Synthesis of Polymeric Membranes for Oil-Water Separation

A Thesis submitted to the Department of Chemical Engineering, School of Chemical and Materials Engineering (SCME), NUST, Islamabad, in the partial fulfillment of the requirement for the degree of

(MS in Chemical Engineering)

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December, 2015

Certificate

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Dedication

Dedicated to my Parents, Family & Teachers

Acknowledgements

All glory and praise be to **“ALLAH ALMIGTHY”** the creator of this universe who bestowed me with health and courage to complete this work. Countless salutations upon **“HOLY PROPHET HAZRAT MUHAMMAD (S.A.W.W)”**.

I would like to thank my respected supervisor **Prof Dr Arshad Hussain** for his support during my complete research work, for his guidance, motivation, patience and valuable knowledge. His guidance was always helpful for me in matters of difficulty. He has been always a source of inspiration for me.

Besides my advisor I would like to thank the rest of my guidance committee: **Dr A Q Malik, Dr Bilal Khan Niazi, Dr Wasif Farooq** for their useful comments and encouragement.

I would also like to thank all the laboratory assistants for their kind help in providing facilities required for research.

Last but not least, I would like to thank my family, friends and class mates for their encouragement.

Tariq Mehmood

Abstract

In this work treatment of oily waste water was studied with the help of polymeric membranes. Membranes were composed of polymeric blend having cellulose acetate and nylon 66 which was never used for membrane purposes. Results of rejection and flux were compared with commercial cellulose acetate membranes. Membranes were synthesized with the help of solution casting. Nylon 66 is a man made synthetic polymer having extraordinary mechanical properties. It is due to its mechanical and thermal properties that it has become the most widely used polymeric material. Membranes were characterized with the help of scanning electron microscopy (SEM) in order to examine morphology of the membrane as well as impact of change in solvent on overall structure of the membrane. Mechanical and thermal properties of blended membranes as well as commercial membrane were also examined with the help of thermal gravimetric analysis (TGA), universal tensile testing machine (UTM). Characterizations of membrane revealed that blending of membrane showed increase in thermal and mechanical properties of membrane as that of commercial membrane. Membranes were tested for flux as well as rejection of oil as a function of nylon 66 compositions and trans-membrane pressure. Result showed that synthetic membrane composed of 2% nylon 66 and DMSO as a solvent give high flux up to 30 L/m^2.h as well as rejection of oil up to 90% whereas commercial membrane showed flux of 22 L/m^2.hr and rejection up to 70%.

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List of Abbreviations

Scanning Electron Microscopy (SEM)

X-Ray Diffraction (XRD)

Energy Dispersive Spectroscopy (EDS)

Thermogravimetric Analysis (TGA)

Cellulose Acetate (CA)

Transmembrane pressure (TMP)

Dimethylsulfoxide (DMSO)

Formic Acid (FA)

Chapter 1

Introduction

1.1 Background

Need of oily waste water treatment is increasing with each passing day owing to rapid increase in pharmaceutical, petrochemical, food and automobile industries [1]. Membrane treatment has been acknowledged as the potential candidate for waste water treatment [1, 2]. Inefficiency of conventional techniques like skimming, air flotation and flocculation for oil water separation impede their usage for water treatment. Their inefficiency paved the way for need of enhancement in membrane technology [3]. Numbers of organic as well as inorganic materials have been utilized in order to synthesize membrane with required properties [4]. Ceramic materials have gained much importance as a membrane material because of their high mechanical and thermal properties [5]. However their synthesis procedures as well as cost hinder their growth. Polymeric membranes have been used for oil water treatment owing to their easy processability and low cost.

1.2 Working principle

Membrane could be defined as a selective barrier between two phases. It allows selective particles to be passed through it however hinder the transport of undesired particles. Rejected components by the membrane are termed as retentae. While particles managed to pass through it are called permeate. Separation of particles takes place in the presence of driving force [6]. Driving force could be pressure gradient, temperature gradient, electrical potential difference [7].

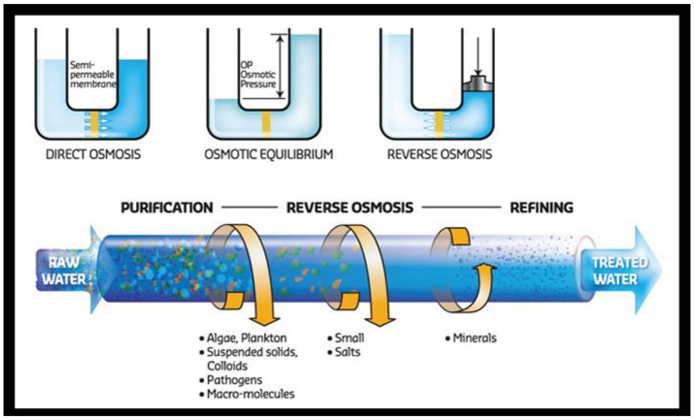


Figure 1-1 Working Principle [40]

1.3 Modes of membrane process

On the direction of flow of feed stream upon the membrane surface, membrane processes have been divided into two modes [8].

- Dead End Filtration
- Cross flow Filtration

1.3.1 Dead End filtration

In the case of small scale separation mostly in batch process, dead end filtration is applicable. In dead end filtration the flow of stream and membrane surface are perpendicular to each other [9].

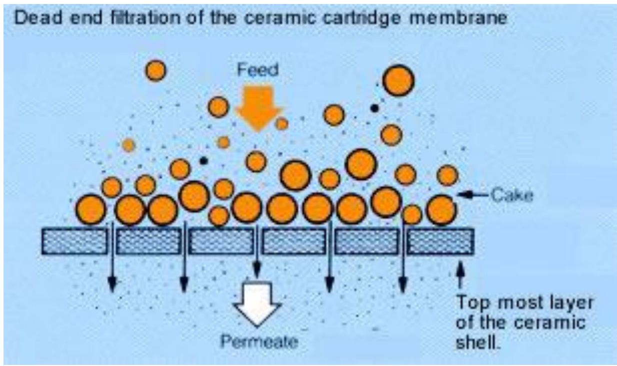


Figure 1-2 Dead End Filtration [40]

1.3.2 Cross-flow filtration

In these type of separation the flow of streams and surface of the membrane are parallel to each other. However permeate travelled through the cross section of the membrane.

These types of filtration are less prone to membrane fouling and mostly used by continuous processes [10].

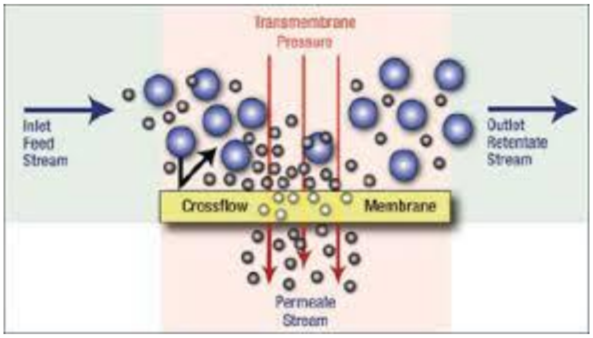


Figure 1-3 Cross flow filtration [40]

1.4 Membrane materials

Membrane materials are broadly divided into two categories:

1. Biological
2. Synthetic

Biological materials are mainly comprised of proteins and fats [8]. These are very sensitive materials and membranes synthesized from these materials have very delicate use. On the other hand synthetic materials consist of organic and inorganic materials. Organic materials are those materials which consist of carbon group whereas inorganic materials have not any carbon group. Organic polymeric materials are more important in membrane technology than inorganic polymeric materials. Ceramics, glass, metal are classified as inorganic materials. Every material has its limitation so the membranes synthesized from these materials will also be having some limitations [3]. Membranes made up of polymeric materials are prone to breakage because some polymers are not so stiff to bear high pressure, on the other hand some ceramic membranes can be operated on very high temperature because ceramics remains unaffected when exposed to high temperature. In some cases flexibility is required; so polymeric membranes are more preferable to inorganic membranes because of long carbon chains. In the case of water separation polymeric membranes are widely used because of their hydrophilicity and flexibility. In water separation processes high temperatures are not required so ceramic or other inorganic membranes do not grab much attention. Several polymers are being used when it come to water separation like cellulose acetate(CA),polysulfone(PSF), polyethersulfone(PES), polyacrylonitrile(PAN) [11, 12]. There are several properties of membrane surface which play crucial role in the desired separation of water. As hydrophilicty of the membrane increases, the separation of water from impurity will also be increased. Membrane porosity is also required for desired separation efficiency; the larger the pores will be the lesser will be the separation or treatment of water [13].

Nature of solution which is going to be treated is also having great importance. Acidic nature of solution may cause harm to the membrane especially if membrane is made up of polymeric material. Inorganic materials are more resilient to acidic solution rather than polymeric materials. Temperature during separation process also affects the texture and properties of membrane materials in the case of polymeric membranes. But ceramic membranes are more heat resistant than polymeric membranes [14].

1.4.1 Cellulose acetate

Cellulose acetate is a polymeric material. It is a naturally occurring polymer obtained mostly from wood. It comprises of repeating units of glucose having formula of $C_6H_7O_2(OH)_3$.

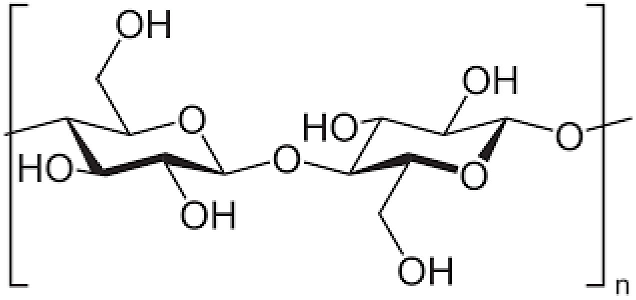


Figure 1-4 Cellulose Acetate [40]

High hydrophilicity of cellulose acetate makes this polymer of great importance. Three hydroxyl active groups in repeating units of cellulose molecule are accountable for hydrophilicty. Strong hydrogen bond is present between cellulose chains which keep it together and not allowed to melt or dissolve in ordinary solvents. Cellulose acetate is a major constituent of the polymeric membranes especially in the field of desalination, reverse osmosis and water treatment [15]. Cellulose acetate is one of the derivatives of cellulose among others like regenerated cellulose, cuprophane and nitro cellulose. In most of the cases cellulose acetate and regenerated cellulose are used for the synthesis of membranes used for the membrane processes like ultrafiltration, microfiltration and dialysis. Whenever cellulose acetate exposed to any harsh environment like acids, bases, or high temperature it encounter permanent degradation which could not be regenerated [11, 16].

1.4.2 Nylon

After revelation of natural polymers like cotton, starch, proteins and wool to the scientists they strived for the synthesis of more delegate polymers which could be modified according to desired requirements and properties. These synthetic polymers comprised of long chains with repeating monomeric units. Nylon is one of the first polymers which were modified to cater specific needs. Carothers synthesized polyamide 6,6 in laboratories at DuPont in 1935 [16]. Nylon was also used in world war 2 for production of parachutes, airplane tire cord, glide tow ropes and military apparel. With the passage of time nylon became widely used in textile industry, plastic industry, and automotive industry. Usage of nylon in membrane field emerged in seventies. Now a day's lot of work has been done in the field of ultrafiltration and microfiltration using nylon as a membrane material [17]. Nylon membranes are widely used in water system owing to their higher hydrophiliciy. Another advantage of these synthetic polymers is that they do not require any kind of wetting agent during the synthesis of these membranes in order to further increase its hydrophilicity. Several thin film composite membranes are being used for the desalination purposes and a large amount of work is in progress to further find opportunities to increase their performance [18].

