“Preparation of Tailor Made Membranes and Their Performance Study Regarding Hydroquinone Removal from Water”

By
RICHA MODI
(14MCHE10)

DEPARTMENT OF CHEMICAL ENGINEERING
INSTITUTE OF TECHNOLOGY
NIRMA UNIVERSITY
AHMEDABAD-382481
MAY-2016

“Preparation of Tailor Made Membranes and Their Performance Study Regarding Hydroquinone Removal from Water”

Project

Submitted in partial fulfillment of the requirements
For the Degree of

Master of Technology
In
Chemical Engineering
(Environmental Process Design)

By
RICHA MODI
(14MCHE10)

Guided By
Prof MILIND JOSHIPURA

DEPARTMENT OF CHEMICAL ENGINEERING
INSTITUTE OF TECHNOLOGY
NIRMA UNIVERSITY
AHMEDABAD-382481

MAY-2016

Declaration

This is to certify that the thesis comprises my original work towards the degree of Master of technology in Environmental Process Design at Chemical Engineering Department, Institute of Technology, Nirma University and not been submitted elsewhere for a degree. Due acknowledgement has been made in the text to all other material used.

RICHA MODI
(14MCHE10)

Undertaking for the Originality of the Work

Richa Modi (14MCHE10), gives undertaking that the major project entitled **“Preparation of Tailor Made Membranes and Their Performance Study Regarding Hydroquinone Removal from Water”** submitted by me, towards the partial fulfillment of the requirements for the degree of Master of Technology in Chemical Engineering (Environmental Process Design) at Chemical Engineering Department, Institute of Technology, Nirma University, Ahmedabad is the original work Carried out by me and I give assurance that no attempts of plagiarism has been made. I understand, that in the event of my similarity found subsequently with any published work or any dissertation work elsewhere, it will result in severe disciplinary action.

RICHA MODI

Date:

Place: Ahmedabad

Endorsed by

Signature of Guide
Prof MILIND JOSHIPURA
Professor
Department of Chemical Engineering
Institute of Technology
Nirma University

Certificate

This is to certify that the Project Report entitled **"Preparation of Tailor Made Membranes and Their Performance Study Regarding Hydroquinone Removal from Water"** submitted by **Ms. RICHA MODI** (14MCHE10), towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in **Chemical Engineering (Environmental Process Design)** of **Nirma University** is the record of work carried out by her under our supervision and guidance. The work submitted has in our opinion reached a level required for being accepted for examination. The results embodied in this major project work to the best of our knowledge have not been submitted to any other University or Institution for award of any degree or diploma.

Project Guides:

Prof MILIND JOSHIPURA
Professor
Department of Chemical Engineering
Institute of Technology
Nirma University

Dr. AMIT BHATTACHARYA
Sr. Scientist in RO Discipline
CSIR- CSMCRI,
Bhavnagar

Dr. S. S. Patel
Head of Department
Chemical Engineering Department
Institute of Technology
Nirma University

Prof. (Dr.) P. N. Tekwani
Director
Institute of Technology
Nirma University

Examiners:

Date of Examination:

ABSTRACT

Contamination of water has been a serious concern all over the world due to exposure to many sources of pollution creating many harm. The main use of pesticides is for benefit of human being, but sometimes, due to improper handling, it may become the powerful enemy of human. Through water as path pesticides easily goes in direct (drinking water) as well as in indirect manner (in food chain). The consciousness among the people regarding the priority to drink safe water is growing. There are various techniques (viz. active carbon filtration, UVirradiation-H_2O_2) to separate pesticides from water. Membrane separation technique is the one which is of importance as due to inherent characteristics such as low cost energy consumption and simple operation. Thus, Membrane separation technique is one of the "Green Technology".

The pressure driven membrane techniques (as in reverse osmosis, nano-filtration) are basically based on the principle of Osmosis. The interfacial polymerization of m-Phenylene Diamine (MPD) (2% in water) and Tri-Mesoyl Chloride (TMC) (0.1% in hexane) is done on Polysulfone membranes on the asymmetric polysulfone membranes induce the salt rejection property in it. The separation of hydroquinone through the membranes showed trend as i.e. the salt rejection decreases on increasing concentrations of salt, the performance removal of hydroquinone is better increasing. The addition of surfactants also increased the separation performance.

Keywords: Hydroquinone, Reverse Osmosis membrane, Rejection, Water, Sodium Chloride.

ACKNOWLEDGEMENT

I am using this opportunity to express my gratitude to everyone who supported me throughout this Project Report. I am thankful for their aspiring guidance, invaluably constructive criticism and friendy advice during the project work. Therefore we would like to extend our sincere gratitude to all of them.

First of all I am thankful to **Dr. Amit Bhattacharya** (Sr. Scientist in RO division, CSIR-CSMCRI, Bhavnagar, Gujarat) for their provision of expertise, technical support and logistical support and for providing necessary guidance concerning project & implementation.

I am also grateful to **Dr. Paramita Ray** (Senior Principal Scientist DC of RO Membrane, CSIR-CSMCRI, Bhavnagar, Gujarat,) for in the implementation. Without their superior knowledge and experience, the project would like in quality of outcomes, and thus their support has been essential.

I would like to express my sincere thanks towards **Prof Milind Joshipura** (Professor), who devoted their time and knowledge in the implementation of this project.

I am also grateful to **Dr. Jayesh Ruparelia** (Professor & PG Coordinator), who devoted their time and knowledge in the implementation of this project.

Nevertheless, I express my gratitude toward our families and colleagues for their kind co-operation and encouragement which help us in completion of this project.

RICHA MODI
14MCHE10

Table of Contents

List of figures

List of Tables

CHAPTER-1

INTRODUCTION

There is no doubt that water is a precondition for all lives on the earth. It keeps us alive literally while being a prerequisite for an integral part of most of our daily activities. Growing pressure on water resources from population and economic growth, climate change, pollution, and other challenges has major impacts on our social, economic, and environmental well-being. With the advancements of new technologies and industrial growth fresh water resources all over the world is being threatened.

There is no doubt that the quantity of sewage is a global factor. It is seen that two million tons of sewage, industrial and agricultural waste is discharged into the world's waterways. The contaminants in waste water include soaps and detergents, cooking oils, pesticides, paint, gasoline, seawater, pharmaceuticals, solid waste and, of course, human waste. As the fresh water resource is limited, the treatment of waste water is foremost required. It also prevents waterways from disposal.

The world’s water is increasingly becoming degraded in quality, threatening the health of people and ecosystems and increasing the cost of treatment. In one study it is seen that 780 million people around the globe still lack access to clean water and thousands perish daily for lack of it[1]. To preserve the fresh water sources and use it economically, the waste water treatment is one of the pathways in water management.

1.1 Techniques of Waste Water Treatment

Providing safe water to all is a challenging task. Continued research efforts in this area for more than few decades result many process/technologies. There are different techniques (viz. active carbon filtration, ozone treatment, membrane separation) to remediate contaminants of water [2]. In this regard, Membrane separation Technique is one of the promising techniques as it does not environment friendly and energy saving for bulk volume of water.

1.1.2 Membrane Separation Techniques: Membrane separation is the most advanced filtration technology utilized to clarify, concentrate and separate continuously molecular or ionic compounds from their solution state. This process is potentially interesting for water processing, in particular in the treatment or recycling of water polluted by micron, submicron and/ or ionic species [3]. There is a number of membrane-based separation techniques, having different driving forces as concentration gradient, applied pressure and electrical potential.

The main advantages of membrane processes as compared to other separation processes are: low energy consumption, simplicity and environmental friendliness. Thus, no additive is required essentially to proceed the separation. That is why; the membrane technology is termed as "clean technology".

Membrane is a physical barrier that allows certain compounds to pass through it, depending on their physical and/or chemical properties. Different types of membrane filtration processes in use are in the purification of water as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electro dialysis etc.

There are different types of polymer materials (viz. cellulose acetate, polysulfone, Poly ether sulfone, Polyvinylidine difluoride, Polyacrylonitrile) available which are used for preparation of membrane according to their application. In case of membrane purification process the flux and separation of desired product is the most important. Separation can be done by depending upon the differences between the matters to be separated viz. size, shape, vapour pressure, solubility, and so on. Membrane filtration is a very efficient and economical way of separating suspended or dissolved components from feed streams [4].

1.3 Aims and objectives

Out of all contaminants present in waste water an aromatic organic compound hydroquinone, we are separating with the help of membrane in this report, as there are possibilities of water contamination with hydroquinone, as hydroquinone occurs in the environment as a result of man-made processes as well as in natural products from plants and animals. Due to its physicochemical properties, hydroquinone will be distributed mainly to the water compartment when released into the environment. The hydroquinone removal studies from water through membranes are carried out through our tailor made membranes. The performance also studied with different total dissolved solutes (TDS) in terms of sodium chloride.

Hydroquinone, also benzene-1,4-diol or quinol, is an aromatic organic compound basically a type of phenol, a derivative of benzene, having the chemical formula $C_6H_4(OH)_2$. Its chemical structure, shown in figure, features two hydroxyl groups bonded to a benzene ring in a para position.

