

# **Fabrication and Analysis of Boron-Nitride Nanosheets based Membranes for Water Treatment**



**By**

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# **Fabrication and Analysis of Boron Nitride Nanosheets based Membranes for Water Treatment**



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for the degree of**

**MS in Chemical Engineering**

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## **Dedication**

This research is dedicated to

My Father.

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## Abstract

The current research aimed to fabricate Cellulose acetate/polyethylene glycol (CA/PEG) based mixed matrix membranes incorporated with two-dimensional boron nitride (BN) nanosheets by non-solvent induced phase inversion (NIPS) process. Synthesized membranes were characterized in terms of surface morphology (SEM), functional groups (FTIR), hydrophilicity (contact angle measurement) and other properties (mean pore radius, porosity). Large macro-voids were formed on cross-sectional morphology of the synthesized membranes by the addition of BN nanosheets. This is also attributed to enhancement of mean pore radius, porosity, and hydrophilicity of membranes. Membranes incorporated with BN nanosheets showed high hydrophilicity and higher water flux values as compared to pure CA/PEG membrane. A decrease in flux was observed at higher concentration of BN nanosheets due to agglomeration of BN nanosheets in the membrane structure. Highest pure water flux of  $54 \text{ Lm}^{-2}\text{h}^{-1}$  and oil rejection efficiency of 96% was stated for CA/PEG membrane with optimum concentration of 0.25 wt% BN nanosheets. Moreover, this membrane showed better anti-fouling property having flux recovery ratio of 94% as compared to pure CA/PEG membrane with flux recovery ratio of 77%.



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## List of Acronyms

CA:	Cellulose Acetate
DMF:	Dimethylformamide
PEG:	Polyethylene Glycol
BN:	Boron Nitride
BNNS:	Boron Nitride Nano Sheets
h-BN:	Hexagonal Boron-Nitride
SDS:	Sodium Dodecyl Sulphate
NMP:	N-methyl-2-pyrrolidone
DI:	De-ionized
MMMs:	Mixed Matrix Membranes
MF:	Microfiltration
UF:	Ultrafiltration
NF:	Nano-filtration
RO:	Reverse osmosis
ES:	Electro-spinning
TE:	Track etching
MSCS:	Melt spinning combined with cold stretching
TIPS:	Thermally induced phase separation
NIPS:	Non-solvent induced phase separation
VIPS:	Vapor-induced phase inversion
PAHs:	Polyaromatic Hydrocarbons
PAC:	Powdered Activated Carbon

NPM:	Nano Porous Membrane
PS:	Polysulfone
PES:	Polyethersulfone
PAN:	Polyacrylonitrile
PVA:	Polyvinyl Alcohol
PEI:	Polyetherimide
PDA:	Polydopamine
GO:	Graphene Oxide
COD:	Chemical Oxygen Demand
SEM:	Scanning Electron Microscopy
FTIR:	Fourier Transform Infrared Spectroscopy
PWF:	Pure Water Flux
O/W:	Oil-Water
TOC:	Total Organic Carbon
FRR:	Flux Recovery Ratio