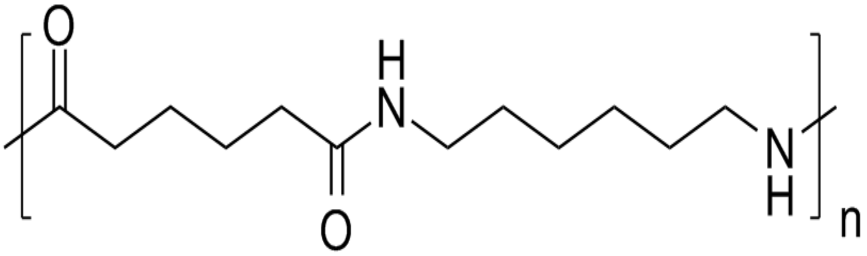


Figure 1-0-5 structure of nylon [40]

Aliphatic polyamides further divided into sub types like (polyamide 6, polyamide 6/6, polyamide 11, polyamide 4). Here the basic difference between these types of polyamide is amount of repeating carbon atoms in the linear main chain of recurring polymer unit [16]. As the number of carbon in the main chain of the repeating polymer unit goes on increasing the numeral with the polyamide also keep on increasing. In the case of polyamide 6/6 the polymer is synthesized with the reaction of hexamethylenediamine and adipic acid. Nylons have regular chains consisting of series of methylene group which is also joined with the hydrogen bonded amide linkage. This strong hydrogen bonding leads to strong intermolecular attraction between different units cause high crystillanity [40]. Nylons gain much importance owing to their strong mechanical properties and their capability of survival in harsh environment. It is due to their high crystillanity that their yield stress, tensile strength, module hardness, abrasion resistance are very high.

Nylons are mostly resistant towards a large number of organic solvents. They are highly resistant towards aliphatic and aromatic hydrocarbons. Crystallanity increases resistance of the nylon so nylon 6,6 and nylon 6 are very resistant. Property of higher hydrophilicity and good chemical resistance in harsh environments as well as in non aqueous environment are some distinct properties which made nylons as important synthetic polymers [16] .

1.5 Importance of solvent

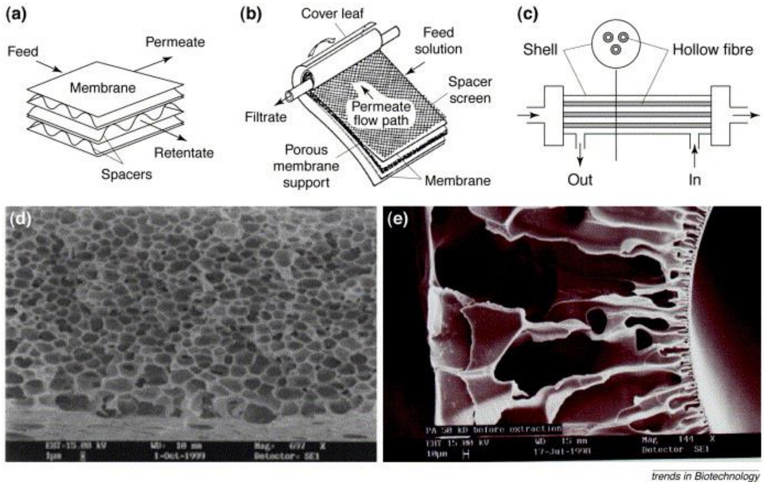
Selection of solvent has great important in the case of synthesis of the polymeric membranes. Solvent plays a major role in the overall morphology of the membrane as well as in pore formation. Solvent for the synthesis of polymeric membrane should be soluble in water so that when the casted membrane comes into contact with the precipitation medium which in most of the cases is water, the solvent present in the film should be dissolved in the water and leave behind a solid membrane having pores in it [8].

1.6 Classification of membrane technology on the basis of morphology

In the case of synthetic membranes the membranes could be divided into two types on the basis of their morphologies.

1. Symmetric Membranes
2. Asymmetric Membranes

Asymmetric membranes find its applications in the field of ultrafiltration, reverse osmosis, pervaporation and gas separation. Asymmetric membranes consist of two layers. The upper layer is termed as selective layer because actual separation is done by this layer whereas the secondary layer is just for support purposes for skin layer to bear high pressures [7]. In the case of symmetrical membranes total resistance applied to the permeated solution is offered only by the skin layer.



trends in Biotechnology

Figure 1-6 Symmetric/Asymmetric membranes [40]

Whereas in the case of symmetrical membranes skin layer is absent. Finger like voids are also ceased to exist. Membrane consists of homogeneous structure from top to bottom. In the case of symmetrical membranes all of the area of the membrane is utilized to separate the required material from waste [7].

1.7 Classification of membrane processes

1.7.1 Pressure gradient:

1.7.1.1 Ultrafiltration

Ultrfiltration process is widely used for the separation of colloids, macromolecules and micro solutes. The average pore diameter of ultrafiltration membranes is in the range of 0.1nm to 300nm [15]. Membranes which are used for the ultrafiltration processes are known as ultrafiltration membranes. These membranes are usually asymmetrical membranes having anisotropic structure. Leob-Sourirajan was the first person who synthesizes such type of membranes so the process through which this type of membrane is synthesized is named after him[15]. These types of membranes consist of anisotropic structure. Anisotropic membranes comprises of two layers. Upper layer or the surface layer is finely porous which is than supported by a much more open layer. Both layers have their individual function. The skin layer actually performs the separation of desired and undesired particles. The micro porous substrate provides the mechanical support in the cases of intense pressure to keep membrane from breakage. Ultrafiltration membranes permeate the desired substances of the solution and hinder the further movement of the undesired particle with the help of pores [19]. These membranes are mostly characterized with the help of molecular weight cut off (MWCO). The two processes ultrafiltration and microfiltration are alike in their processing but the sole difference between the two is the size of pores. Ultrafiltration membranes contain pores of shorter diameter as compared to microfiltration membranes. The range of ultrafiltration membranes pores diameter is between 10-1000Å ranges whereas the pore diameter of microfiltration membranes is in the ranges of 0.1-10µm. In ultrafiltration process feed could be introduced both in batch as well as in continuous way. But the continuous feed is preferable to the batch process. One of the advantages for preference of continuous process is turbulence over the surface of the membrane. The other advantage of continuous feed system is that the composition of the feed is maintained due to continuous mixing of the feed [15].

1.7.1.2 Microfiltration:

Microfiltration membranes are those membranes which have pores diameter of 0.1-10µm. These type of membranes fall between the ultrafiltration membranes and conventional filter papers. Microfiltration membranes are widely used for the separation of the suspended particles in the solution. Microfiltration membranes are divided into two major types.

1. Depth filters
2. Screen filters

Screen filters contain pores having fewer diameters than the size of undesired particles. So particles which have diameter larger than these pores could not pass through these membranes and can be easily separated. The other type of microfiltration membranes is depth filters. The filters comprises of pores having larger diameter than particles which is to be separated. So when particles come in contact with these membranes they can easily penetrate through these membranes but separation of these particles takes place in the constriction across the membranes [8]. Separation could also be achieved in these membranes through absorption. Depth filters have more surface area available for the separation than screen filters. Absence of membranes defects and pore uniformity is crucial in microfiltration membranes because any permeation of undesired particles is detrimental for the membrane durability [7].

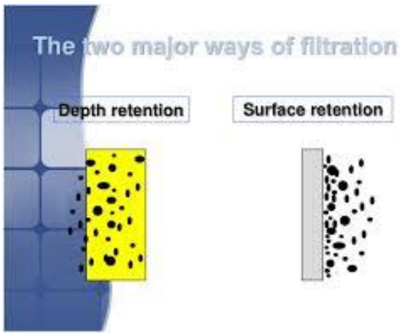


Figure 1-7 Dead end/screen filtration [40]

1.7.1.3 Reverse Osmosis

Reverse osmosis process is widely used for desalination of water [15]. Polymeric materials are widely used for the synthesis of the reverse osmosis membranes. Cellulose acetate is most used polymer due to its high hydrophilicity and rejection for the salts. There are several categories of reverse osmosis membranes.

1. Brackish water and sea water desalination reverse osmosis membranes. Having pressure range of 200-1000 psi.
2. Low pressure membranes having pressure range of 100-200 psi having salt solution of 200-5000 ppm.
3. Hyperfiltration membranes used for the separation of solutes from several organic salt solutions.

1.7.1.4 Nanofiltration

Membranes which fall in between the category of reverse osmosis membranes and ultrafiltration membranes are called nanofiltration membranes. These membranes are also called lose reverse osmosis membranes [15]. Nanofiltration membranes are widely used for the salt rejection but they have lower efficiency than the reverse osmosis membranes. Mostly nanofiltration membranes have rejection of sodium chloride between 20 and 80 %. Whereas in the cases of reverse osmosis these salt rejection range increase to 90% and in the case of ultrafiltration this rejection of salts reduces to less than 5 %. The materials which are used to synthesize these types of membranes are cellulose acetate and interfacial composite membranes [7].

1.7.2 Classification on the basis of porosity

Several types of techniques are used for the synthesis of membranes having different porosity. Preparation technique of membrane have large impact on the morphology, pore structure and permeation properties. Mainly there are three types of membranes characterized on the basis of the pore diameter. These are

1. Porous membranes (it include Ultrafiltration, Microfiltration)

2. Nonporous membranes (Gas separation, dialysis, pervaporation)
3. Carrier membranes.

1.7.2.1 Porous Membranes

These types of membranes comprises of pores having large diameter. In these types of membranes separation take place with the help of diameter of pore. If the diameter of pore is less than the diameter of the undesired particles than the separation will occur. Ultrafiltration and microfiltration process are examples of these type of separation.

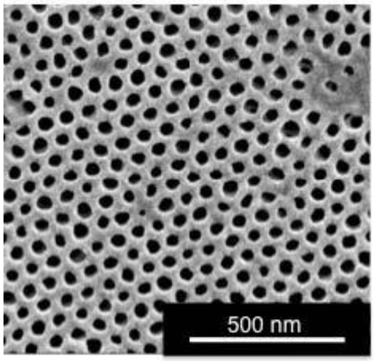


Figure 1-8 porous membranes [40]

1.7.2.2 Nonporous Membranes

In these types of membranes pore diameter is not so much influential. Here the properties of the constituent polymers play crucial role in the separation of the two streams. Solubility and diffusivity of several polymers with the solution which is going to be separated should be tested with care because higher selectivity of the polymer will give best yield [7]. Pervaporation, dialysis and gas separation process use these types of membranes.

1.7.2.3 Carrier mediated transport

In these types of transports the separation is not done by the membrane itself but the membrane is loaded with special carries which ultimately facilitates the separation of the particles. The carriers could be either mobile or could be static[7].

Table 1-1 Classification of membrane membranes on the basis of porosity

Pore Types (nm)	Membrane Types (nm)	Species	Dimensions (nm)
Macropores (>50)	Microfiltration (50-500)	Yeasts & fungi Bacteria Oil Emulsion	1000-10,000 300-10,000 100-10,000
Mesopores (2-50)	Ultrafiltration (2-50)	Colloids Viruses Protein	100-1000 30-300 3-10
Micropores (0.2-2)	Nanofiltration (≤2) Reverse osmosis (0.3-0.6)	Water Organic antibiotics Inorganic ions	0.2 0.3-0.8 0.2-0.4

1.8 Membrane transport theory

Ability to control the permeation rate of two different species is an important property of membrane. There are two well defined models which explain overall phenomena take place in order to separate different species.

1. Solution diffusion model
2. Pore flow model

1.8.1 Solution diffusion model

Solution diffusion model advocate that diffusion is the most important phenomena through which membrane separate desired species from undesired one. According to this model permeate first dissolve into the membrane material through surface and then pass through the cross section of the membrane. In this type of process, separation of two species taken place on the basis of the difference of solubility's of the materials in the membrane materials [40]. Diffusion rate of the material through the membrane also play important role in the transport of the material. Specie which has higher solubility in the membrane material will pass more quickly as compared to the species which have less solubility in the membrane material.

1.8.2 Pore flow model

In this type of model the property of membrane materials are least concerned. According to this model separation of materials through the membrane taken place with the help of pores available in the membrane. Particles having less diameter than pores available at the surface of the membrane will penetrate through membrane but particles having large diameter than pores available at the surface will be retained [7].

