations it was 8.36. However in station 2 and 3, the pH values in the water column were consistently low in all the observations with average values 6.5 and 6.7, respectively. During Post-monsoon and summer monsoon, in the surface waters at station 8, pH values were observed as 6.8 and 8.2, respectively whereas in pre-monsoon the values was 7.6.

3.4 Dissolved Oxygen (DO)

The dissolved oxygen content in the study region varied from 2.25 to 5.41 ml L^{-1} in the surface layer

and from 0.35 to 4.8 ml L^{-1} in the bottom layers. However, in summer monsoon, oxygen content was comparatively low in the bottom waters (Figure 3), indicative of a monsoon condition (Sarala Devi et al., 1979). The highest surface oxygen value (5.41 ml L^{-1}) was at station 7 in post-monsoon and the lowest (2.25 ml L^{-1}) at station 2 in the same season. In the bottom layer, the highest oxygen value was reported at station 10 in pre-monsoon and the lowest at station 10 in summer. In pre-monsoon, the oxygen concen-trations in the surface and bottom waters showed little vertical water column variation. However in summer monsoon, dissolved oxygen concentration in the surface and bottom waters varied marginally, indicating the existence of a highly stratified water column.

3.5 Nitrate-Nitrogen (NO_3-N)

During the observational period, nitrate concentrations in the study region showed inconsistent distributional pattern with values ranging between 3.98-68.4 μmol L^{-1}. Lower values of nitrate were observed during post-monsoon whereas in summer monsoon higher values were observed in the bottom and surface waters of the study region (Figure 2 and 3). The nitrate distribution in the backwaters during post-monsoon seems to be a typical pattern with minimal nitrate values, suggesting the contribution from the sea, when the estuary is under the grip of marine conditions.

3.6 Nitrite-Nitrogen (NO_2-N)

Nitrite concentrations during the observational periods are shown in figure 2 and 3. The distributional pattern post-monsoon showed depleted levels of nitrite concentration (<0.73 μmol L^{-1}) in the water column along the entire study area except the bottom waters of station 10 (Figure 3). A gradual increase in concentration was observed in the surface waters towards the northern channels during the study period (Figure 2). Station 2 in the upstream recorded a highest value of 1.32 μmol L^{-1} in post-monsoon and station 1 recorded a high value of 1.1 μM in summer at the surface. During pre-monsoon, an exceptionally high peaking of nitrite was also observed at station 7 at the southern end of the study region prominently in the deeper waters (1.53 μmol L^{-1}). The bottom waters showed fluctuating nitrite concentrations during all the seasons (Figure 3).

3.7 Ammonia-Nitrogen (NH_4-N)

The observations in post-monsoon revealed a marginal increase in ammonia concentration in the surface waters in almost all the stations except station 10 towards the bar mouth (Figure 2). During this season, ammonia concentration showed an irregular distributional pattern with values ranging from 7.98 to 59.64 μmol L^{-1}. In pre-monsoon and summer monsoon the concentration reduced to a low range of values varying between 26.41-4.45 μmol L^{-1}. Generally the northern part of the estuary possessed higher concentration values. The bar mouth region (Station 10) seems to be declined in ammonia except in pre-monsoon.

3.8 Phosphate-Phosphorous (PO_4-P)

During summer period the estuarine waters can be seen rich in phosphate at the surface as well as bottom layers with values ranging between 2-7.5 μmol L^{-1} with a gradual down slopping towards the bar mouth. Enrichment in the phosphate content in the surface waters were observed in many of the stations during this period (Figure 2). Station 10 (bar mouth) registered low phosphate during pre-monsoon. Comparatively low values of phosphate were observed during post-monsoon season throughout the entire study area. In summer, an exceptionally high value of phosphate was recorded at station 3 at the northern end of the study area (Figure 2).

3.9 Silicate-Silicon (SiO_4-Si)

The distributional pattern of silicate exhibits high concentration in the fresh water region with a gradual seaward decrease in the surface and bottom waters irrespective of the seasons (Figure 2 and 3). Silicate values ranged between 4.5 and 112.44 μmol L^{-1} in the estuarine waters. The maximum value in the estuary was at the surface waters of station 2 in post-monsoon. The deeper waters of this station contained comparatively higher silicate concentration (92.86 μmol L^{-1}). The maximum silicate value during summer monsoon was recorded in the surface waters at station 6. In summer and pre-monsoon, silicate concentrations in the study area were considerably reduced.