# Chapter 1

## Introduction

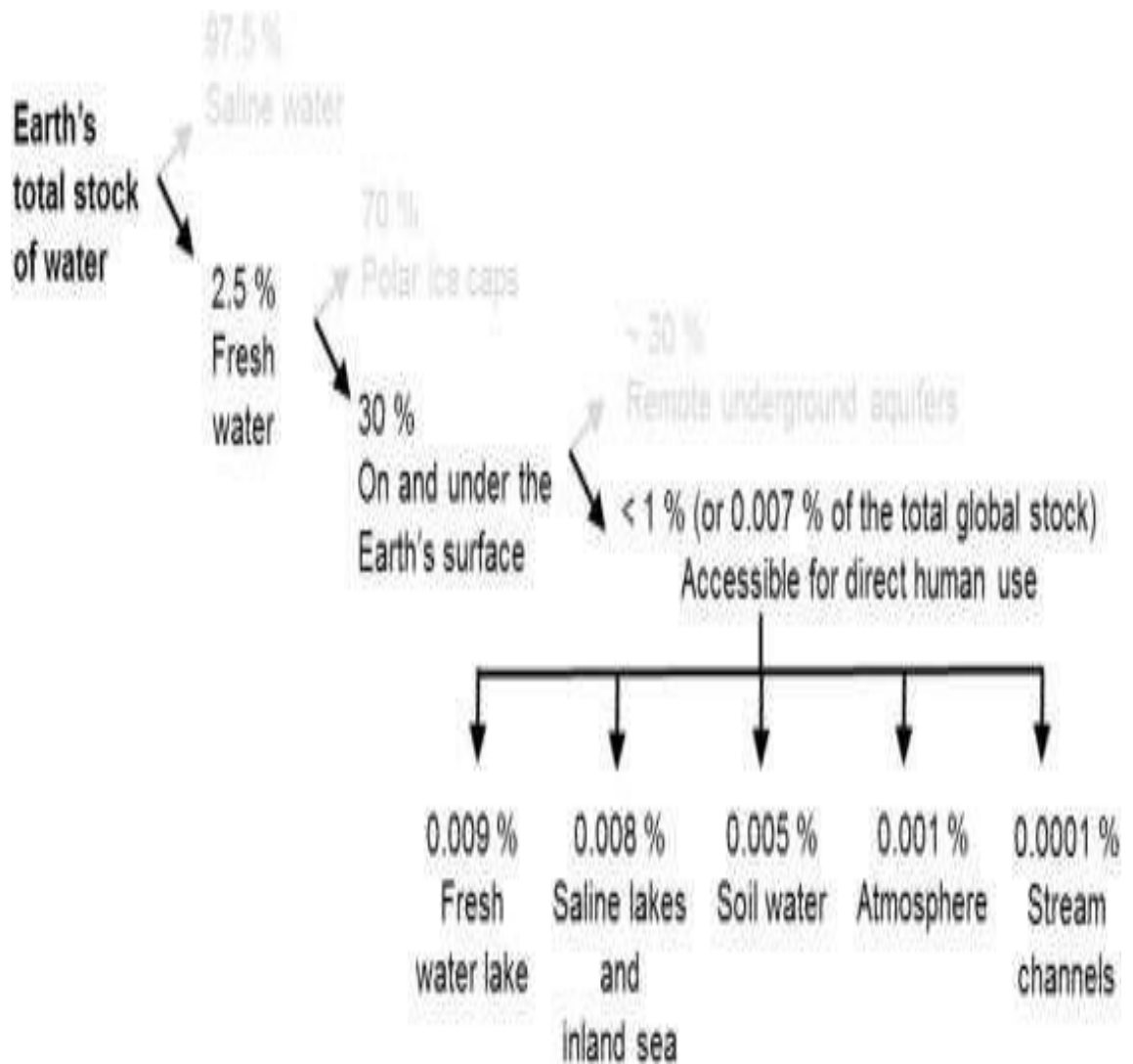
### 1.1 Background

Water is essential for life and needed in various human activities. Therefore, access to clean and freshwater nowadays is a serious concern across the globe. Subsequently, sustainable management of freshwater resources has gained tremendous importance on a global scale [1].

Globally, water is obtained from two different sources that are conventional and non-conventional sources. Conventional sources contain lakes, rivers, rainfall, snowmelts, and aquifers, which can be used directly or after a small treatment. Non-conventional sources include brackish water, seawater, municipal water, etc. Further usage of non-conventional sources requires proper treatment. Global freshwater resources are shown in figure 1.1.

Freshwater is naturally occurring and generally obtained from natural sources such as lakes, rivers, rainfall, etc. Water containing less than 1000 mg of dissolved solids per liter is known as fresh water. Of all the water available on the earth, only 2.53% is fresh water and is trapped inside glaciers and deep underground. Freshwater sources require no or a little treatment to be consumed as freshwater [2]. On contrary, non-conventional water resources are used for agricultural and other cleaning purposes. However, water from the aforementioned resources requires certain treatment processes before utilizing it. They are treated in many ways such as desalination of seawater and brackish water; collection, treatment, and reuse of agricultural drainage water [3].