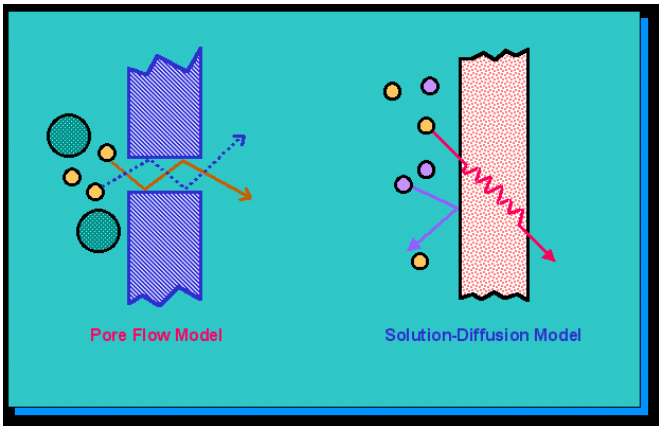


Figure 1-9 Solution diffusion/pore flow model [40]

1.9 Problem Statement

Both of the polymers nylon 66 and cellulose acetate are widely used for membrane synthesis. There are some hurdles which impede their growth in the field of membrane technology. These are as follows:

- Low flux of cellulose acetate based membranes in the case of oil water treatment.
- Low flux of nylon based membranes in water treatment.
- Mechanical and thermal properties of the cellulose acetate membranes are not satisfactory.
- Less hydrophilicity of the membrane surface.
- High fouling in the case of cellulose acetate based membranes.

1.10 Research objectives

In order to address these lope holes in cellulosic membranes for oil water separation this study encounter these problem and provide solution to certain problems faced by polymeric membranes. Overall objective of this research are as follows:

- To synthesize and characterize polymeric membrane comprising of cellulose acetate and nylon 66 polymeric blend.
- Effect of solvent on overall morphology and structure of the membrane.
- To study the overall flux of permeate and rejection of oil as a function of nylon 66 concentration.
- To study the effect of trans-membrane pressure on the overall flux of membrane as well as on the rejection of oil.
- To test mechanical properties of the newly fabricated membrane with the help of tensile testing machine.
- To study thermal properties of the synthesized membranes.

1.11 Scope of study

The research mainly focused on the synthesis of blend membrane composed of cellulose acetate and nylon 66. Membranes have been characterized with the help of SEM, TGA and Tensile Test. In order to examine flux of the membrane the prepared membrane has been tested for oil water separation and for flux calculation. Effect of transmembrane pressure on overall flux as well as rejection of oil has also been tested with the help of synthesized membranes. Effect of change in solvent over morphology and functioning of the membrane has also been observed.

Chapter 2

Literature survey

Number of industries like pharmaceutical, petroleum refinery and food is increasing with unprecedented pace which also causes global problems. During processing, water comes in contact with number of pollutants for instance hydrocarbons, hazardous chemical, and sewage sludge from boilers, cooling towers and heat exchangers. Waste water produced by these industries is not reusable and have drastic impacts on living species. This discharged oily water severely damages aquatic life as well as pollute ground water which is the biggest dilemma of the present time. With the increase in population, demand of clean water is also increasing, particularly areas having shortage of this precious resource. If the water pollution increases with the same pace the time will come when there will be scarcity of water even for basic needs. Nowadays treatment of this oily water is the biggest challenge in hand. Recycling of polluted water or reduction of pollutants up to acceptable level by its treatment is considered to be the only way out in these grim circumstances. Conventional techniques are also being used for the treatment of oily waste water like decanting, biological treatment, chemical treatment, gravity separation, skimming, air flotation, coagulation and flocculation [3, 11]. Such processes require number of chemical and biological solvents to treat waste water which could cause devastated affects on mankind [3]. Some drawbacks limit their usage as suitable techniques for water treatment which are listed below:

- High cost
- Usage of toxic compounds
- Large space required for installation
- Generate polluted components.

These drawbacks insist researches to search for suitable treatment processes which produce less hazardous pollutants [3].

Table 2-1 Conventional techniques for treatment of oily waste water [20]

Conventional Technique	**Advantages**	**Disadvantages**
Solvent extraction	Fast process and very efficient	Incur high cost which inefficient removal of heavy metals
Centrifugation	No solvent is required An easy technique	High energy is required Economically not viable
Forth floatation	Low energy requirement	High viscosity of oil is not acceptable
Ultrasonic irradiation	No chemical is required Easy process	Equipment is very high Heavy oils could not be treated
Pyrolysis	Can treat large amount of oil More fast and effective	Operating as well as maintenance and capital cost are very high
Oxidation	Removal of PHCs from oil sludge	Environmentally not benign. Chemical intensive process. High cost
Land Farming	Much maintenance is not required.	Pollute underground water. Sand pollution

Membranes are considered as the strong participant in the treatment of polluted water. Rapid growth has been witnessed in membrane technology both at academic and industrial level. In the case of treatment of oily waste water membrane give high efficiency due to their capacity of separating oil from water [1]. Membrane technology is being used in number of process for the treatment of waste water. The membrane technology is overtaking the conventional treatment process because it does not offer any chemical exposure during and after its processing. Porous membranes have been widely used for the treatment of oily waste water. There are several techniques through which porous membranes could be synthesized.

2.1 Preparation of synthetic membranes

2.1.1 Phase inversion

Phase separation is a process in which the polymeric solution comprised of polymers mixed in specified amount blended together is transformed from one state to other state (From liquid state to the solid state). Through this process the morphology and pore size could be tailored according to the needs of the process. Phase inversion include in itself number of techniques which have different procedure but give same output in the shape of solid polymeric membranes having pores of desired size [8]. These processes are:

2.1.1.1 Precipitation by solvent evaporation

In this type of process the specified amount of polymers is dissolved in the desired amount of solvent to form am homogeneous solution. Polymeric solution is then casted on the suitable support which could be glass support or non woven support. The casted solution is allowed to evaporate in an inert atmosphere (mostly in nitrogen environment). The solvent of the polymeric solution will be evaporated leaving behind the solid membranes having very dense structure [7]. Water vapors are not allowed to come in contact with these membranes while drying because they will distort the structure of membranes.

2.1.1.2 Precipitation from vapor phase

In this type of process the polymeric solution is casted on the solid surface. Surface is allowed to evaporate in the vapor atmosphere. When vapor come into contact with the casted membrane the membrane become solidify by diffusion of nonsolvent into the casting solution. The morphology of the membrane could be manipulated by changing the concentration of nonsolvent in the vapor phase and span of drying through vapor phase [8].

2.1.1.3 Precipitation by controlled evaporation

In this process the polymer is mixed with the solvent and nonsolvent in order to form the solution. The solvent is more volatile than the nonsolvent. When the solution is allowed to evaporate, the solvent will evaporate leading to the solid membrane having pores of different sizes in it [7].

2.1.1.4 Immersion Precipitation

This technique is most widely used when it comes to synthesis of asymmetrical membranes. In this process the polymer is dissolved in the desired solvent in specified amount so that a homogeneous solution could be formed. This polymeric solution is casted on the solid support with the help of doctor blade. Thickness of the membrane is controlled with the help of doctor blade. The casted solution is allowed to evaporate for 30 s. Solvent will evaporate leaving behind pores in the membrane. After evaporation the casted solution is immersed in a coagulation bath. Coagulation bath consist of nonsolvent. The solvent which is used to make a homogeneous solution must be readily soluble in the nonsolvent so that precipitation of the membrane could occur [8].

2.2 Membranes used for oil-water treatment

Polymeric material is widely used for the synthesis of polymeric membranes because of their extraordinary properties required in membrane processes. Wenjuan Chen et al. (2009) studied two different membranes composed of polyacrylonitrile(PAN) and the other one is based on cellulose acetate grafted with polyacrylonitrile. Polyacrylonitrile membranes offer high water flux but also showed poor antifouling property. In order to get high flux as well as high antifouling property a new membrane was synthesized composed of cellulose acetate grafted with polyacrylonitrile. This new synthesized membranes was tested for flux and antifouling property and results were very promising. This novel membrane gave high permeation flux as well as high antifouling property. Free radical polymerization was done in order to graft polyacrylonitrile on cellulose acetate. Phase inversion procedure was used to get the desired asymmetrical membrane. Grafted membrane offer high flux in the case of ultrafiltration of oil and water as well as showed high antifouling property. Oil droplets deposited on the membrane surface of the membrane could also easily remove from surface with the help of simple hydraulic washing. Flux of the membrane was also recoverable. It was estimated that the flux of the membrane after three runs was about 110 $l/m^{2}\cdot h$ in the case of oil water system[21].

Hong-Jian Li et al. synthesize polymeric membrane comprised of cellulose acetate for oil and water separation. The membrane was of hydrophilic in nature comprises of celluloseacetate/monohydrate/N-methylmorpholine-N-oxide (NMMO.H_2O/polyethylene glycol (PEG 400). Experiments showed that the total retention of the membrane for oil was more than 99% and total oil contents in the permeate was calculated about 10mg/l. Flux reduction of the membrane was the result of concentration polarization which repel oil droplets as well as water contents and reduce contact of oil droplets with the membrane. Cake layer was formed on the surface of the membrane due to continuous contact of the oil droplets with the cellulose acetate. This cake layer results in the increase in concentration polarization. The membrane was also tested for different ph environments in order to test the ability of the membrane to work in harsh environments. Author conclude that the cellulose acetate consisting membrane have potentials to be used for the separation of oil from water in oily emulsions [11] .

Yu et al. (2006) modified polyvinylidene fluoride based membranes with nano sized inorganic alumina particles in order to purify the oily waste water stream. These membranes were applied in hollow fiber module for ultrafiltration. Oily waste water stream was supplied by oil field. Results obtained after the processing of membrane reveal that the oil contents in the permeate stream reduced to 1 mg/l. suspended particles in the permeate stream also reduced to less than 1 mg/l which is desirable by oilfield drainage. The used membrane is than cleaned with different solvent to carry out another separation. SEM of the fouled membrane was also carried out which showed that the presence of the inorganic nanoparticles enhances the ability of membrane to resist fouling. Through washing of membrane with 1 wt% OP-10 type surfactant the complete recovery of the flux can be achieved.

Song et al. (2006) synthesized Tubular carbon membranes for microfiltrations having uniform pore structure with lower cost were prepared through coal. Coal is very cheap material and readily available in every corner of world. It was revealed that pore size of membrane was directly related to particle size of the coal. In this study the effect of pore size, cross flow velocity and transmembrane pressure on permeate flux was investigated. It was calculated that as the pore size and transmembrane pressure increases the flux of the membrane goes on decreasing because large particles in the waste stream block the pores of membrane which resultantly reduce the overall flux of permeate. On the other hand the cross flow velocity results into increase in permeate flux because high cross flow velocity will remove the sedimentation layer which form at the surface of the membrane as the process of separation proceed. Optimum conditions for the efficient working of membrane were calculated as the pore size of 1.0μm, transmembrane pressure of 0.10MPa and cross flow velocity of 0.1m/sec. when the oil contents of permeate was calculated it was obtained that 97% of oil was rejected by the membrane having oil contents 10mg/l [22].

Zhang et al. (2009) tested membranes made up of polysulfone for the treatment of oily waste water streams. Results showed 99.16% rejection of oil from the oily waste stream having oil concentration of 0.67 mg/l. The research also concluded that the composite membranes synthesized in the study can also be considered feasible for the separation of oil [23].

Yang et al. (2011) successfully synthesized dynamic membranes having high efficiency for the oily waste water separation. They deposited Mno2 particles on surface of the Kaolin layer leading to a Kaolin/MnO2 dual layer composite membrane. The Kaolin layer composed of KMnO4 and Kaolin having concentrations of 0.1 and 0.4 g/l. Results reveal that as the oil concentrations rises the flux of the permeate decreases but oil rejection increases. These membranes become stable in neutral or alkaline system having oil retention of 99%.