3.10 Chlorophyll *a*

Distribution of chlorophyll *a* showed marked spatial variation in the estuarine waters (Figure 2 and 3). Throughout the study period, estuarine waters showed high chlorophyll concentration except the northern and bar mouth stations. In the estuarine waters maximum chlorophyll concentration was found at station 4 (54.3 mg/m^3) and station 5 (48.4 mg/m^3) during pre-monsoon. Chlorophyll concentrations were reduced considerably during summer monsoon throughout the study area. Post-monsoon observations recorded a fluctuating chlorophyll *a* concentrations in the surface waters (Figure 2).

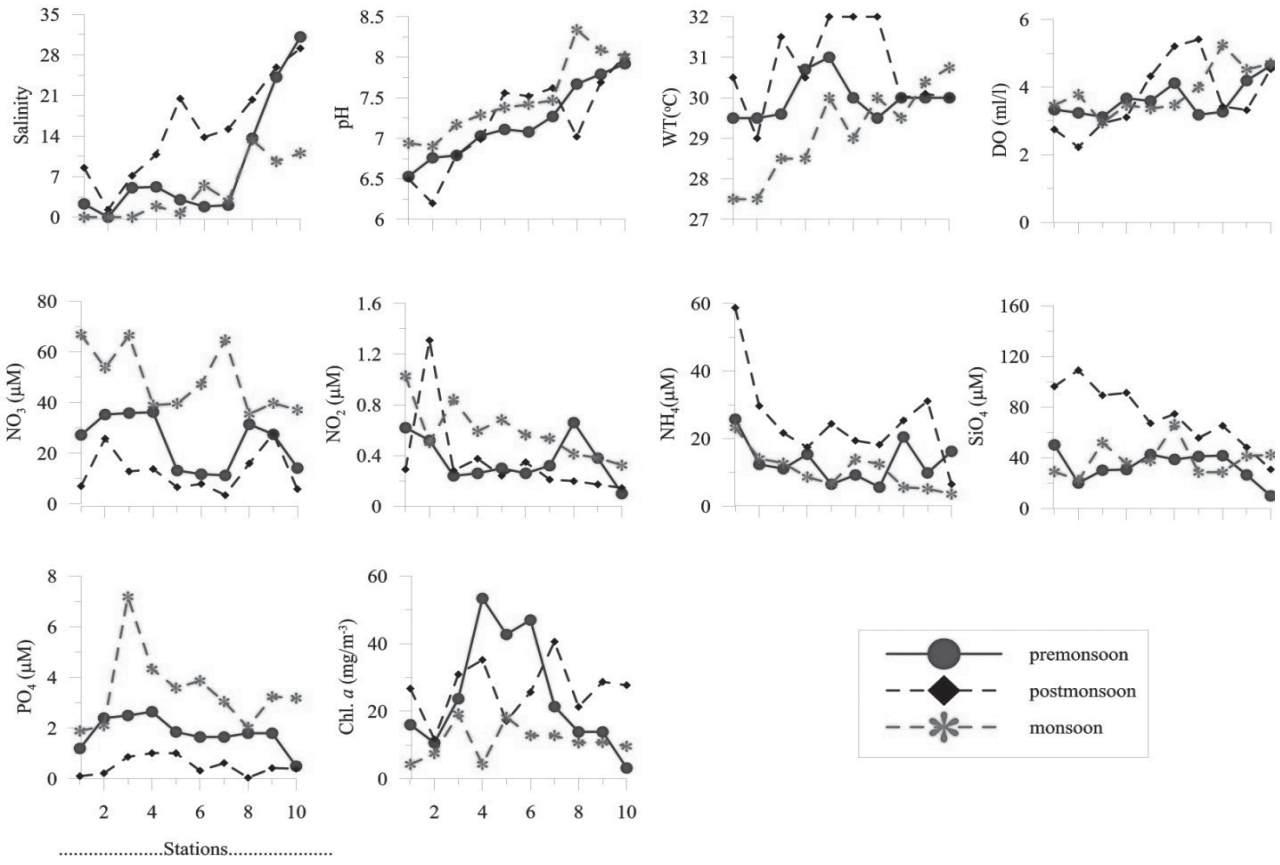

Figure 2: Salinity, pH, Water temperature, Dissolved oxygen, Nutrients and Chlorophyll in the surface waters of the Cochin estuary