Figure 1.1 Structure of hydroquinone ($C_6H_6O_2$) [5]

Physical Properties:

M.P. - 172-175 °C (lit.)
B.P. - 285 °C (lit.)
Molecular Mass - 110.11
Density - 1.32 kg/m^3

solubility - H_2O: 50 mg/mL, clear
Water Solubility - 70 g/L (20 ºC)
Stability - Stable [6].

Chemical Properties:

It is a white granular solid or white needlelike crystals or crystalline powder.

General Description-

Light colored crystals or solutions. May irritate the skin, eyes and mucous membranes. Mildly toxic by ingestion or skin absorption.

Air & Water Reactions:

Darkens on exposure to air and light. Miscible in water. Solutions become brown in air due to oxidation. Oxidation is very rapid in the presence of alkali.

Health Hazard-

Hydroquinone is very toxic; The probable oral lethal dose for humans is 50-500 mg/kg, or between 1 teaspoon and 1 ounce for a 150 lb. person. It is irritating but not corrosive. Fatal human doses have ranged from 5-12 grams, but 300-500 mg have been ingested daily for 3-5 months without ill effects. Death is apparently initiated by respiratory failure or anoxia.

Sources of Hydroquinone Contamination-

- Hydroquinone is released to the atmosphere from its production and use, such as during methyl methacrylate manufacture and in the production of coal tar chemicals.
- It may be released in the effluent of photographic processes and from coal gasification condensate water.
- Individuals who develop black and white film may be exposed to hydroquinone, as it is a common component of developing solutions.
- Hydroquinone has been detected in cigarette smoke and in diesel engine exhaust [7].

CHAPTER-2

LITERATURE REVIEW

2.1 Reverse Osmosis (RO)

Reverse osmosis (RO) is an innovative membrane based technology to purify water by separating the dissolved solids from feed stream resulting in permeate and reject stream for a wide arena of applications in domestic, industrial and wide array of applications. Reverse osmosis or other membrane separation processes has an innovative vision which is extremely targeted towards environmental pollution control problems and environmental restrictions. Reverse osmosis has the ability to counter our present day environmental pollution control issues. Membrane separation processes will slowly enhance towards a ground breaking procedure. It is seen from literature review that RO technology is used to remove dissolved solids, colour, organic contaminants and nitrate from feed stream [8].

RO is the most important process of desalination of brackish (1000-5000 ppm salt) or sea water (about 35000 ppm). All dissolved salts, inorganic molecules and organic molecules of molecular weight of approximately 100 Daltons can be removed from water by using RO membranes. It can separate particles of size 0.0001 to 0.001 µm (1 to 10 Å) [4].

2.2 History of Membranes

The word membrane originates from the Latin word ‘membrana’ which means a skin. Membrane is a barrier which separate two phases and restricts transport of various chemical in selective manner. In 1748, Abb'e Nollet defined the term 'osmosis' to describe permeation of water through a diaphragm. In 1887, Traube and Pfeffer developed technique to measure the osmotic pressure solution and behaviour of ideal dilute solution using Van't Hoff equation. Bechhold devised a technique to prepare nitrocellulose membrane of graded pore size, which he determined by a bubble test in 1907. After that, microporous collodion membranes were commercially available by the early 1930s.

The golden age of membrane technology began in 1960 with investigation of the Loeb and Sourirajan for the preparation of first asymmetric skinned cellulose acetate RO membrane. These membranes consist of an ultrathin, selective surface film on a much thicker but much more permeable microporous support, which provides the mechanical strength. By 1980, microfiltration, ultrafiltration, reverse osmosis, electro dialysis, nanofiltration and gas separation processes were developed. The first major development was the Monsanto Prism membrane for hydrogen separation and inorganic membrane dominated by ceramic membrane found in large scale commercial application [4].

2.3 Pressure- Driven Filtration Techniques

Membrane separation techniques are driving force dependent. Depending upon the applied driving forces it can be categorized as pressure driven filtration technique, electrical potential dependent, concentration gradient dependent, thermal dependent etc. Pressure - driven separation processes are widely used in different applications. In case of water desalination and purification pressure-driven separation techniques are mostly used. The separation ranges of pressure-driven techniques are mentioned in the figure. Depending upon the size of the solutes different techniques should be applied. Following are the various kinds of pressure-driven techniques:

Microfiltration (MF)

MF is widely used for separation of suspended particle, bacteria, fragmented cell or colloids from solution using membrane pore size approximately 0.1 to 10 µm. MF done by size exclusive mechanism, reject particle size of 0.2 to 10 µm at low operation pressure 0.2 to 3.5 bar. It's removes little or no organic matter. These membranes are used for the treatment of high organic loading water, cutting oil emulsion and juice, wine or beer clarification and recovering precipitated metals.

Ultrafiltration (UF)

UF is pressure driven process in which water and low molecular weight substances pass through the membrane while high molecule species are retained. It provides macro-molecular separation up to 10 nm size. Colloids, proteins, microbiological substances can be removed by UF processes.

Nanofiltration (NF)

NF membranes have a nominal pore size of approximately 0.001 microns and MWCO of 1,000 to 100,000 Daltons. NF occurs mainly due to electrostatic interaction and also by size exclusion. It rejects neutral molecules by size exclusion and multivalent salts by electrical charge. NF can remove nearly all cysts, bacteria, viruses, and humic substance. Dissolved salts can also beremoved in certain extent.

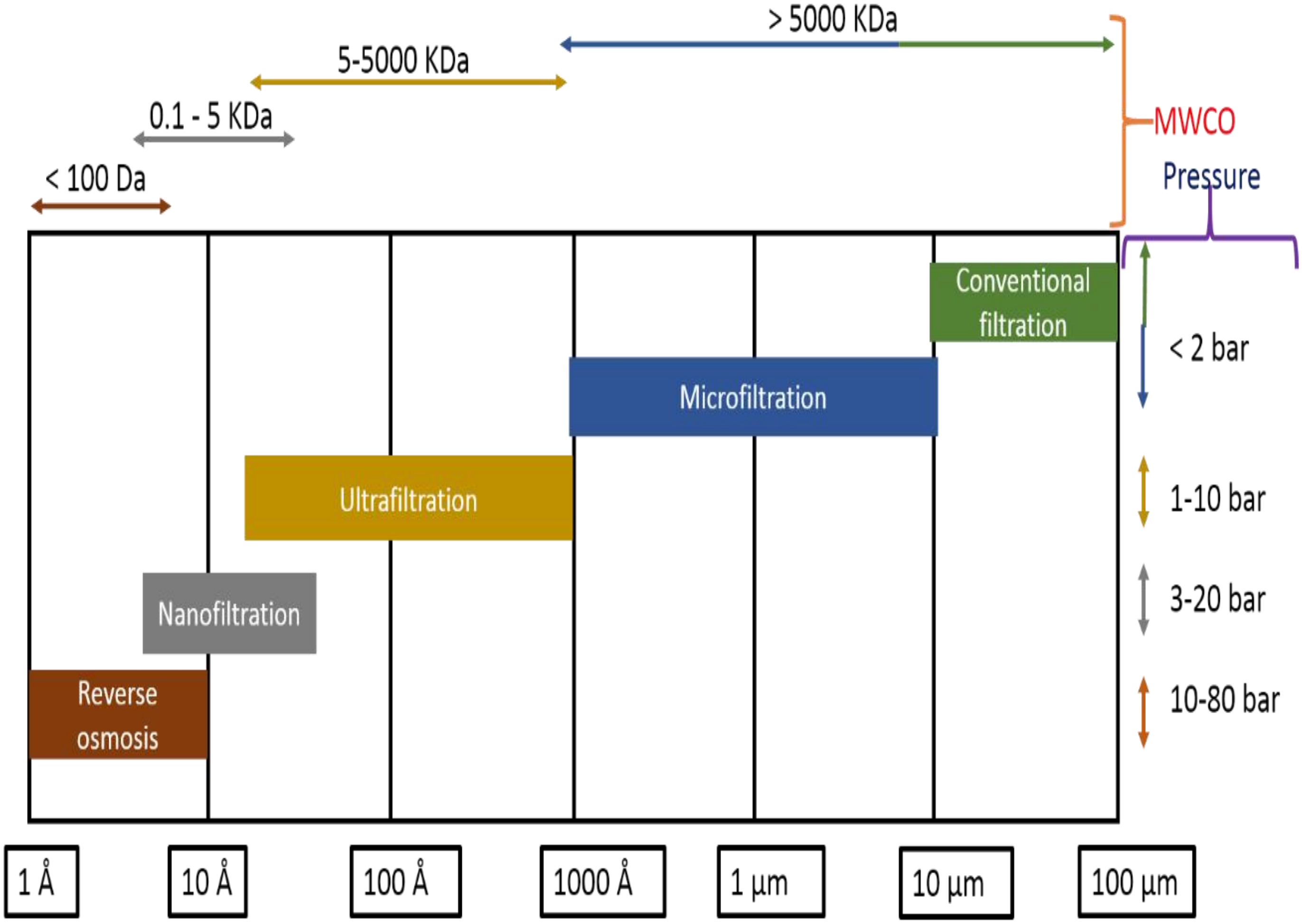

Figure 2.1 Separation ranges of different pressure-driven membranes

2.4 Classification of Membranes

Synthetic membranes can be fabricated from organic or inorganics which include metal or ceramic (aluminium oxides, silicon carbides, zirconium oxides), homogeneous or heterogeneous polymer films and liquids. Ceramic membranes chemically, thermally, mechanically very stable, biologically inert, eco-friendly and have long working life span. Liquid membranes refer to synthetic ones where liquid layer works as a separation barrier.