Hua et al. (2007) used ceramic membranes for the treatment of oily stream through cross flow type microfiltration. Having pore size of 50 nm. This study concluded that with the change of parameters like pressure, flow and temperature the flux of the membrane also changes. Oil components were reduced to 92.4% in the permeate stream. Modeling was also done in order to test the results obtained from the experiments. Model for accumulation volume for permeation was developed. Results obtained from the model justified all the results obtained from the experimental procedure. Model showed that the transmembrane pressure greatly influence the permeate flux [24].

Cui et al. (2008) synthesize microfiltration membrane comprises of NaA zeolite hydrothermaly synthesized on α-Al2O3 tubes. Testing of this membrane the separation of oil from oil water emulsion reveals that more than 99% of oil was rejected from the membrane and permeate stream carry only about 1mg/l of oil with flux of about 85 l/m2.h. With the passage of time the flux of the membrane reduces due to fouling of the membrane. In order to recover the flux of the membrane, it was backwashed with the help of hot water or alkali solution. These zeolitic membranes are cheaper than other ceramic membranes. NaA zeolites are synthesized from reagents of silica and alumina. Reactions temperatures are also not so much severe [25].

Um et al. (2001) investigate the effect of gas injection in the cross flow mechanism for ultrafiltration membranes. Nitrogen gas was introduced in homogeneous oil emulsion. It was revealed that when the gas was exposed into the liquid the flux of the membrane increased extraordinary as was expected through film theory model. Addition of gas changed the emulsion from homogeneous to heterogeneous gas liquid phase. With injection of nitrogen gas it causes turbulence over the surface of the membrane as well as produce bubbles. Gas efficiency in the membrane separation can be predicted by the amount of bubbles in the mixture. If the bubbles are present in a greater amount than a specified amount the flux will decrease same will be the case if bubbles are too less in the mixture. The effect of cross flow velocity on the overall flux of the membrane was also studied. Results showed that as the cross flow velocity as the flux of the membrane increase with greater pace even in the absence of gas injection. This increase in flux could also be attributed due to effect of turbulence dampening because of bubble compressibility [15].

Abadi et al. (2011) engineered ceramic Microfiltration membrane comprises of (α-Al2O3) having tubular shape for the treatment of oil emulsions. Permeate collected after the membrane separated the oil from water have oil and grease contents about 4 mg/l. Microfiltration process reduce the total suspended solids, turbidity and oil and grease contents to about 100%, 98.6% and 85%. Total organic components of the waste water reduced to 95% after being passed through ceramic membrane. Microfiltration was also compared with conventional technique like biological methods and results showed that the microfiltration can replace conventional techniques. Moreover the effects of the transmembrane pressure, temperature and cross flow velocity over flux and total oil contents were also investigated. Backwashing was carried out for the fouled membrane and results revealed that 95% of flux recovery can be made by doing periodic backwashing. For long term operation chemical cleaning was required to recover flux [26].

Mittal et al. (2001) synthesize composite membrane comprising both ceramic and polymeric materials having hydrophilic properties. Major contents of membrane were clay, kaolin and binding material. Dip coating technique was used to prepare this membrane. Top layer of membrane was composed of cellulose acetate which was first dissolved in acetone and then dipped for 10 sec in order to produce top layer. Membrane was characterized with the help of several characterization techniques like SEM, XRD, TGA, and permeability test of the membrane for oil water separation was also conducted for the composite membrane. Porosity and pore size of the membrane was calculated with the help of mass of cellulose acetate and hydraulic permeabilities. It was concluded that as the pressure and oil contents in the feed increases the flux of the membrane decreases. It was observed that the rejection of the membrane increases with the course of time. Maximum rejection done by this membrane was about 93%. Material used for the synthesis of this membrane was also cheap so this membrane was also cost effective [27].

Salahi et al. (2013) worked in the nano-porous membranes fabricated in the form of sheets. These nano-porous membranes were made up of polyacerylonitlie (PAN) having pore size of 10 nm for the treatment of oily streams in desalter. Treated water obtained from this process was under the given limit of environmental discharge [28].

Sarfraz et al. (2012) worked on the hybrid system of the NPM-PAC in order to control the fouling of membrane. Results demonstrated that the fouling of membrane comprising of NPM (Nano Porus Membrane) decreases as the amount of PAC (Powdered Activated Carbon) increases. An optimal amount of PAC which could increase the flux of membrane of NPM is about 300 ppm. If the amount of PAC goes on increasing it will than reduce the flux of membrane because the resistance of cake layer will increase. Organic removal of waste water was also increase when NPM membrane coupled with PAC concentrations. The incorporation of PAC in NPM membranes increased the removal effencies of the COD and Total Organic Carbons to 90.2% and 97.6%. Rejection of oil and chemical oxygen demand increased to 90%. Flux also increases to 133.8 l/m2.h [28].

Zong et al. (2003) studied the effect of separation of oil from oily waste by using microfiltrarion with a conventional technique named as flocculation. For flocculation a flocculent named as 3530S which is one of a derivative of polyacrylamide. Optimal condition was implemented for the flocculation which was dosage of flocculent as 70mg/l, temperature of 40^{o}C and stirring for 90mins. After flocculation the microfiltration unit was placed. The membrane fouling in microfiltration was decreased and flux of membrane increases owing to the pretreatment of feed stream in the flocculation unit. Membrane used in the microfiltration unit was made up of ZrO_2. It was revealed that the oil rejection increased by using flocculation before the microfiltration as compared to using alone microfiltration. Effects of transmembrane pressure and cross flow velocity on amount of oil in permeate and chemical oxygen demand was also checked. Results showed that with the increase in transmembrane pressure the flux of the membrane also increase but the oil rejection of the membrane decreases. The optimal conditions for the efficient working of membrane were selected as 0.11 MPa transmembrane pressure and 2.56 m/s cross flow velocity. Cross flow velocity also increased the flux of permeate but the relation is not proportional [29].

Maria Tomaszewska et al. (2005) studied the integrated process of Utrafiltration and reverse osmosis for the treatment of oily waste water. A system was designed in which the ultrafiltration was succeeded by reverse osmosis. Results showed that when oily waste water passed through ultrafiltration 95% of oil was removed and remaining oil was removed by reverse osmosis. Complete removal of oil was achieved through this combination of two techniques. In ultrafiltration, permeate only contain 10 ppm of oil contents but complete removal of turbidity and total suspended solids was achieved. Oil removal efficiency of reverse osmosis membrane was 85% and 70%. Reverse osmosis membranes also removed phosphates and cations to about 90%. It was calculated that permeate obtained from reverse osmosis membranes did not contain oil contents [30].

Amir et al. 2014 synthesize a membrane composed of polyethersulfone and cellulose acetate. Polyethylene glycol (PEG400) was also added into the membrane dope in order to increase number of pores in the membrane. Cellulose acetate was added into PES to increase overall hydrophilicity of the membrane and to gain the desired structure for oil water separation. In this research two membranes were compared Made up of Polyethersulfone and PES/CA/PEG400. These membranes were compared on the basis of Pore size, morphology, hydraulic resistance, flux calculation and oil rejection. With the addition of cellulose acetate in polysulfone, sponge like structure was obtained with number of pores in it. Cross flow system was used for the evaluation of oil in water separation. Pore size and thin outer skin layer was showed by SEM. Increase in water flux is a result of high hydrophilicity of PES/CA membrane. Membrane under consideration gives water flux of 27 l/m^2 oil rejection of 88% [12].

Patricia Poletto et al. (2011) prepare membranes from two different recipes. Blend of water/formic acid/polyamide 66(PA66) and other one consists of water/hydrochloric acid/polyamide 66(PA 66). It was showed that each solvent has its own impact on the overall morphology and permeance. This effect was the result of behavior of different solvent with different solvent. When membrane was tested with the help of electron microscope it was showed that the membrane structure was of asymmetrical structure. Membrane composed of two layer skin layer and porous support having larger pores the skin layer. Membrane synthesized from HCl solvent was having more thick skin layer (around 23µm) as compared to the membrane fabricated from FA solvent (around 10µm). Skin layer thickness determines the capacity of the membrane to absorb water. It was concluded that membranes having thin skin layers absorbs more water and have more porosity as compared to the membranes having thick skin layers. Porosity of the membrane made up of HCL solvent was having less porosity (15%) as compared to the porosity of the membranes made up of FA of approximately (50%). Membrane was also tested for pure water flux. Same trend was also noticed during the calculation of pure water flux. As the thickness of the skin layer of the membranes decreases the flux of the pure water goes on increasing [31].

Table 2-2 Literature review

Year	Author	Conclusion
2006	Hong-Jian Li et al.	Synthesized cellulose acetate based ultrafiltration membranes and conduct oil water separation test. Results showed that permeate flux was calculated about 7.6 $l/m^2.h$. Membrane showed high rejection of oil upto 99%.
2014	Amir et al.	Synthesize polymeric membrane based on polyethylene styrene and cellulose acetate. PEG-400 was also added into the polymeric solution. Synthesized membrane showed higher flux and rejection of oil values as compared to PES membranes.
2009	Wenjuan chen et al.	Ca-g-PAN membranes were synthesized through the process of Free radical polymerization. Membranes was tested for oil water separation and results

		showed higher flux and selectivity as compared to cellulose acetate membranes.
2011	Patricia Poletto et al.	PA 66 based membranes were prepared with the help of two different solvents. Effect of solvent on overall moerphology and strucuture of membrane was studied. Membrane was also tested for permeation of pure water. Membrane made up of formic acid provides more flux as compared to membrane synthesized with the help of HCL.

Chapter 3

Experimental Techniques

3.1 Materials and Methodology

3.1.1 Material

Cellulose acetate was purchased from sigma Aldrich. The molecular weight of the cellulose acetate was 30000 g/mol. Cellulose acetate was available in powder form. No pretreatment was required for the further usage of cellulose acetate. Nylon 66 was purchased from Zytel DuPont. Nylon 66 was available in the pellet form. DMSO was procured from Sigma-Aldrich, purity of 99%. It has transparent color. Formic acid was also procured from Sigma Aldrich having purity of 98%.

3.1.2 Membrane Synthesis

3.1.2.1 Dimethyl sulfoxide based membranes

Specified amount of nylon 66 was added into DMSO. Solution was allowed to stir for 5 hours with the help of magnetic stirrer. Temperature was also provided with the help of heating plate in order to get homogenized solution. After complete dissolution of nylon in DMSO, specified amount of cellulose acetate was added. Solution was allowed to stir until homogeneous solution could not be attained. Sonication was done for complete dispersion of both of the polymers. The solution was sonicated for half an hour for complete dispersion. During this step lot of air bubbles trapped in the solution. In order to get rid of these air bubbles the solution was placed in shelf undisturbed partially uncovered. After removal of the air bubbles the next step was to cast the membrane on the glass surface. Casting is very useful technique for the synthesis of polymeric membranes. Glass slab was used for the casting of membrane. The solution was poured on the glass slab. Doctor blade was used for spreading of the membrane solution in order to get film of required thickness. Doctor blade confirms the homogeneous thickness of the membrane. Casted membrane was then left for 40 sec to evaporate solvent leaving behind pores in the membrane. Than the casted film was immersed in the nonsolvent medium which was water. As discussed earlier the solvent used was soluble in water, so as the film was immersed in the water the solvent present in membrane dissolved in water leaving behind solid white polymeric membrane. It took almost half an hour to complete the precipitation of membrane. Solvent dissolved in water leaving behind pores of different diameter in the structure of the membrane. When the precipitation of membrane completed it was preserved in plastic bag.