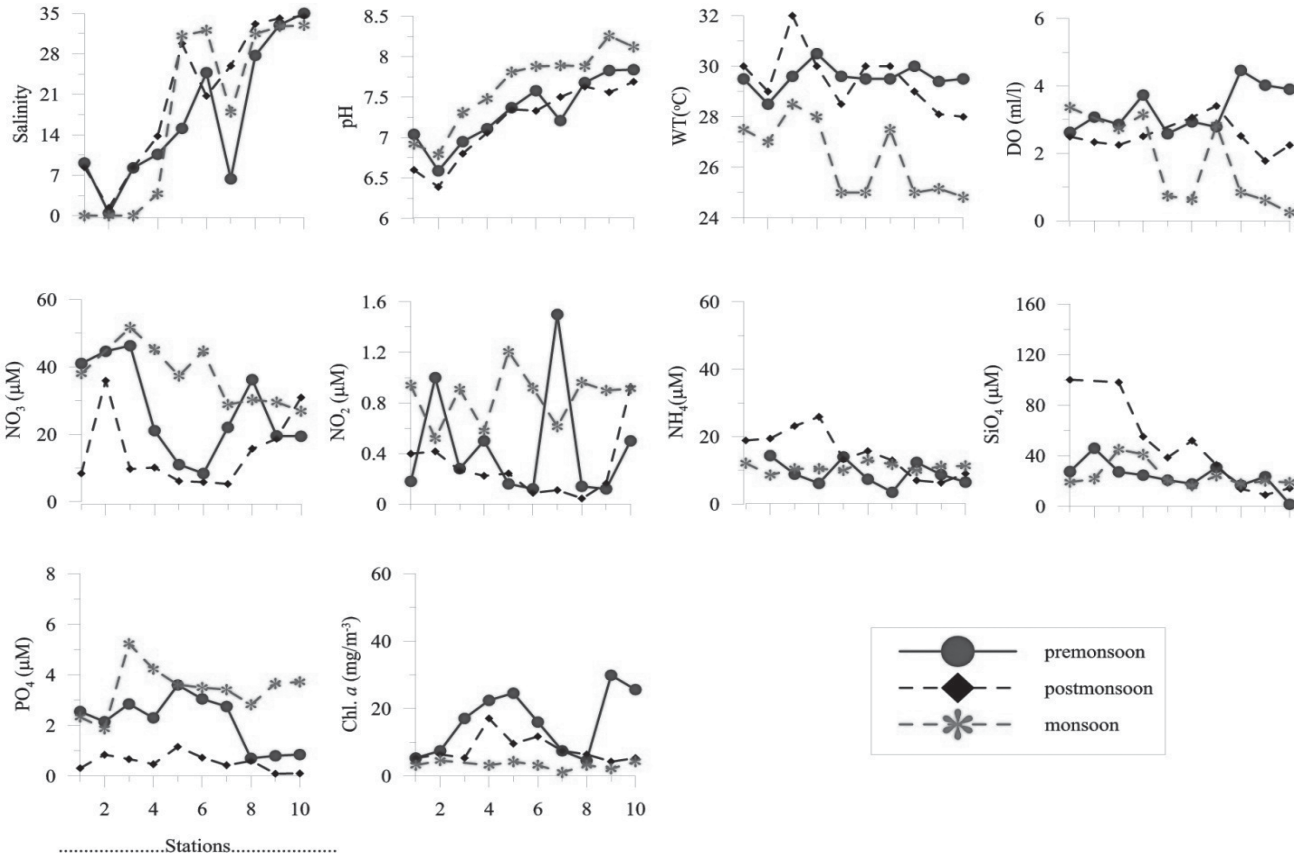

Figure 3: Salinity, pH, Water temperature, Dissolved oxygen, Nutrients and Chlorophyll in the bottom waters of the Cochin estuary

4. Conclusion

The present study deals with the environmental assessment of the central part of the Cochin estuary. The surface waters of the study region were generally rich in dissolved oxygen than the bottom waters. Comparatively high nutrient values and chlorophyll *a* values were recorded in the surface waters of the estuarine region. Whereas the coastal waters were characterized by low nutrient concentrations and low chlorophyll *a* values. Despite the comparatively high intrusion of the nutrient depleted coastal waters, during the study period, considerably high nutrient values and chlorophyll *a* values observed indicate the tendency of the system to be eutrophic and deteriorated. Even though the system is susceptible to hydrographic and biotic disturbances due to the ongoing developmental activities in the study region, its environmental setting is hardly affected, as the observed hydrographic features do not show any significant deviations from the prior observations for the same period.

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Bedia, J., et al. "Iron Catalysts by Chemical Activation of Sewage Sludge with FeCl3 for CWPO." *Chemical Engineering Journal*, vol. 318, June 2017, pp. 224–30. *ScienceDirect*, doi:10.1016/j.cej.2016.06.096.

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