In case of pressure-driven separation processes, polymeric materials are mainly used. The tailor-made features make the polymeric membranes very attractive in the separation field. Polymeric membranes can be of various thickness having homogeneous or heterogeneous structure. Depending upon the way of preparation various types of membranes can be formed with different structures.

2.4.1 Symmetric membranes-

Symmetric membranes are homogeneous in nature. These membranes have uniform structure throughout the entire membranes. The porous structure may be cylindrical, web or slit in shape. Thicknesses of these membranes are relatively higher and thus have only limited application in gas separation and electro dialysis.

2.4.2 Asymmetric membranes-

Asymmetric membranes are heterogeneous in nature. These membranes can be categorized as

i. Integral-asymmetric with a porous layer.
ii. Integral-asymmetric with a dense skin layer.
iii. Thin-film composite membranes.

Porous integral-asymmetric membranes are used in ultrafiltration, microfiltration, and dialysis whereas integral-asymmetric membranes with a dense skin layer are used in the reverse osmosis and gas separation.

2.5 Polysulfone (Characteristics, Properties)

Polysulfone, as polymer material, has been produced since 1960s. The presence of phenoxy phenyl sulfone in the Polysulfone chain makes it special. It is one of the important materials in the membrane science and technology. The reason for it is the appliance of polysulfone to a high glass transition temperature polymer of high mechanical, thermal and chemical resistances. Polysulfones are used in the preparation of asymmetric membrane with different pore sizes (microfiltration and ultrafiltration membranes) in the active layer [9].

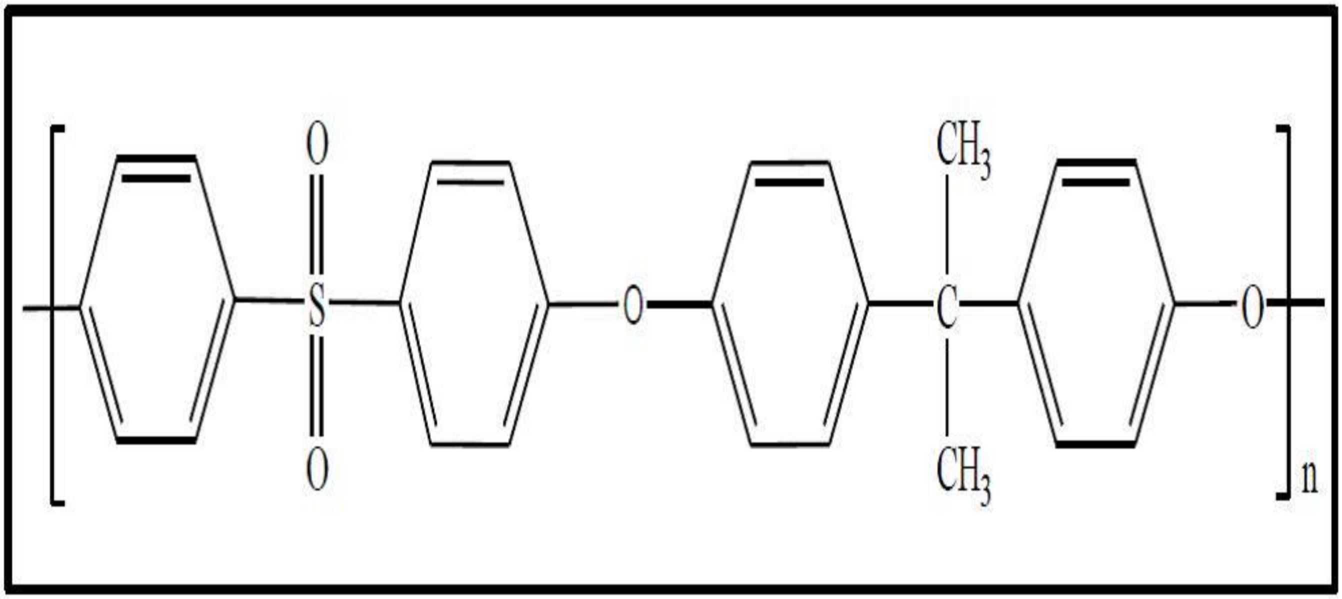

Figure 2.2 Chemical structure of Polysulfone [4]

Polysulfone has:

- Excellent resistant to inorganic acids and bases,
- Withstands repeated exposure to steam sterilization,
- Resistance to hot water,
- Good thermal properties,
- Can be used for food, water and medical applications [4].

In our study, the TFC RO membrane is comprised of top ultra-thin skin polyamide layer, polysulfone porous support. Non-woven fabric is used for better mechanical strength. The membranes are extensively used for water desalination and other industrial applications. The top polyamide layer is the selective layer which is responsible for permeability and selectivity.

2.6 Polysulfone Membranes Preparation by Immersion Precipitation / Wet Phase Inversion

Polysulfone membranes are prepared from conventional wet-phase inversion technique. In this technique a polymer solution is cast into a film and then the polymer precipitates by immersion into a non solvent; the non solvent (water, for example) rapidly precipitates the polymer on the surface of the cast film, forming the very thin, and dense skin layer of the membrane. The polymer beneath the skin layer precipitates more slowly, results in a more porous polymer sub layer [10].

The wet phase inversion technique allowed formed asymmetric porous membrane. In this technique initially homogeneous polymer solution becomes thermodynamically unstable and phase separates into “polymer-poor” and “polymer-rich” phases. The polymer poor phase forms the membrane pores and polymer rich, solid phase forms the membrane homogeneous structure. Wet phase technique porous membrane formed by diffusion exchange between solvent and non-solvent in the polymeric substrate .Polymer membrane is cast on a non-woven polyester fabric because fabric is provide more stability, tautness and fabric have highly porous structure [4].

2.7 Preparation of Asymmetric Polysulfone Membrane By Machine Casting

Polysulfone (PSf) membranes were prepared by conventional phase- inversion technique. PSf membranes (15 w/w %). were prepared. Homogeneous PSf solutions were prepared by dissolving PSf in DMF at 60˚C with constant stirring. After the homogeneous mixing of PSf it was kept 3-4 h for the complete removal of air bubbles. Thereafter the solutions were casted on polyester fabric fitted on proto- type casting machine and immediately immersed into a non-solvent gelation bath containing RO water. This results in the de-mixing of solvent (DMF) and non-solvent (water) which leads to the formation of membrane. Schematic of the preparation of membranes are presented in the following scheme.

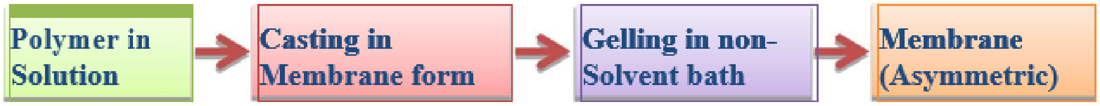

Figure 2.3 Different steps in preparation of Polysulfone membrane in Special Casting Machine [4].

2.8 Thin film composite membranes (TFC)

TFC are typically made out of a thin polyamide layer deposited on top of a Polysulfone porous layer on top of a non-woven fabric support sheet. The three layer configuration gives the desired properties of high rejection of undesired materials (like salts), high filtration rate, and good mechanical strength. The polyamide top layer is responsible for the high rejection and is chosen primarily for its permeability to water and relative impermeability to various dissolved impurities including salt ions and other small, unfilterable molecules.

2.8.1 Preparation of Thin film composite membranes

Polyamide composite membranes are prepared by the interfacial polymerization of m-Phenylene Diamine (MPD) and Tri-Mesoyl Chloride (TMC) on the surface of the prepared polysulfone membranes. The interfacial polymerization of m-Phenylene Diamine (MPD) (2% in water) and Tri-Mesoyl Chloride (TMC) (0.1% in hexane) is done on Polysulfone membranes surface (14 x 11 cm) fitted on glass tray and cured at temperature 80°C for 2 minutes.

The thin film composite membranes are capable of desalting the water. The vast use of thin film composite membranes in terms of desalination membrane has prompted us to separate organics from water. Our first approach is to see the potentiality regarding the separation of electrolytes. In this regard the performances of salt separation of the membranes are included.

2.9 Theories of Transport of Salt In Membranes

By applying appropriate theory, it is possible to correlate the transport of solvent and solute with the structural parameters of the membrane, i.e., porosity, pore size, charge density and effective thickness of the rejection layer.

Brief features of some of these theories are –

SOLUTION-DIFFUSION: Transport mechanism is that ions & solvent dissolve in the polymer matrix of the membrane & diffuse independently (uncoupled) of each other through the membrane.

KIMURA-SOURIRAJAN THEORY: Solvent preferentially absorbs at the membrane solution interface. It then moves through the capillaries of the membrane by viscous flow in which the flux is directly proportional to the effective pressure. The solute passes through the pores of the membrane by diffusion.