3.1.2.2 Formic acid as solvent

Polymeric membrane was also prepared with the help of formic acid as a solvent. Phase inversion technique was used for the synthesis of the membrane with the help of formic acid as a solvent as was used for the synthesis of membrane in the case of DMSO. Solvent was procured from (Sigma Aldrich). Same amount of polyamide (nylon66 and cellulose acetate) was used for the synthesis. Polyamide (nylon 66) was weighed with the help of weighing machine and placed in the beaker having formic acid of specified amount. The beaker was then placed on the heating plate and stirred with the help of magnetic stirrer. Stirring was done at room temperature. Solution was allowed to stir for 4-5 hours in order to get fully homogeneous solution having transparent color. Cellulose was than weight with the help of weighing machine and then introduced in the homogeneous solution of nylon and formic acid. Stirring of the solution was resumed. Solution was allowed to stir overnight to get homogeneous solution. When cellulose acetate completely dissolves in the solution it showed transparent color. Sonication of the solution was done for complete dispersion of nylon and cellulose acetate in the solvent. Sample was sonicated for about 3-4 hours. Solution was then allowed to remove air bubble by placing it in dark place for overnight.

Solution was than casted on the glass plate with the help of doctor blade. Homogeneous thickness was ensured with the help of doctor blade. Casted solution was allowed to evaporate for 40 sec so that the formic acid could evaporate through the casted membrane leaving behind pores. Casted film was then placed in the coagulation bath having non solvent which is distilled water. Precipitation of membrane takes place and the color of the casted membrane changed from transparent to white. Membrane was allowed to precipitate completely by its immersion in nonsolvent bath for 30 minutes. Membrane after complete precipitation separates itself from the casted surface.

Table 3-1 Composition wt%

Solution	Cellulose acetate (wt %)	Nylon 66 (wt %)	DMSO (wt %)
D1	11	2	87
D2	11	3	86
D3	11	5	84

Table 3-2 Composition (wt %)

Solution	Cellulose acetate (wt %)	Nylon 66 (wt %)	Formic Acid (wt %)
F1	11	2	87
F2	11	3	86
F3	11	5	84

3.2 Membrane Testing

3.2.1 Equipment

For the testing of membrane flux and rejection performance, membrane testing unit was used. Testing unit consists of feed tank and permeate collection point. Membrane was placed in the membrane cell. Membrane was supported with the help of Teflon support so that it can bear high pressure during testing. A centrifugal pump was placed in the membrane testing unit to flow the feed in the membrane cell with the required pressure. Pressure gauge was mounted on the retentate side of membrane testing unit in order to monitor the transmembrane pressure. Ball valve was fixed near pressure gauge to manipulate the transmembrane pressure in order to monitor the effect of the change in the transmembrane on flux and rejection of membrane. Schematic diagram is shown in the figure 3.3.

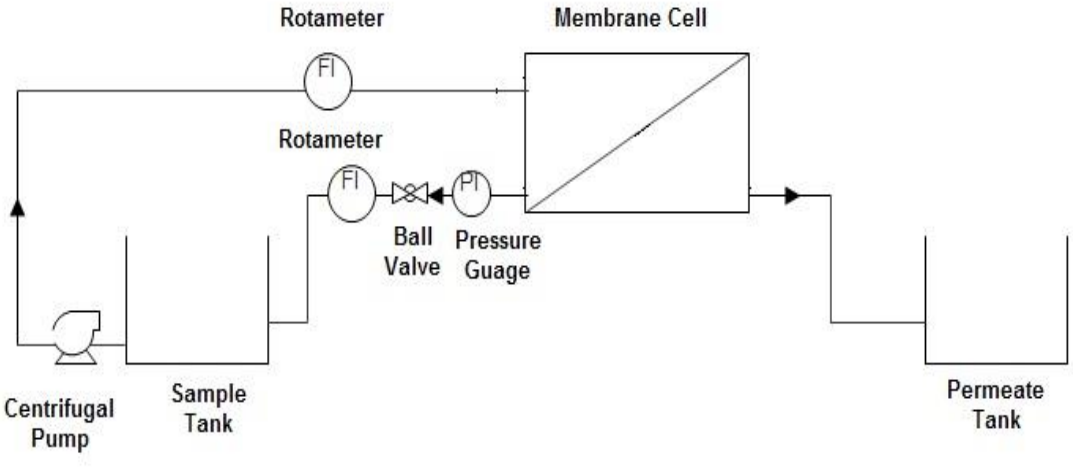


Figure 3-1 Schematic Diagram

3.2.2 Conditions

Feed entered into the membrane cell at atmospheric pressure. Similarly atmospheric pressure was applied on the permeate side. Pressure in the membrane cell at the feed side is manipulated as (0.5,1,1.5) bar with the help of ball valve mounted on the retantate stream. No temperature was applied in the feed tank so the feed entered into the tank at atmospheric temperature. Similarly the temperature of the permeate side is also at room temperature.

3.2.3 Processing

Emulsion was prepared by mixing suitable amount of oil in water. Surfactant was also added in the solution so as to form a stable oil water emulsion (9:1). Feed entered into the membrane cell with the help of centrifugal pump. As the feed entered into the membrane cell, it came into contact with membrane. The membrane consisting of pores allowed water to pass through its cross section but oil droplets owing to large size trapped into the membrane. Feed which could not pass through membrane pass over the membrane and discharge into the feed tank. Permeate than collected into the permeate chamber. Feed again entered into the membrane cell and process continued. The retentate stream rejected from the membrane cause stirring in the feed tank so no stirrer in the feed tank was required.

3.2.4 Extraction of oil

Permeate was collected into the beaker having volume of 100ml. Oil droplets which managed to find their way through membrane pores because of strong adhesion with water molecules are required to analyzed in order to get overall performance of the membrane. Liquid - liquid extraction was done to separate these oil droplets from water. Permeate solution was poured into 500 ml separating funnel and placed it on stand. Hydrochloric acid was used to change the nature of permeate from basic to more acidic. 1 ml of hydrochloric acid was added with the help of pipette in 100ml to get desired ph (<2) of permeate solution. Separating funnel was then closed with the help of placing cock on its mouth and stirred for 2 minutes. Sample of permeate solution was collected into glass tube for the measurement of its ph. Ph was measured with the help of ph meter by dipping its nobe into the glass tube having permeate. Ph of permeate should be less than 2. After calculating ph of permeate add 5.5 ml of n- hexane into separating funnel with the help of pipette. Placed stopper on the mouth of the separating funnel and shook it well for 2 minutes. Release the gases produced as a result of shaking by removing the stopper. Leave the funnel undisturbed for 10 minutes so that sufficient time could be given to split permeate into two separate layers, one layer of oil contents and other of water. Conical flask of 100 ml was rinsed with water and then dried in oven. When the flask completely dried, it was weighed with the help of analytical balance. Drip drains the lower layer of water into the beaker. It took 3-4 minutes. Filter paper was placed in the funnel and mounted this funnel into pre weighed conical flask. 1 gm of sodium sulfate was also added onto the filter paper which was placed into funnel. Drip drains the solvent layer into the pre weighed conical flask through filter paper. Repeated the above procedure twice in order to get complete extraction of oil droplets from permeates. Evaporate the solvent from conical flask by heating it in hot water bath. When only a few milliliter of the solvent left into the flask it was placed into steam bath for 15 minutes at the temperature of 70^{o}C. Removed the flask from the steam bath and put it into desiccators to absorb the moisture and brought the temperature of flask to the room temperature. The cooled flask was than weighed on analytical balance. Difference between weight of unused flask and oil containing flask will show the amount of oil permeated through the membrane.

3.3 Characterization Techniques

Characterization of membrane is very crucial part of research which helps to investigate the morphology and structure of the membrane. Morphology and structure of the membrane is responsible for the separation carried out by the membrane. Chemical composition as well as morphology of the membrane was determined with the help of X-ray diffraction (XRD), Thermogravimetric Analysis (TGA), Scanning Electron Microscope (SEM), Tensile testing. Water permeation was also calculated by carrying out pure water flux and rejection determination.

3.3.1 Energy Dispersive X-ray Analysis (EDX)

In this technique high intensity electron beams are thrown on the sample with the help of electron microscope in order to interact with the atoms of the sample. This high intensity electron beam scattered the electron present in the sample. These scattered electrons are captured by microscope and draw images. In the meanwhile another phenomenon also takes place. In these phenomena when electron beam strike at the atom of the sample they become excited and try to stable themselves. When electron beam hits the atom, electrons from the outer shell jump from valance shell to the inner shell. This displacement of the electrons results in the emission of characteristics X-rays from the atom. In nature every atom has its own valance energies so everyone has their own characteristic x rays. In EDX analysis these characteristic X-rays are used by the electron microscope and it identify the constituent materials on the basis of characteristic X-ray. With the help of a semiconductor material for the detection of X-ray and multi channel analyzer the characteristic X-rays in electronic counts. These electronic counters are accumulated as a spectrum and displayed in the form of chemical analysis of the sample. The electron microscope also shows the topography of the material. EDX also provide information regarding the composition of the sample.

3.3.2 Scanning Electron Microscopy

Morphology of the membrane plays very crucial role in the overall performance for the desired application. In order to study the morphology of the membrane scanning electron microscopy of the membrane was carried out. In order to investigate the morphology of the membrane the dried polymeric membrane was dipped in liquid nitrogen and then fractured in order to get the fibrous cross section of the membrane. The membrane was than sputtered with gold. Membrane morphology of cross section and surface was than studied with the help of JEOL JSM-6490A scanning electron microscopy.

3.3.3 Thermogravimetric analysis

Thermogravimetric analyzer (TGA) is a useful laboratory analyzer to characterize material. This analyzer finds its application in number of fields for instance pharmaceutical, food, and petrochemical.

TGA measures behavior of weight changes occur in a material with respesct to change in temperature or time with in controlled atmosphere. In this analyzer sample is exposed to controlled temperature and change of weight in sample is than measured. This shows the behavior of material under certain temperature range.

TGA comprised of a furnace having sample pan in which sample is placed. A sample pan is also supported with balance pan which showed the overall weight of material. Control temperature is than provided in the furnace and in order to control the environment purge gas is also introduced. Results obtained from temperature are plotted against two axis (X axis, Y axis). X axis shows the temperature/time applied to the material in the furnace in terms of ^{o}C/min whereas the Y axis displayed the overall mass loss in the term of weight %.

Sample preparation is an important step which requires some attention. Following are some steps which should be kept in consideration while preparing the sample for TGA analysis.

1. Sample weight should be under the limit of 2-50 mg.
2. Bottom of pan should be covered with the same material.

3. Each run should contain same amount of the sample for the sake of comparison among the samples.
4. Maximum of the area of material should be exposed to temperature.
5. Sample nature should be kept into consideration while setting the temperature.
6. Temperature scanning rate is mostly in the range of 10-20 ^{o}C/min.

In most of the case the inert atmosphere is provided in furnace with the help of nitrogen gas so that no degradation could be taken place due to reactive gas.

3.3.4 X- Ray Diffraction

X-ray diffraction is also one of the useful techniques to analyze the crystalline behavior of the material. Information regarding unit cell dimension can be identified with the help of this technique. This characterization technique utilizes Scherer equation in order to detect the structure of crystal and its atomic spacing.

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad 3.1$$

X rays generated from the cathode ray source play crucial role to identify the required information regarding crystal size and atomic spacing. When X rays come into contact with the sample their wavelength and electromagnetic radiation encounter some changes which later on detected and processed in order to get the desired information. Surface are of the specimen is calculate by utilizing following formula:

$$S = 6 \times \frac{10^3}{\rho L} 3.2$$

3.3.5 Flux Calculation

In order to calculate the overall flux of membrane, cross flow membrane testing unit was utilized comprised of feed tank, permeate collector and centrifugal pump. Effect of trans membrane pressure was examined with the help of ball valve mounted on retentate stream. Centrifugal pump was also installed to flow the feed in the membrane cell. Flow meters are also placed on the testing unit on both feed stream and retentate stream. Oil in water emulsion was prepared by mixing lubricating oil with water in different proportions at 900rpm speed for 30 minutes. Membrane was washed with the help of distilled water in order to place it in the membrane testing unit for the determination of permeate flux. Membrane was placed on the teflon support to prevent it from breakage under high pressures. Total membrane area which was exposed to the feed was about $0.0094m^2$. Flux was calculated for varying trans membrane pressures. 0.5,1 and 1.5 bar. Flux of permeate was calculated through the expression.

$$J_w = \frac{Q}{A\Delta t} \quad 3.3$$

J_w denote the flux of permeate (ml/m^2hr), where Q denotes the quantity of volume which is permeated through the membrane (ml), A shows the area of the membrane which is exposed to the feed (m^2) whereas ΔT shows the sampling time for permeate.

3.3.6 Oil Rejection

Percentage rejection of oil was also calculated with the help of method used for oil and grease calculation. N-hexane and HCL was used for the calculation of oil contents in permeate and feed streams. Concentrations of oil in feed and permeate was calculated through this process. Rejection was calculated through the following expression:

$$R (\%) = (1- \frac{Cp}{Cr}) \times 100 \quad 3.4$$

Chapter 4

Results and Discussions

4.1 Morphological Study

4.1.1 Morphological study of Commercial membrane

Commercial membrane was examined with the help of Scanning Electron Microscopy. Images revealed that the membrane was having homogeneous structure. Membrane composed of spongy structure with pores of large diameters at the surface of the membrane as shown in figure 4-1. Cross sectional images of C1 showed that membrane was having homogeneous porosity throughout membrane cross section as shown in Figure 4-2. In most of the cases membrane having finger like voids along its cross section are more preferable to the membrane having spongy cross section in the case of oil-water treatment [21].

4.1.2 Morphological study of D type membranes

Synthesized membrane composed of cellulose acetate (CA) and nylon 66 was also characterized through SEM. Surface images revealed that nylon is finely dispersed in the matrix of cellulose acetate. This showed that nylon 66 and cellulose acetate are compatible with each other. Moreover hydrophilicity of membrane surface has been enhanced by addition of nylon 66 as shown in figure 4-1. Pores were also available at the surface which confirmed the ultrafiltration structure [15]. Cross section of membrane was also examined through scanning electron microscopy. Membrane was composed of two layer; 1) skin layer, 2) porous support. Cavities were available across the cross section of the membrane separated by honey comb structure. It showed that the morphology of the membrane confirmed asymmetrical structure [32] as shown in figure 4-1. Porosity of the skin layer as well as availability of cavities across the cross section of the membrane could be justified by the fact that DMSO has higher affinity with nonsolvent (in this case is water). Less amount of nonsolvent dissolve high amount of solvent resulted in the production of cavities across the cross section of the membrane as well as pores on the surface. Literature has also confirmed that affinity of solvent with nonsolvent results in the production of finger like cavities as well as thin skin layer [32].

4.1.3 Effect of nylon 66 concentration on morphology

Effect of nylon 66 concentrations in polymer solution on surface as well as across its cross section was examined with the help of scanning electron microscopy of membrane. Results showed that as the concentration of nylon 66 increased in the polymer solution from 2 to 5% increase in surface roughness was noticed as shown in figure 4-1. Similar behavior of nylon 66 was observed in the study of Dar-Jong Ling et al [33]. Nylon became more prominent on the surface of the membrane. Surface of membrane was having porosity owing to less width of the skin layer.

Figures 4-1 showed cross sectional images of the membrane prepared with different concentration of nylon 66 in polymeric solution. Viscosity of the solution was increase by addition of nylon 66 [15]. Delay in liquid liquid demixing resulted in reduction of porosity [32]. Diameter of pore was reduced whereas pore to pore distance was increased [32]. When concentration of nylon 66 was less large cavities were witnessed shown in figure 4-2. As the amount of nylon increase in polymer solution the number of cavities were replaced with solid material having less porosity [34].

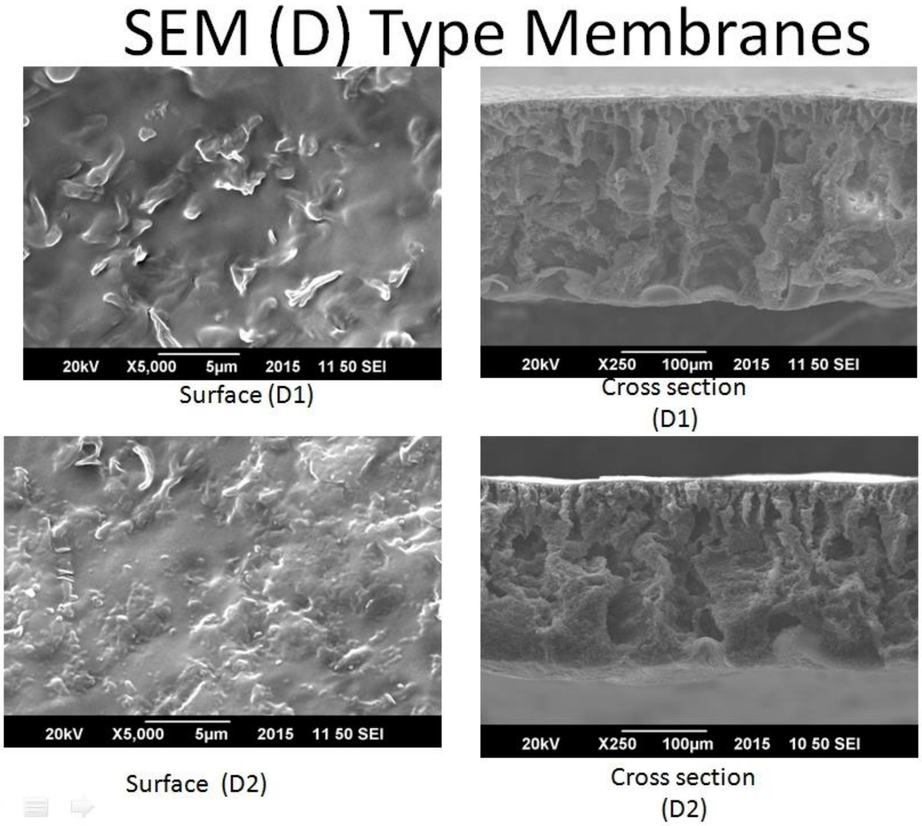


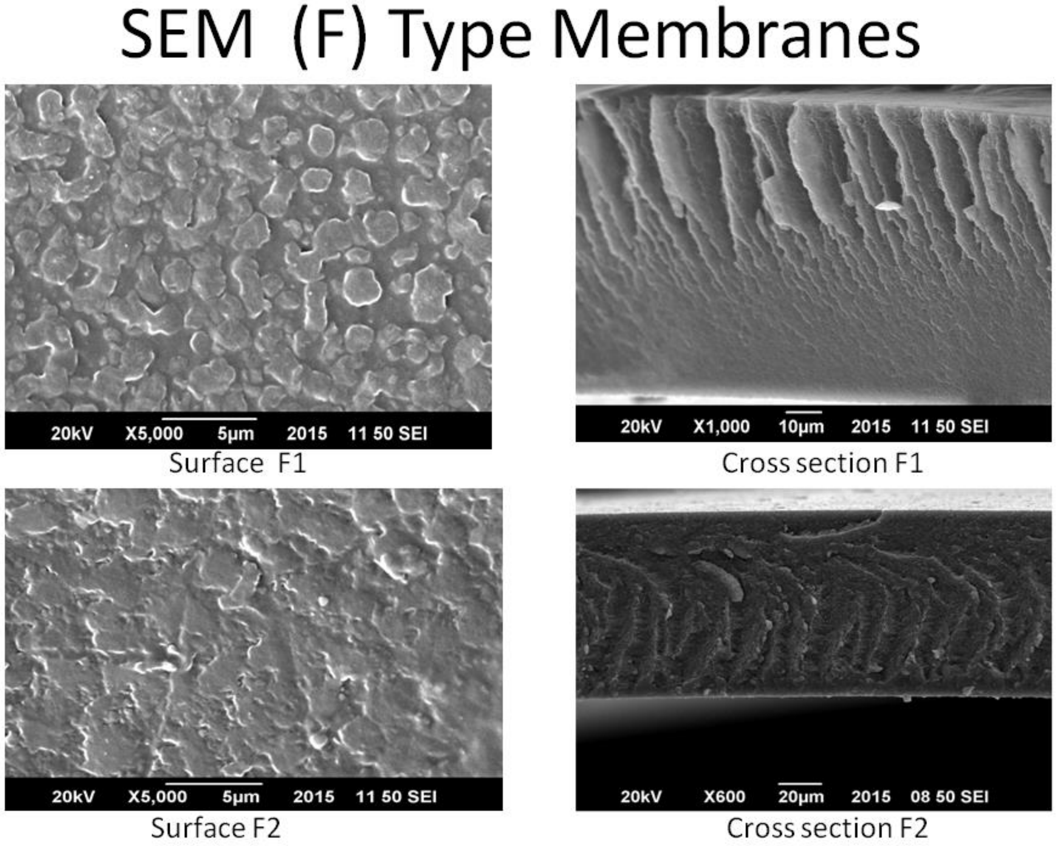
Figure 4-1 Surface and cross section images of D type membranes with nylon 66 compositions of 2 and 5 %.

4.1.4 Morphologyical study of F base membranes

Membranes prepared with the help of formic acid as a solvent was also studied with the help of scanning electron microscopy. Results showed that nylon was homogeneously dispersed on the surface of the membrane as shown in figure 4-2. Presence of nylon 66 on the surface of the membrane increased surface roughness. Cross sectional study of the membrane revealed that the membrane conformed asymmetrical structure. Membrane composed of skin layer followed by porous support as shown in figure 4-2. Porous support of the skin layer composed of pores of different diameters. Decrease in overall porosity of the membrane as well as compact structure across cross section could be the effect of affinity of solvent with non solvent [32]. Affinity of formic acid was low which resulted in compact structure of the membrane.

4.1.5 Effect of Nylon 66 concentration

Effect on nylon concentration on overall morphology of the membrane was also examined with the help of scanning electron microscopy. Results showed that as the concentration of nylon increased from to 2 to 5 wt% in membrane solution, roughness of the surface increased shown in figure 4-2. Increase in nylon 66 concenteration also effect cross section morphology of the membrane. As the amount of nylon 66 increased the thickness of skin layer was increased. Moreover the cavities available at the cross section of the membrane also ceased to exist. Same effect was noted by Tai hong yang et al. [32]. Increase in polymer amount resulted into late liquid-liquid demixing. Slow liquid-liquid demixing cause decrease in porosity as shown in figure 4-6,4-8. Moreover the pore to pore distance was increased leading to less porosity of the membrane [34].


SEM (F) Type Membranes

Surface F1

Cross section F1

Surface F2

Cross section F2

Figure 4-2 SEM images of surface and cross section of F type membranes, Nylon 66 composition of 2 and 5 %.

4.2 Thermogravimetrical Analysis

Thermo gravimetrical analysis was also done in order to analyze thermal stability of synthesized membrane [35]. D1 and F1 membranes were selected for mechanical testing owing to their high flux. Figure 4-3 showed thermo gravimetric curves for D1 membranes in inert atmosphere on heating rate of 15^{o}C/min. TGA curve showed three weight losses at the temperature of 60-70°C, 320-400°C and 420°C. In the case of synthesized membrane first drop in TGA curve at 70°C is due to loss of moisture remaining in the membrane. Major weight loss of membrane was witnessed from the temperature 320-400. Drop in curve would be the result of degradation of cellulose acetate. Last drop in TGA curve started from 420°C leading to the overall decomposition of membrane.