EXTENDED NERNST PLANCK: Convection, diffusion & electrical potential gradient control the movement of ions through the membrane pores. The ions show selectivity by Donnan partitioning & steric effects.

2.10 Separation of Pesticides from water

The pesticide water pollution is a threat to mankind. Different potential techniques are mentioned here to purify the pesticide polluted water. Of them, membrane separation techniques made a major breakthrough in the remediation of pesticide polluted water. The use of membranes has clear advantages over the other methods. It is economical, needs less energy and thus makes the environment less polluted. The clean technology is recently the subject of attention. Pressure driven membrane techniques (as reverse osmosis, nanofiltration) are based on the principle of Osmosis. [4].

CHAPTER-3

MATERIALS AND METHODS

3.1 Materials

Polysulfone (Udel, P-3500, Solvey Advanced Polymers, USA), N, N, Dimethyl Formamide (Loba Chemie,India), Non-Woven polyester fabric (Filtration Sciences Corp.,USA), are used to prepare the asymmetric Polysulfone membrane. m-Phenylene Diamine (Across, India) and Trimesoyl Chloride (Aldrich, India) are used for the preparation of thin film composite (TFC) membranes (interfacial polymerization).

Hydroquinone (Sisco) the prime material is used. Reverse osmosis treated water is used in the experiment. Sodium chloride (CDH) is used for the salt rejection performance of the membranes. Sodium lauryl sulphate (SLS i.e. anionic) (Fisher Scientific) used as surfactants to study the effect in hydroquinone separation of the membranes.

3.2 Methods

3.2.1 Preparation of Asymmetric Polysulfone Membranes

Polysulfone membranes are prepared from conventional wet-phase inversion technique. A homogeneous solution of Polysulfone of 15% (w/w) in dimethyl formamide is prepared by slow dissolution of Polysulfone beads at 45°C by continuous stiring. Thin film of polysulfone solution is casted over the non-woven polyester fabric by moving the fabric over the guide roller using a proto-type casting machine as shown in Figure below schematically. The polymeric solution casted on fabric is then immersed into the non-solvent gelation bath which is water here. This results in the de-mixing of solvent (DMF) and non-solvent (water) which leads to the formation of membrane

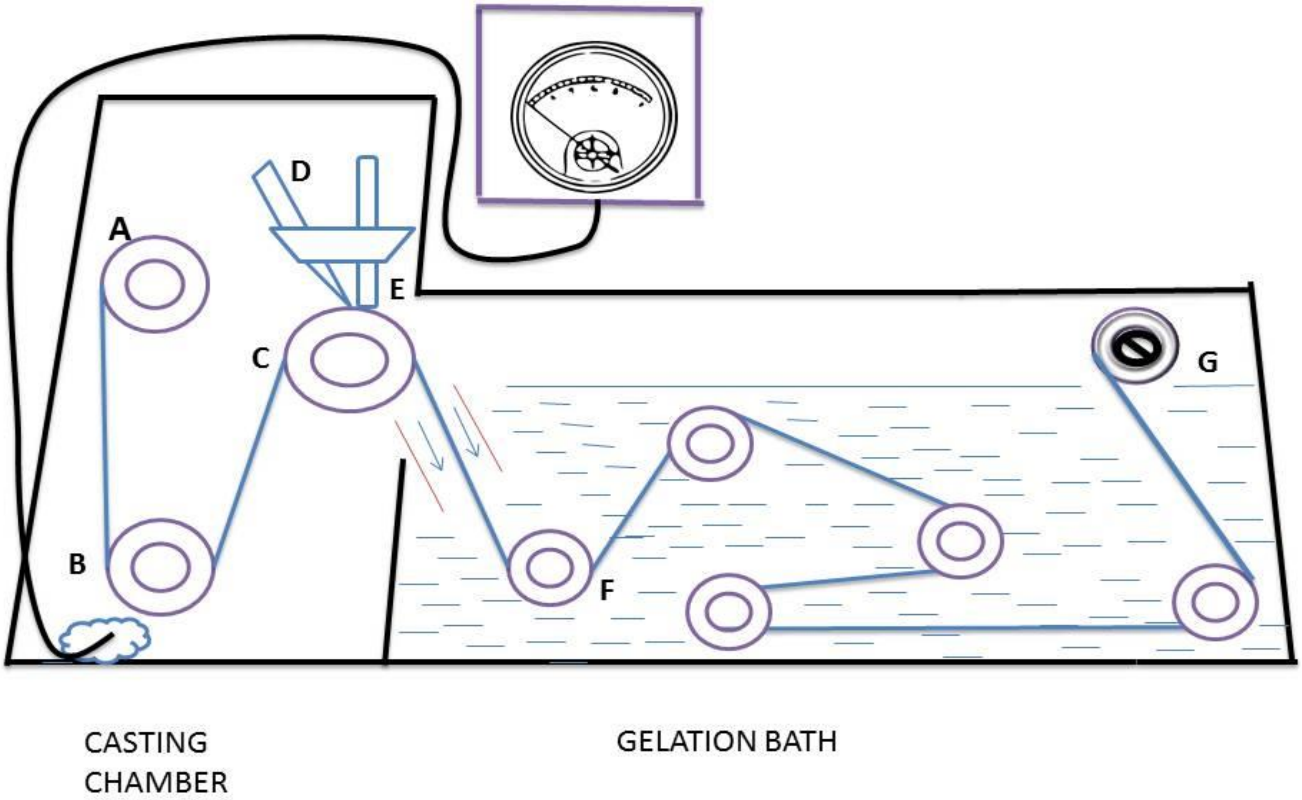

Figure 3.1 Schematic presentation of special casting machine for preparation of polysulfone support membrane.

A. Mounting roll, B. Speed control sensor, C. Casting blade, D. Micrometer, E. Gelation bath, F. Non solvent water, G. Receiving roller, H. Speed control device**.**

3.2.2 Preparation of Thin film composite membranes

Polyamide composite membranes are prepared by the interfacial polymerization of m-Phenylene Diamine (MPD) (2% in water) and Tri-Mesoyl Chloride (TMC) (0.1% in hexane) on the surface of the prepared polysulfone membranes (14 x 11 cm) fitted on glass tray and cured at temperature 80°C. The schematic presentation of the thin film composite membrane along with the reaction pathways are presented in the figure below.

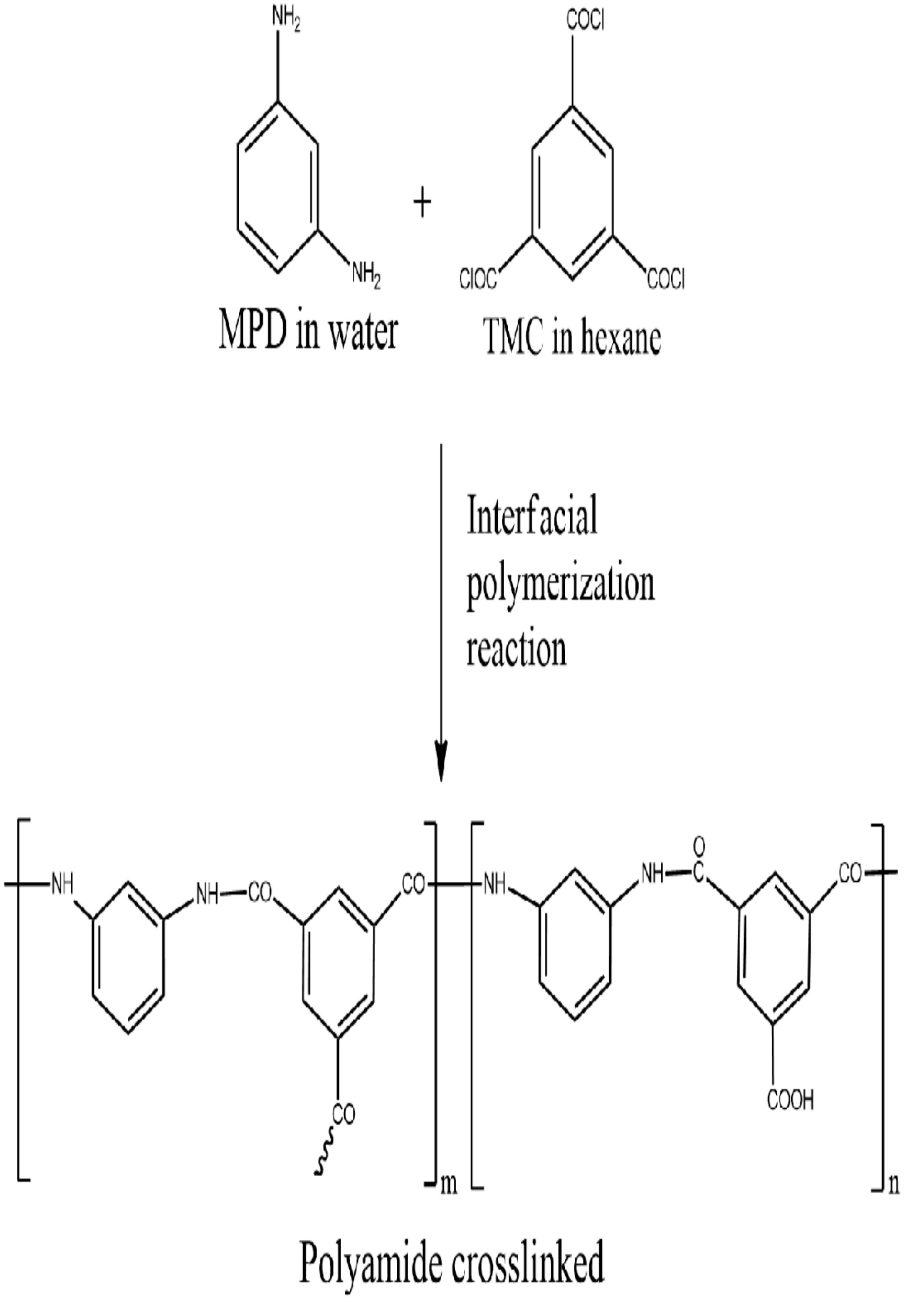

Figure 3.2 Formation of Thin Film Composite Membrane [11]

3.2.3 Preparation of Hydroquinone solution

An appropriate amount of Distilled Water is taken to dissolve 5mg/L Hydroquinone. Different Concentrations of salt Sodium Chloride (200 to 1000 mg/L) are added in to the feed solution separately to study the effects in separation performances.