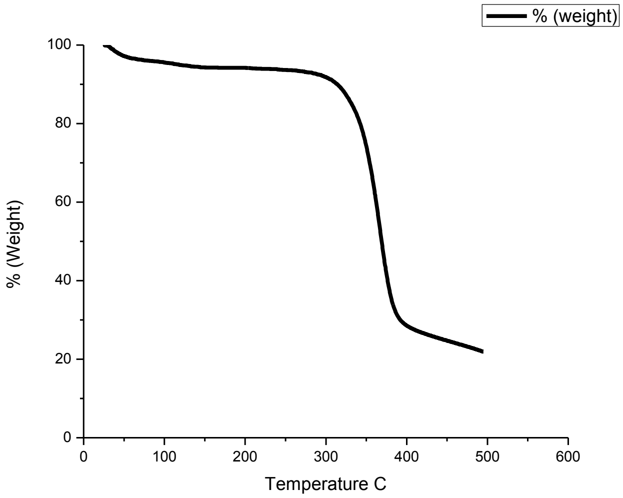


Figure 4-3 TGA of D1

Thermal sustainability of F type membrane was also examined with the help of thermogravimetric analysis. Result showed that initial drop in curve was at about 30°C. This drop in curve would be due to evaporation of moisture remaining in the membrane. Major drop in curve was noticed at 300°C. Cellulose acetate would be started to decompose which resulted drop in TGA curve. Literature has also confirmed that decomposition of CA started at about 260°C. Drop in curve continued up till 400°C. After complete decomposition of cellulose acetate, Nylon began to decompose. As shown in figure 4-4.

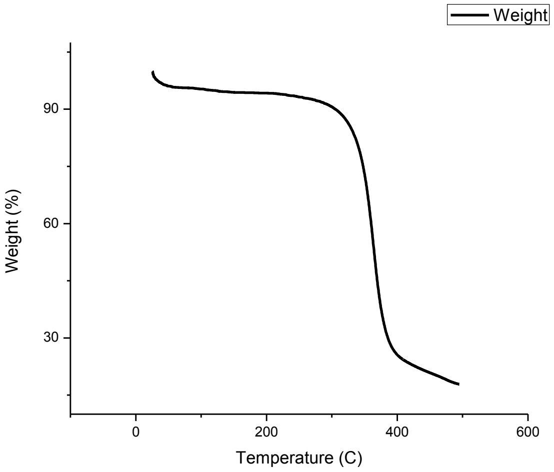


Figure 4-4 TGA of F1

TGA of commercial membrane composed of cellulose acetate was also done in order to compare thermal properties. Conditions were same in all cases. TGA curve of C1 membrane showed that major drop in curve was noticed at about 175°C. Drop continues until 240°C leading to complete degradation of membrane as shown in figure 4-5.

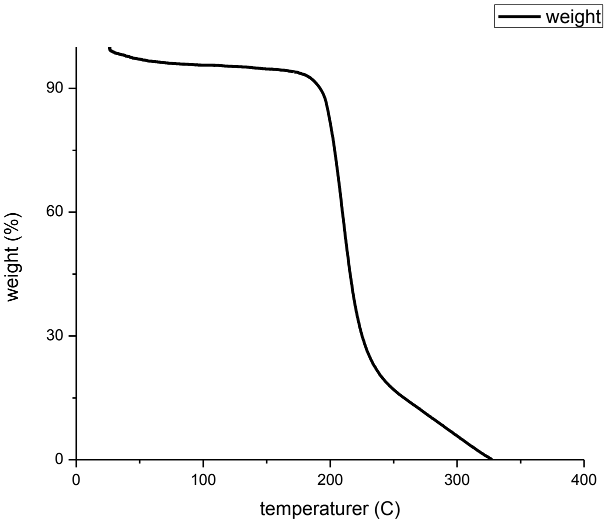


Figure 4-5 TGA of C1

TGA results showed that synthesized membrane is more resistant to high temperature and showed less mass loss even at high temperature as compared to commercial membranes. In synthesized membranes the major drop in TGA curve is due to the decomposition of cellulose acetate. Literature has confirmed that the decomposition of pure cellulose acetate membrane started around 260°C [35]. On the other hand complete degradation temperature of pure cellulose acetate is around 350-400°C. Results showed that thermal stability of the synthesized membrane was increased to about 25°C. Moreover solvent has no significant effect on the thermal properties of the membrane. This finding also suggests that both of the polymers are compatible with each other and addition of nylon 66 enhance thermal properties of cellulose acetate [36].

4.3 Tensile testing of membranes

Mechanical properties are having great importance in the field of membrane technology. Pressure gradient is the most important driving force for the required separation through membrane. Membrane should be having good mechanical properties in order to become useful in high pressure environment [37]. In the case of asymmetric membranes mechanical properties are not as good as that of symmetrical or dense membranes. Asymmetrical membranes composed of large cavities followed by skin layer which deteriorate the mechanical strength of the membrane. Whereas symmetrical membranes have no finger like voids and compact in structure provide good mechanical properties [37]. Both synthesized and commercial membranes were tested in order to examine their mechanical properties.. It was observed that commercial membrane show high tensile strength up to 9 MPa. Such a high tensile strength could be justified with the help of cross sectional SEM image. It was revealed through SEM image that commercial membrane has symmetrical structure along its cross section. Such a compact structure will result in high tensile strength. On the other hand elongation at break of commercial membrane was about 2.9%. Less elongation of the commercial membrane could be justified by the porous structure of the membrane. SEM images showed that membrane was having pores in it which will reduce the overall flexibility of membrane. So its elongation at break will be reduced. Synthesized membrane D1 having cellulose acetate and nylon 66 blended with the help of dimethylsulfoxide was also tested for its mechanical properties and results were satisfactory. D1 membrane showed tensile strength of 10Mpa and elongation at break about 2.5%. Nylon is having excellent mechanical properties and good thermal properties. When nylon was added into the matrix of cellulose acetate it will also impart its mechanical and thermal properties to the overall properties of the membrane. So the increase in the tensile strength of the membrane can be attributed to the addition of nylon 66 in cellulose matrix It has been confirmed from the literature that tensile strength of cellulose acetate membrane having asymmetrical structure has maximum tensile strength of 6.9 MPa [37]. On the other hand reduction of elongation at break could be justified by cross section structure of the membrane. As SEM images revealed that the membrane was having asymmetrical structure with large cavities. It will result in decrease in elongation. Structure was not compact so elongation will not be high. When synthetic membrane F1 composed of nylon 66 and cellulose acetate blended membrane having formic acid as the solvent was tested for their mechanical properties results were very promising. These membranes showed tensile strength of about 14.3 MPa and elongation at break of approximately 6%. These results could also be justified through SEM images. It was revealed through surface images of the membrane that nylon 66 was homogeneously dispersed on the surface of the membrane in cellulose acetate matrix. Such a homogeneous dispersion of nylon will impart the inherent mechanical properties of nylon 66 to the overall properties of the membrane. Elongation of the membrane was also increased owing to the cross sectional structure of the membrane. Membrane was having finger like voids after the skin layer. But finger like cavities were not too much vide. Moreover the cavities were succeeded with porous sponge structure which will provide more elongation without any breakage in the membrane.

Table 4-1Tensile testing

Membrane	Tensile strength Mpa	Elongation at break %
C1	9 ± 0.2	2.9±0.1
F1	14.3±0.3	6±0.2
D1	10±0.2	2.5±0.2

4.4 Flux

Permeate flux of the membranes were calculated by varying transmembrane pressure and nylon 66 composition.

4.4.1 Commercial membrane

Commercial membrane was placed in membrane testing unit in order to calculate overall flux.

4.4.1.1 Flux as a function of Transmembrane pressure

Membrane was tested for different transmembrane pressures in order to examine the effect of transmembrane pressure on overall flux. Results showed that as the transmembrane pressure across the membrane increased the overall flux of the membrane also increased as shown in figure 4-. Increase in flux could be attributed to the fact that as the driving force of the system increases its flux will also increases[38]. Pores on the surface of membrane resulted in increase in flux. A sharp decrease in flux was witnessed after a certain time. Decrease in flux over time could be the result of pores blockage as well as the production of resistance layer at the surface of the membrane. Figure 4-6 showed the effect of transmembrane pressure on overall flux of the membrane.

4.4.2 D type Synthesized Membranes

Synthesized membranes composed of DMSO as a solvent were also examined in order to calculate overall flux.

4.4.2.1 Effect of composition on flux

Composition of nylon 66 in overall polymeric solution was also varied in order to check the effect of nylon 66 on the flux of membranes. Results showed that as the composition of nylon 66 increased from 2-5 wt% the flux of membrane decreased. Such a behavior could be justified from SEM images. As the amount of nylon 66 increases in the polymeric solution the cavities were replaced by solid areas across the cross section of the membranes. Moreover increase in nylon 66 amount results in increase in surface roughness. Surface roughness will result in more adhesion of oil droplets over membrane surface and result in formation of resistant layer [39]. Surface images of membrane also showed that increase in amount of nylon 66 hinder contact of cellulose acetate with water at surface. It will reduce the efficiency of cellulose acetate at the surface which results in overall reduction of flux. Both of the membrane materials (cellulose acetate and nylon 66) swell when exposed to water [38]. So swelling of polymeric solution will reduce the overall porosity of the membrane. Figure 4-6 showed flux of membrane as a function of composition.

4.4.2.2 Effect of trans-membrane pressure on Flux

Effect of trans-membrane pressure was also studied on the overall flux of the membrane. Results showed that as the trans-membrane pressure across the cross section of the membrane increased the overall flux of the membrane was also increased. Increase in membrane flux could be attributed to the low thickness of the skin layer. Increase in trans-membrane pressure may cause some deformation in polymeric chains as well as in pores dimensions [24]. More permeate would be passed through the voids produced as a result of chain movement. But with course of time the flux of the membrane decreased because oil droplets which managed to pass through the surface of the membrane block the pores available on surface as well as cross section of the membrane. Moreover the formation of resistant layer at the surface of the membrane also decreased the overall flux of the membrane. Figure 4-7 showed the effect of TMP on membrane flux.

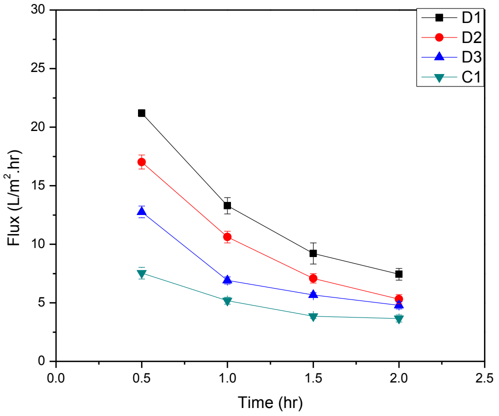


Figure 4-6 Flux as a function of nylon 66 composition

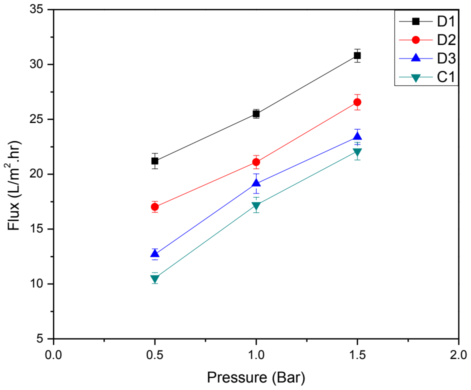


Figure 4-7 Flux as a function of TMP

4.4.3 F type synthesized membranes

Membranes composed of formic acid as a solvent were also tested in order to examine overall flux.

4.4.3.1 Flux as a function of composition

Flux of the membranes was calculated as a function of composition of nylon 66. Results showed that as the amount of nylon 66 increased in polymeric solution the overall flux of the membrane decreased. These results could be justified with the help of SEM images. SEM images showed that as the amount of nylon increased in polymeric solution, the thickness of the skin layer was increased result in reduction of flux. Moreover increase in polymer composition results in delayed liquid-liquid demixing [32]. As a result more compact structure was witnessed having less porosity. So flux of the membrane will be reduced. Increase in surface roughness was also witnessed as the amount of nylon 66 increased in polymeric solution. Surface roughness increased the probability of resistant layer formation at the membrane surface [39]. Flux will be reduced. Figure 4-8 showed the behavior of flux as a function of amount of nylon 66.

4.4.3.2 Flux as a function of trans-membrane pressure

Membrane flux was also calculated as function of trans-membrane pressure. Pressure across the membrane was varied and flux of the membrane was calculate in order to examine the effect of pressure. Result showed that as the trans-membrane pressure increased across the membrane, flux was enhanced. Increase in flux could be attributed to the change in dimension of pores as well as change in polymeric chains taken place due to high pressure [38]. As the pressure across the membrane increased the driving force was enhanced, high amount of water penetrate through pores available at surface as well as across the cross section of membrane. But owing to greater thickness of skin layer of F based membranes than D type membrane the change in flux was not high enough. Figure 4-9 showed the effect of trans-membrane pressure on the overall flux of the membrane.

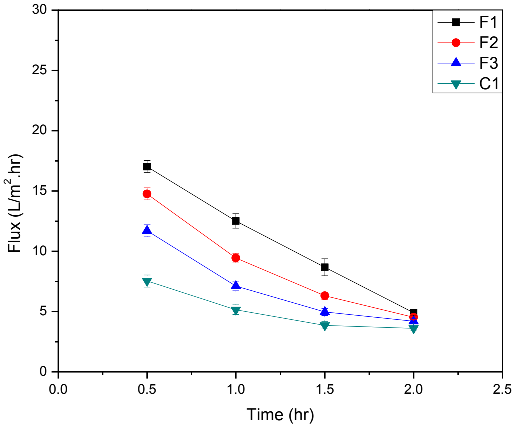


Figure 4-8 Flux of F type membranes as a function of nylon 66 composition

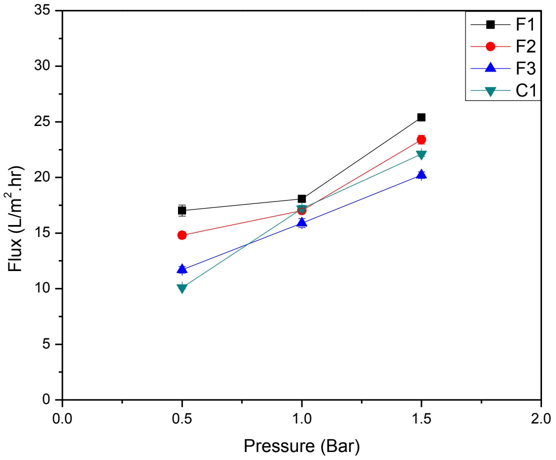


Figure 4-9 Flux as function of TMP (F type)

4.5 Rejection of oil

Permeate was treated in order to calculate amount of oil which managed to pass through the membrane. Oil and grease extraction method was used to examine the amount of oil.

4.5.1 Rejection of commercial membranes

4.5.1.1 Rejection of membrane as a function of trans-membrane pressure

Rejection of commercial membrane was also calculated as a function of trans-membrane pressure in order to examine the effect of pressure on the working of membrane. Results showed that as the transmembrane pressure across the membrane increases, overall rejection of the membrane decreased. This behavior of the membrane could be due to the pore blockage or the formation of resistant layer over the surface of the membrane [38]. Increase in transmembrane pressure across the membrane resulted in higher penetration of oil droplets across the cross section of the membrane. Which resulted in more concentration of the oil in permeate stream as well as resulted in pore blockage. Figure 4-10 showed the effect of transmembrane pressure on membrane rejection.

4.5.2 Rejection of synthesized membranes

Synthesized membranes based of DMSO were also tested for the calculation of efficiency in the case of oil water treatment.

4.5.2.1 Membrane rejection as function of composition

Membrane rejection was also calculated by varying the composition of the polymeric solution. Amount of nylon 66 in polymeric solution was varied and its affect on membrane rejection was studied. Results showed that as the amount of nylon 66 increased in the overall composition of the membrane, overall rejection of the membrane was increased. This increase in rejection could be attributed to change in structure occurred as the amount of nylon 66 increased in the polymeric solution. Overall membrane porosity decreased as well as the thickness of skin layer was increased. As a result more oil will be rejected and could not be passed through the cross section of the membrane. Moreover nylon 66 is best barrier to oil and lubricant so as the amount of nylon 66 increases in the polymeric solution the amount of oil in the permeate decreases. Figure 4-10 showed the rejection of membrane as a function of nylon 66 concentrations.

4.5.2.2 Rejection as a function of trans-membrane pressure

Synthesized membranes composed of DMSO were also tested for the rejection of oil as a function of trans-membrane pressure. Results showed that as the trans-membrane pressure across the membrane increased, overall rejection of the membrane decreased. Decrease in overall rejection of the membrane could be justified by the structure of the membrane. Thin skin layer o allowed more oil droplets to pass across it when exposed to high trans-membrane pressure. Moreover due to formation of cake layer the already dispersed oil droplets across the cross section of the membrane managed to penetrate through the cross section of the membrane resulted in the increase in oil concentration of permeate. High trans-membrane pressure exert extra pressure over the chains of polymeric materials as well as the pores available at the surface and cross section of the membrane. This exerted pressure resulted in the change in dimension of membrane pores and cause reduction in membrane rejection cause decrease in membrane rejection. However stiffness imparted by nylon 66 to the membrane also reduce the effect of high pressure on membrane [36] and rejection of membrane was not rapidly decreased. Figure 4-11 showed the effect of trans-membrane pressure over the membrane rejection.

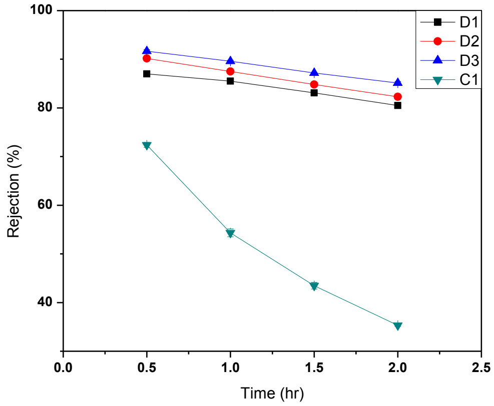


Figure 4-10 Rejection of D type membranes as a function of nylon 66 composition

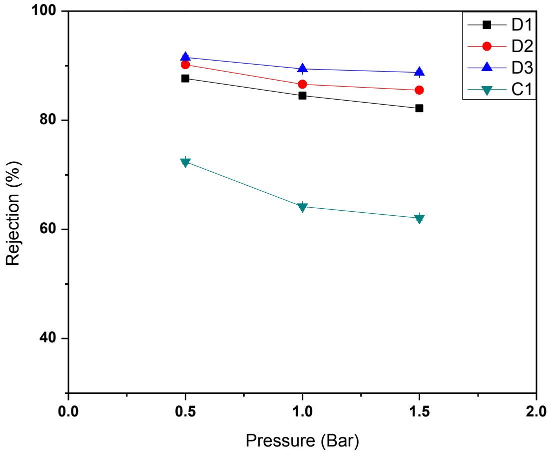


Figure 4-11 Rejection as a function of TMP (D type)

4.5.3 Rejection of F based membrane

Synthesized membranes composed of Formic acid were also tested in order to examine their efficiency for oil rejection.

4.5.3.1 Rejection as a function of membrane composition

Composition of nylon 66 in polymeric solution was varied and effect of composition on overall rejection of the membrane was tested. Result showed that increase in the concentration of nylon 66 in polymeric solution resulted in the increase in oil rejection of membrane. Such a behavior could be attributed to the fact that nylon 66 is a best barrier to the permeability of oil and grease. So increase in the amount of nylon 66 in polymeric solution enhances the efficiency of the synthesized membrane. Moreover SEM images showed that increase in polymeric composition resulted in a change in membrane structure from open to compact. More compactness of the membrane structure will further hinder the movement of the oil across the cross section of the membrane. Increase in nylon 66 concentration resulted in dense skin layer which will resist the penetration of oil droplets into the cross section of the membrane. Figure 4-12 showed the rejection of membrane as a function of nylon 66 compositions at constant pressure of 0.5 bar.

4.5.3.2 Membrane rejection as a function of transmembrane pressure

Rejection of the synthesized membranes was tested by varying transmembrane pressure. Reuslts showed that increase in transmembrane pressure across the membrane resulted in decrease in overall rejection of membrane. High pressure across the cross section of the membrane caused some deformation of the polymeric chains as well as pores available at the surface and cross section of the membrane. More amount of oil droplets managed to pass through the cross section o the membrane which resulted in the decrease in the efficiency of the membrane. But it was also noted that the rejection of the membrane was higher than the rejection of DMSO based membranes. This increase in rejection of the membrane might be due to the stiffness provided by nylon 66 to the overall properties of the membrane and high miscibility of nylon 66 in formic acid. Figure 4-13 showed the rejection of F based membrane at different trans-membrane pressures.

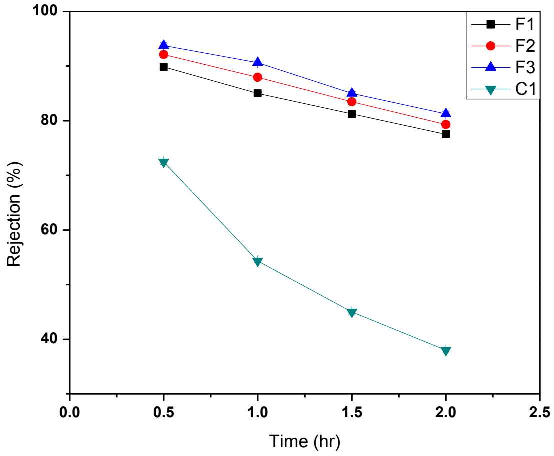


Figure 4-12 Rejection of F type membranes as a function of nylon 66 composition

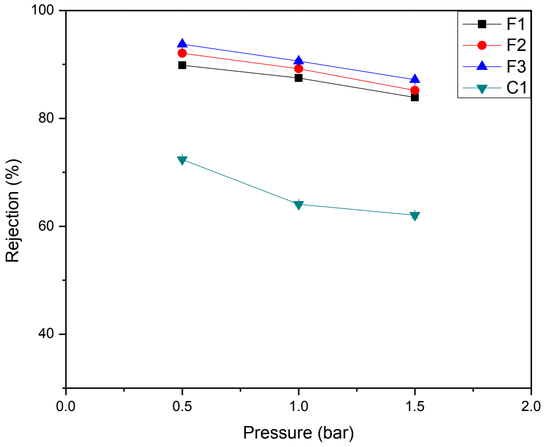


Figure 4-13 Rejection as a function of TMP (F type)

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

Nowadays treatment of oily waste water with the help of membrane technology is gaining much importance. Owing to pollution caused by conventional process they are unable to grab much attention in the field of water treatment.

In past different materials had been tested in order to get desirable membrane for treatment of oily waste water even in harsh environment. But incompetency of membrane materials in order to get desired rejection as well as high flux force researchers to strive for new materials which can fulfill the requirements.

In order to get high flux as well as high rejection polymeric materials have been blended together to get desired properties. In this study nylon 66 was blended in cellulose acetate with different compositions (2,3,5) wt% in order to enhance the thermal and mechanical properties of the membrane. Impact of addition of nylon 66 on the hydrophilicity of the membrane of the membrane was also studied with the help of flux and rejection measurement. Solvent for membrane synthesis was varied in order to get insight about the effect of change in solvent over morphology of the membrane.

Results showed that by blending of nylon 66 with cellulose acetate resulted in high membrane flux as well as high rejection. But increase in the amount of nylon 66 resulted in flux decline but rejection was increased. Thermal and mechanical properties of synthesized membrane were enhanced as a result of blending.

5.2 Recommendations

Synthesized membranes have great potentials in the field of water treatment. Owing to high hydrophilicity of synthesized membranes, they can be used for the treatment of water. Porosity of membrane can be enhanced by incorporating hydrophilic additives in synthesized membranes to enhance its applications. Varying the condition of immersion precipitation can tailored the membrane structure.

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