3.3 Analytical tools and techniques Used

The techniques adapted in this particular study are as follows:

3.3.1 Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

FTIR offers quantitative and qualitative analysis for organic and inorganic samples. Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information [12].

In this study, ATR-FTIR (Perkin Elmer Spectrum GX with a resolution ± 4 cm^{-1} incident angle 45°) is carried out to get the evidence of newer functional groups on Polysulfone & Thin Film Composite Membranes.

3.3.2 Scanning electron microscope

SEM is an imaging / scanning microscope which uses electron beams to get information about the surface of the sample. The primary electron beam interacts with the matter and produces the secondary electrons as signals which contain information about the surface of the sample. This is very much useful in having as insight about the sample’s surface topology or morphology. The surface of the sample to be analyzed should be conductive to interact with electrons else it is made conductive by coating a fine layer of gold by sputter coater. The images obtained are black and white as no visible light is employed.

Here in this study morphological pattern of Polysulfone & Thin Film Composite Membranes is characterized by Scanning electron microscopy to have an insight about the surface topology and cross section of the membranes. Scanning Electron Microscope (SEM) images of the samples were taken using JSM-7100 F.

3.3.3 Contact angle

Contact angle measurements are done by sessile drop method (DSA 3, KRUSS, Germany) at room temperature (25°C). The membrane sample is fixed on the glass plate to be analysed. The water drop of 1μl is placed onto the membrane surface by a micro-syringe pointed vertically down onto the sample surface. To avoid the penetration of the water drop into the membrane pores, the drop image is immediately captured, recorded and then analysed by using image analysis software. The average value is obtained from at least 10 measurements tested for each membrane. Here in this study contact angles are done to characterize the nature of membrane surfaces in terms of hydrophobicity and hydrophilicity.

3.3.4 High Performance Liquid Chromatography

HPLC stands for “High-performance liquid chromatography” (sometimes referred to as High-pressure liquid chromatography). HPLC is a chromatographic technique that can separate a mixture of compounds. HPLC is the advanced technique of chromatography which is based on the principle of adsorption and partitioning. It is a form of column chromatography used frequently to separate, identify, and quantify compounds based on their characteristic polarities and interactions with the stationary phase in the column. High performance liquid chromatography is a powerful tool in analysis, it yields high performance and high speed compared to traditional columns chromatography because of the forcibly pumped mobile phase.

3.3.5 Zeta Potential

The zeta potential is indicates the stability. The value of zeta potential denotes the degree of electrostatic repulsion existing between adjacent, similarly charged particles in a dispersion When the potential is small, attractive forces may exceed this repulsion and the dispersion may break and flocculate here, Zeta Potential of TFC is carried out.

3.3.6 X – Ray Diffraction (XRD)

It is a novel and non destructive method of chemical analysis and a variety of x –ray techniques are available in practice. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. It is based on the scattering of x-rays by crystals.

X-ray diffractometer (PANalytical Empyrean), Cu K α radiation as monochromator was used to prove the changes the relative amorphous character for the respective membranes**.** XRD is a technique to identify crystalline phases and orientation, structural properties, thickness of thin films and multi-layers, atomic arrangement. Here, XRD of both Polysulfone & TFC is carried out & relevant peak is obtained.

CHAPTER-4

RESULTS AND DISCUSSIONS

The preparation of asymmetric membrane can be done by different methods, of them, wet phase inversion is employed a lot as it is simple and low cost one. In the phase inversion technique the chemistry plays between the polymer: Polysulfone and its solvent: N, N dimethyl formamide and non-solvent water.

The choice of Dimethyl formamide solution for dissolving the Polysulfone is preferred because of its slow dissolution and it does not lead to fast and poorly controlled non-homogeneous deformation [13].

4.1 Characterizations based on analytical tools

4.1.1 Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

Figure 4.1 shows the FTIR-ATR spectra of the (a) Polysulfone membranes .The strong reflectance at 1586-1400cm^{-1} is related to the benzene ring stretching mode.The sulfone bands can be observed at 1152cm^{-1}.Asymmetric C-O stretching frequencies occur at 1324 and 1239cm^{1}.

In Figure 4.1 (b) the 1648cm^{-1} peak is observed because of C=O stretching polyamide structure, the C-N stretching at 1546cm^{-1} and amide (polyamide peak at 786cm^{-1} shows the presence of Polyamide (cross-linked) structure on the thin film composite (TFC) membrane .

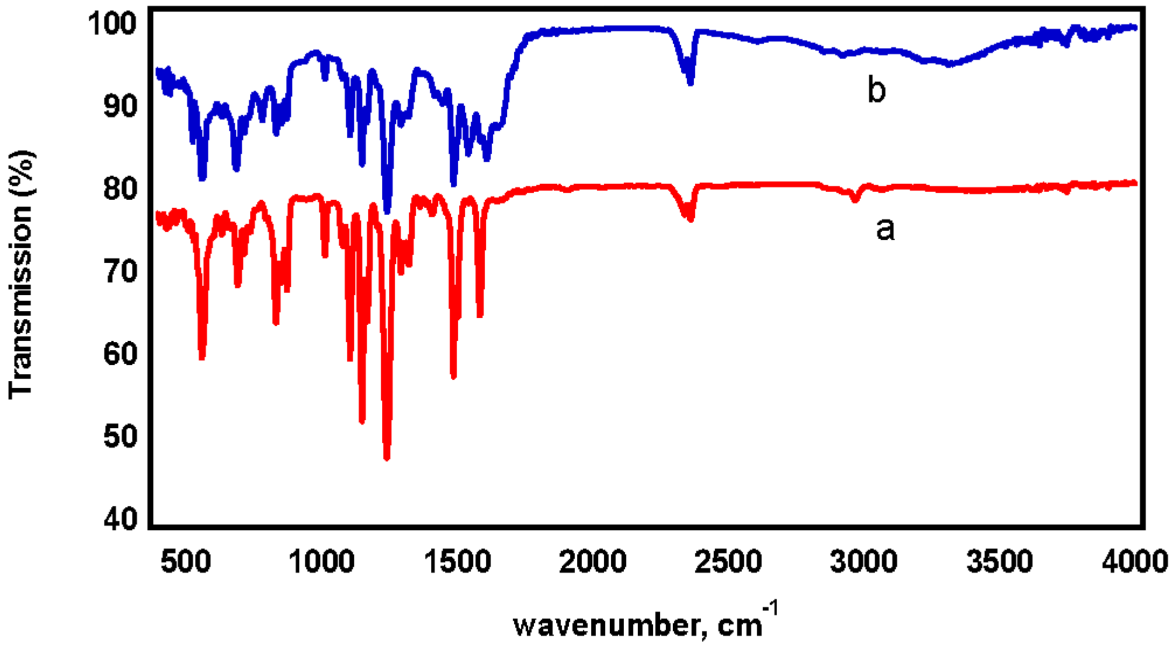

Figure 4.1 FTIR-ATR spectra of Polysulfone (a) and thin film polyamide composite (b) Polysulfone membranes

4.1.2 Contact Angle

Polysulfone is hydrophobic in nature. The contact angle study shows that the water is favorably tried to retain its structure as droplet, rather than spreading over the membrane surface.

In the TFC, due to the polyamide formation the topographic surface is relatively hydrophilic in nature.It means the drop is rather spreaded. The measurement of contact angles shows that Polysulfone is having contact angle 74.12° where as the TFC shows contact angle 60.32°. The schematic diagram is shown in Figure 4.2.

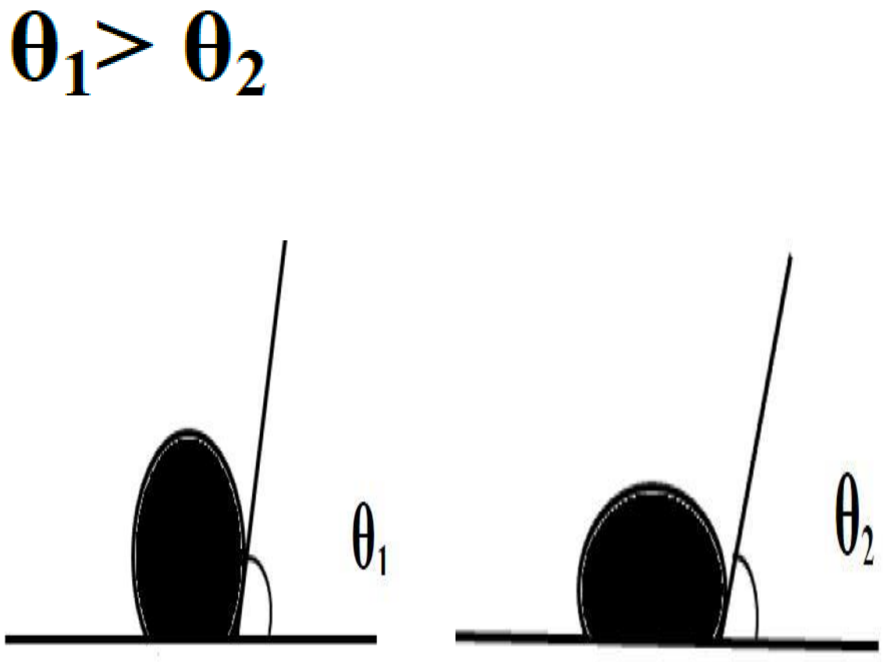

Figure 4.2 Schematic presentation of hydrophobic (Polysulfone) (a) & hydrophilic (TFC) (b) surface in terms of contact angle.

4.1.3 Scanning Electron Microscope

The Scanning Electron micrograph study shows that there is distinct difference in the morphology of the virgin Polysulfone membrane (Figure 4.3 a) and thin film composite membranes (Figure 4.3 b).

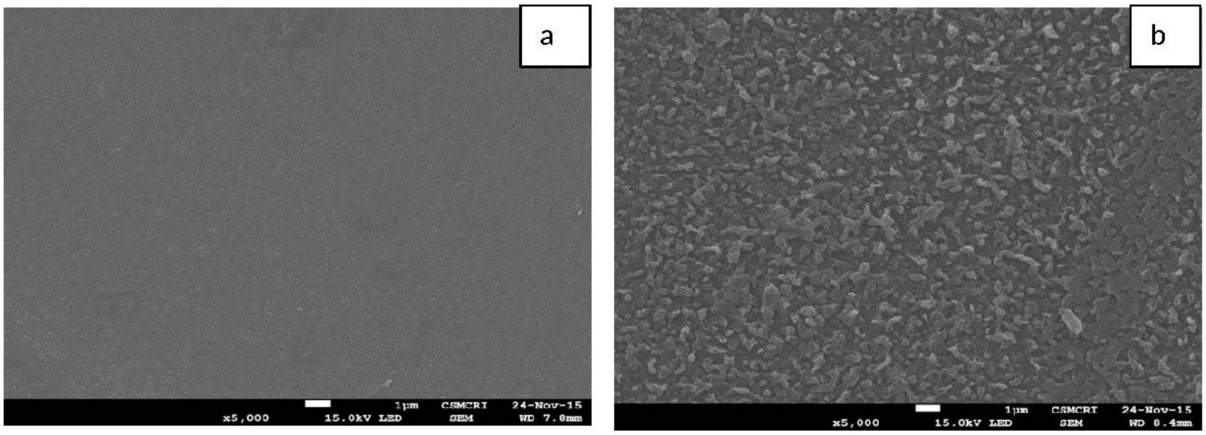

Figure 4.3 Scanning electron micrograph of (a) PS (b) TFC membranes

4.1.4 Zeta Potential

The zeta potential is carried out by making 0.1m (M) solution (i.e. 0.149 gm/2L) of KCl in neutral, basic & acidic medium. In acidic at pH=3.42, (4.74): in neutal at pH=6, (-13.9 mV) & in basic at pH=9.5 (-17.04) as shown in table 4.1

Table 4.1 Showing values of Zeta Potential

pH	**mV**
3.42	4.74
6	-13.9
9.5	-17.04

4.1.5 X – Ray Diffraction (XRD)

XRD of both Polysulfone & TFC is carried out & same peak is obtained. The peak is due to X-ray diffraction from the {19} planes as shown in figure 4.4, for both PS &TFC membranes.

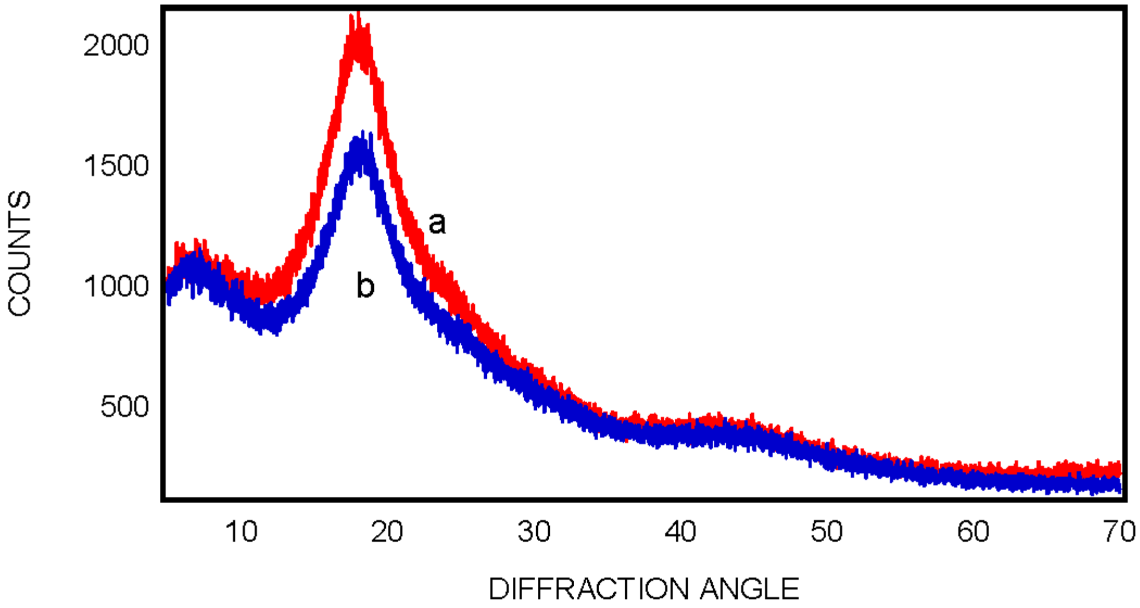

Figure 4.4 Showing XRD pattern of both PS & TFC

4.2 Characterizations in terms of separation performances

4.2.1 Based on Salts

The salt rejection performances of thin film composite membranes were performed. The transport phenomena of salt through the thin film composite membrane can be explained by different theories (preferential sorption, electrical) [14]. The preferential sorption theory was suggested by Kimura and Sourirajan [15]. In their view solvent will preferentially sorp (in this case water) on the membrane flows through the capillary motion through it and thus the separation occurs. In chemistry perspective the formation of –COOH functionality in the cross-linked polyamide is the key to repel the salt and as well as polar compounds [16].

To compare the performance of the membranes different salts concentration viz. (200, 500, 800, 1000 ppm) have taken. For evaluating the separation performance of membrane, first the membrane is cut in area of 0.00159 m^2, then dip this membrane in RO water for 24 hrs. Now the membranes are operated in Cross Flow Filtration Kit.

$$J_W=\frac{Q_p}{a}=A(\Delta p-\Delta\pi)$$

Where,

J_W is Water flux ($Lm^{-2}h^{-1}$),

Q_p is Permeate i.e. product water flow rate,

a is membrane area,

A is water permeability coefficient,

Δp is operation pressure,

$\Delta\pi$ is osmotic pressure difference between feed & permeate solution.

$$\Delta\pi = BRTC_S$$

Flux B is the number of dissociated ions from the dissolved solute (salt).

ΔC_S is salt concentration difference upstream & downstream.

The salt passage rate through the membrane can be described using the solution diffusion as

$$J_S = J_W C_P = B\Delta C_S$$

J_S is salt flux,

B is salt permeability coefficient for a given salt solution system.

The salt rejection (%) & permeate flux under various salt concentrations are assembled in table 4.2. Under an operating pressure of 200 psi, the permeate flux decreased from 2.283 lmh ($l/m^2/h$) to 13.207 lmh($l/m^2/h$) as NaCl concentration increasing from 200 ppm to 1000 ppm.

Table 4.2 The salt rejection (%) & permeate flux (ml) under various salt concentrations.

Membrane	200 (mg/L) (ml/20min)	500 (mg/L) (ml/20min)	800 (mg/L) (ml/20min)	1000 (mg/L) (ml/20min)
I	89% (10)	75% (14)	64.3% (07)	58.9% (07)
II	83% (10)	75% (13)	74.86% (09)	60.8% (07)
III	90.3% (12)	79% (11)	64.3% (10)	57.4% (07)
IV	84% (11)	79% (09)	62.4% (10)	58.03% (06)

The decrease was due to higher osmotic pressure $\Delta\pi$ at a higher salt concentration, reducing the net driving force (Δp - $\Delta\pi$) as shown in the equation.

$$J_W = A(\Delta p - \Delta\pi)$$

The salt flux (J_S) was calculated from the permeate flux (J_w) & salt concentration in the permeate

(C_P) by equation as:

$$Js = J_W C_P$$

It is obvious that increasing salt concentrations enlarges the salt concentration difference (ΔC_S) between feed & permeate. It also increases the salt flux (J_S) due to higher salt concentration across the membrane. As shown in table 4.3, average rejection, flux & conductivity.

Table 4.3 Data showing Average Rejection, Flux & Conductivity.

Parameters	**200 (mg/L)**	**500 (mg/L)**	**800 (mg/L)**	**1000 (mg/L)**
Rejection average (%)	86.575	77	66.465	58.7825
Flux (ml/20 min)	10.75	10.25	09	07
Flux (J_W) ($lm^{-2}h^{-1}$)	20.283	19.3396	16.98	13.2075
Conductivity (C_P) (m/cms^2)	26.85	115	268.28	412.175
Flux (J_S)	544.5986	2224.054	4555.394	5443.801

It demonstrates that the flux increased with the salt concentration difference, with slope equal to salt permeability coefficient (B) as:

$$J_S = B(\Delta C_S)$$

The estimated B value from figure was 2.28*10^4 gm^{-2} sec^{-1} at 25^0C & operating pressure of 200 psi. B is the salt permeability coefficient membranes.

4.2.2 Based on Hydroquinone with the addition of salts in different water matrix

At neutral pH-

An appropriate amount of Distilled Water is taken to dissolve 5mg/L Hydroquinone. Different Concentrations of salt Sodium Chloride (500,800 and 1000 mg/L) are added in to the feed solution separately. It was observed that the salt separation decreases with increase in its concentration from 500 to 1000.

The hydroquinone separation is in decreasing trend in the presence of salt concentration varying from 500, 800, 1000 ppm. The performance behavior can be explained by the factors (viz. Pore swelling, salting out). The repulsion between the ions in the pores makes it effectively more size and thus the separation of hydroquinone falls. In simple view the ‘salting out’ is the competition of water of hydration between the organics and salt molecules. It causes the loss of hydration of the organics and thus decreases the hydrated size of the feed solutes. The active size of the molecules has the spontaneity to pass through the membrane and as a result separation decreases. The variation of the flux is also in decreasing trend. The rejection and flux data obtained are shown in figure 4.5.

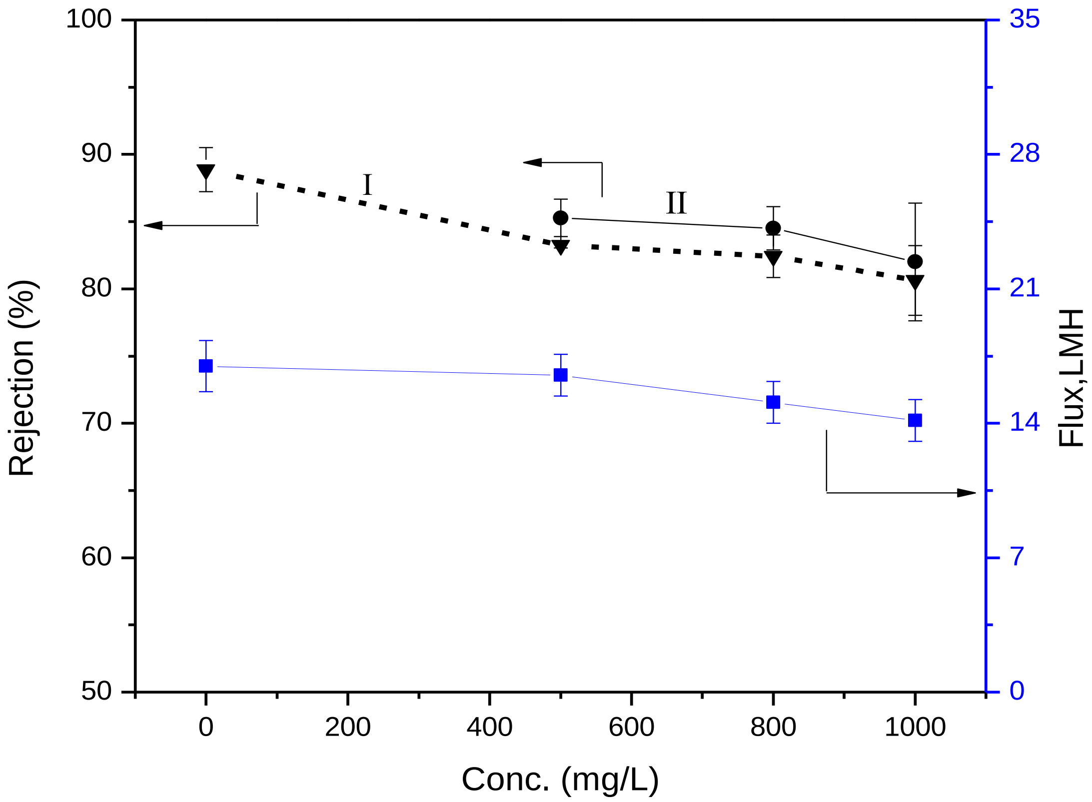

Figure 4.5 Separation performance of hydroquinone in different NaCl concentrations (I) and NaCl (II) at pH 6.4 through thin film composite membrane

At acidic pH-

The variation of membrane separation performances of hydroquinone mixed with different concentrations of NaCl (viz. 500, 800, 1000) in acidic pH is studied. The pH effect is much more prominent in NaCl separation. The decrease is pronounced in low pH, though the rejection of NaCl decreases with rising NaCl concentration.

The H^+ rejection increases as pH increases in permeate. This is reflected from pH studies. The competitive rejection of Na^+ (i.e. NaCl) decreases. Though the hydroquinone separation in NaCl in acidic pH shows similar behavior as in neutral pH, but the decrease is not so much reflected, as the NaCl separation is prominent.

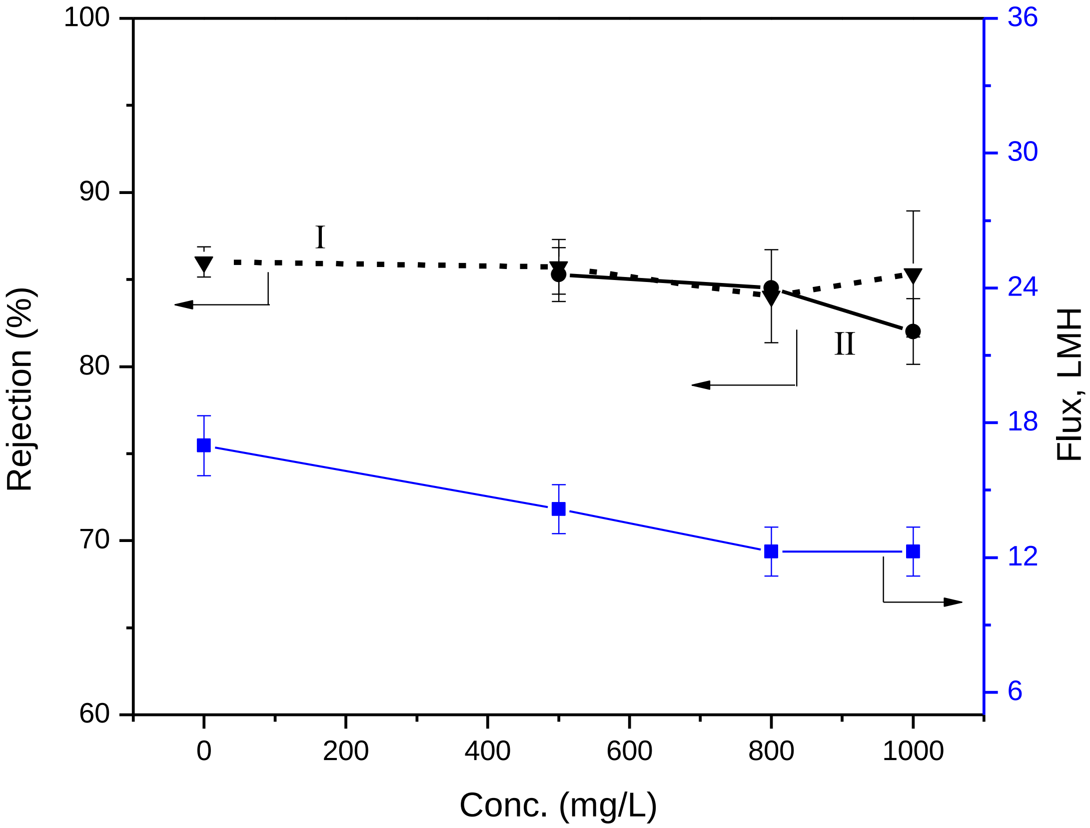

Figure 4.6 Separation performance of hydroquinone in different NaCl concentrations (I) and NaCl (II) at pH 3.5 through thin film composite membrane

CHAPTER-5

Energy Saving Technique

5.1 To increase the separation performance of Hydroquinone through membrane by:

5.1.1 Addition of Chemicals (Surfactants):

With the addition of surfactants the hydroquinone separation will be influenced. The physicochemical properties of surfactants in aqueous solution, when concentration is slowly increased, in general vary continuously with the amount of surfactant.

As we know that surfactants are those compounds which lower down the surface tension between liquid-liquid or between liquid and solid. Aqueous Surfactants are mainly organic compounds containing hydrophobic groups at their tails as well as hydrophilic groups as head are mainly classified on the basis of their nature (viz. anionic, cationic and non-ionic). Thus, surfactant having both water insoluble and water soluble component.

On adding surfactants into hydroquinone solution, the systems get partition into interface and reduce system’s free energy as they:

1. Lowers down the energy of the interface (energy of the interface is area times surface tension),
2. Removes the hydrophobic parts of the surfactant which is in contact with hydroquinone water solution.

Here, we are adding sodium lauryl sulfate (SLS) surfactant to 5mg/l in hydroquinone solution basically in distilled water at varying surfactant concentration viz.50, 100, 150, 200 and 250 mg/l. SLS is an anionic surfactants having an anionic functional groups at their head as sulfate.

To enhance the separation performances of membranes for hydroquinone separation, man-made surfactants (viz. sodium lauryl sulphate (anionic, critical micelle concentration (cmc): $8x10^{-3}$ mol/L) is used.

Critical micelle concentration (cmc) is that concentration at which surfactant molecules associates into small aggregates called micelles and is the crucial physical parameters of the surfactants. On diluting surfactant solution below the cmc results in non associated surfactant molecules.

5.2 Basic property of SLS-

General: Sodium lauryl sulphate (SLS) is basically a form of synthetic detergent used as a cleaning agent and as surfactant (used for bubbles making). SLS is of high pH. SLS is derived from coconut and palm oils which are not so expensive; therefore SLS is a cheap and an effective cleansing and foaming agent [17].

Structural Formula: CH_3- $(CH_2)_{11}$-O-SO_3-Na^+

Appearance: White powder

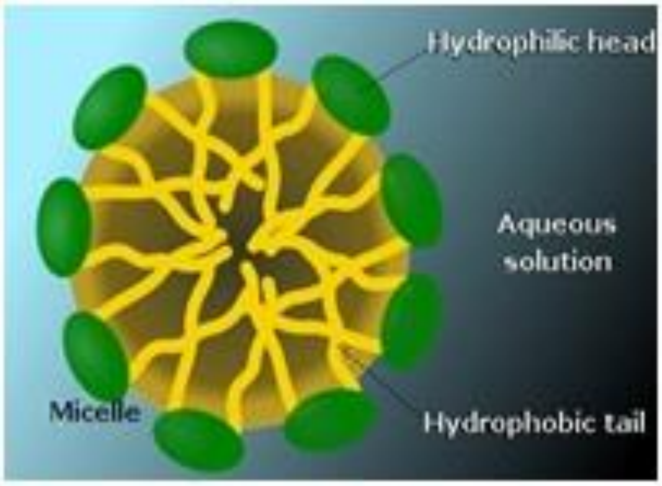

Figure 5.1 Illustration of a micelle [17].

Here, the study is carried out well before cmc values of surfactants, considering low pressure driven TFC membrane. Addition of SLS exerts significant influence in hydroquinone separation. The separation performance is depicted in Table 5.1. Shows improvement in separation performance with the increase in SLS concentrations.

Table 5.1 Data showing the obtained Rejection.

50 (mg/L) **(ml/20min)**	**100 (mg/L)** **(ml/20min)**	**150 (mg/L)** **(ml/20min)**	**200 (mg/L)** **(ml/20min)**	**250(mg/L)** **(ml/20min)**	**5 (mg/L)** **(ml/20min)**
Hydroquinone +SLS	**Hydroquinone +SLS**	**Hydroquinone +SLS**	**Hydroquinone +SLS**	**Hydroquinone +SLS**	**Hydroquinone**
79.7% (13)	86.0 % (12)	89.2% (11)	90.9% (11)	94.8% (13)	79.2% (12)
76.5% (18)	85.0% (15)	88.2% (13)	89.9% (13)	96.9% (15)	76.4% (14)
81.2% (23)	86.1% (23)	88.0 % (21)	89.3% (20)	95.3% (19)	76.4% (23)
80.7% (17)	87.4% (16)	89.4% (15)	90.6% (15)	96.9% (17)	79.2% (17)

Hydroquinone gets entrapped in hydrophobic tail and thus gets larger in size and not passes through the pores of membrane, which results in increase in separation performance thus enhanced rejection.

CHAPTER-6

Conclusions:

Out of all contaminants present in waste water an aromatic organic compound hydroquinone, we are separating with the help of membrane in this report.This project report experimented the use of Reverse Osmosis low pressure thin film composite membrane (TFC) as an effective method for hydroquinone removal from water. Polysulfone (PSf) membranes were prepared by conventional wet phase- inversion technique. Thin film composite membranes was prepared by polyamide coating on Polysulfone asymmetric membrane.

Characterization of these Polysulfone membrane and TFC was done.FTIR shows the presence of Polyamide (cross-linked) structure on the thin film composite (TFC) membrane. The measurement of contact angles shows that Polysulfone is having contact angle 74.12° whereas the TFC shows contact angle 60.32°.The Scanning Electron micrograph study shows that there is distinct difference in the morphology of the virgin Polysulfone membrane and thin film composite membranes.

As this are negatively charged TFC so repels positively charged NaCl .The hydroquinone separation obtained in neutral pH was 80.63% in 1000mg/L NaCl solution whereas in acidic pH, NaCl separation was influenced much more compared to hydroquinone.

To increase seperation performance efficiency of membrane addition of SLS is done as 50 to 250 (mg/L) on Hydroquinone solution. Addition of SLS shows a promising result with enhancing seperation at 200 psi by saving energy.

REFERENCES:

1. “Sustainable Water Management” Local to Global, Pacific Institute, http://pacinst.org/issues/sustainable-water-management-local-to-global.
2. Bhattacharya A., “Remediation of pesticides polluted waters through membranes, Separation and Purification Reviews”, (2006) 35: 1-38.
3. Cheriyan M., “Ultrafiltration and Microfiltration Handbook”, (1998), p-9, Technic Pub Co, USA.
4. Mayank Saxena, A. Bhattacharya, “Removal of Atrazine from water by low pressure thin film composite membrane”, M.Tech thesis, (2012).
5. Hydroquinone Wikipedia, the free encyclopedia, https://en.wikipedia.org/wiki/Hydroquinone, 11/5/2015.
6. Chemicalbook,“Hydroquinone”,http://www.chemicalbook.com/Chemical Product Property ENCB6717931.htm,123-31-9, 11/18/2015.
7. Technology Transfer Network Air Toxics Web site, “Hydroquinone”, US EPA, http://www3.epa.gov/airtoxics/hlthef/hydroqui.html, 11/24/2015.
8. Sukanchan Palit, “A Short Review Of Applications Of Reverse Osmosis And Other Membrane Separation Procedures”, International Journal Of Chemical Sciences And Applications, Vol 3, Issue 2, 2012, 302-305, http://www.bipublication.com.
9. Blanco J. F., Sublet J., Nguyen Q., Schaetzel P., “Formation and morphology studies of different polysulfones–based membranes made by wet phase inversion process” J. Memb. Sci. (2006) ,283(1-2), 27-37.
10. Baker R., “Membrane and module preparation”, Membrane Separation System, (1990) -2, US DOE Report DOE/ER/30133-H1.
11. Ze-Xian Low, Qi Liu, Ezzatollah Shamsaei, Xiwang Zhang and Huanting Wang, “Preparation and Characterization of Thin-Film Composite Membrane with Nanowire-Modified Support for Forward Osmosis Process”, *5*, (2015), 136-149.
12. Analytical Laboratories,”Fourier Transform Infrared Spectroscopy (FTIR) Analysis”, http://www.intertek.com/analysis/ftir, 11/26/2015.
13. Freger V., “Swelling and morphology of the skin layer of polyamide composite membranes: An atomic force microscopy study”, Environ. Sci. Technol., (2004), 38(11): 3168-3175.

14. Bhattacharya A., Ghosh P., “Nanofiltration and Reverse Osmosis Membranes: Theory and application in separation of electrolytes”, Review in Chemical Engineering, (2004), 20(1-2): 111-173.
15. Sourirajan S., “Reverse Osmosis a great separation technique” in: Reverse Osmosis and Synthetic Membranes, Theory, Technology and Engineering, S. Sourirajan (Ed.), National Research Council,Canada, Ottawa, Canada, 1977, Chapter 1 (1-3).
16. Yogesh, Bhattacharya A., Popat K. M., Ganguly B., Brahmbhatt H., “Studies on the separation performances of chlorophenol compounds from water by thin film composite membranes” Macromol. Res., (2008),16(7), 590-595.
17. “Chemistry in Surfactants, Home & Personal Care Products, Oleochemicals and Edible oil: Sodium lauryl sulphate (SLS)”, http://surfactantschemistry.blogspot.in/2013/07/sodium lauryl sulphate SLS.html.