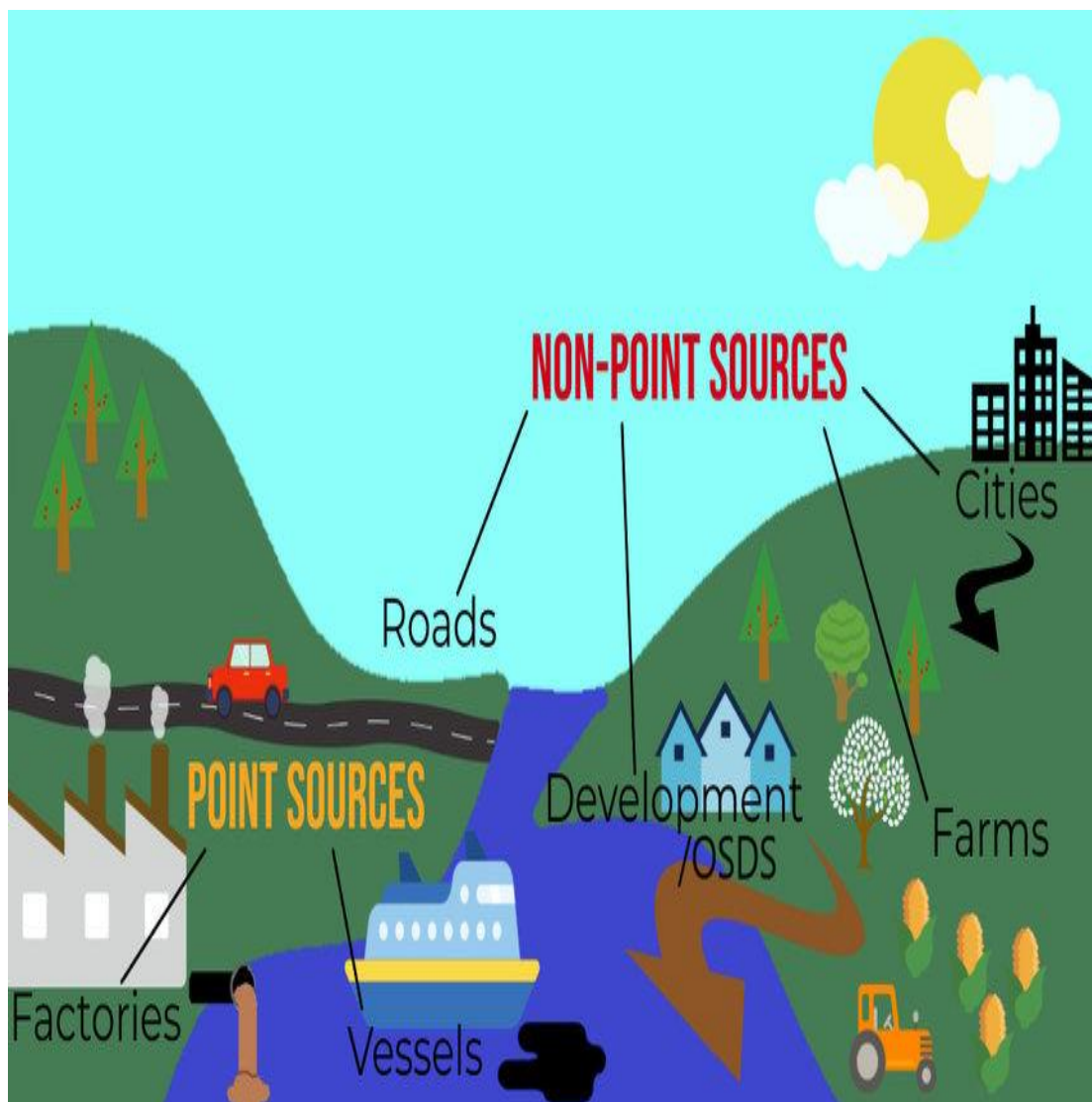


*Figure 1.1 Total global stock of freshwater for human use*

## 1.2 Water Pollution

Water pollution is one of utmost concerns for environmentalists these days. It is defined as the condition when the concentration of harmful chemicals or microorganisms in water bodies such as ground water, oceans, rivers, and lakes reaches to a point where it poses threats to aquatic as well as human life. Being a universal solvent, water dissolves almost everything in it, that is why it can be easily contaminated as well. Surface water and ground water are considered to be most affected water bodies.

When there is a single source of pollution or when the pollution in water body is coming from one point then this is called point source pollution from example effluent coming from drainage pipe of an industry and oil spill from a ship carrying oil tanker. When multiple sources are discharging effluent in a single water body then this is termed non-point source pollution. Different point and non-point sources of pollution are shown in figure1.2. Transboundary pollution is situation when the pollution entering the water body at one-point scatters to hundreds and thousands of miles away for example, radioactive waste from nuclear power station discharged to a nearby river [4].



*Figure 1.2. Point and Non-point sources of pollution*

Water pollution does not start from within the water itself. Most of it comes from land from point and non-point sources. Water pollution can be caused by a number of reasons including domestic sewage, industrial wastewater, and agricultural waste being discharged into a water body. Other reasons are acid rain and global warming. Apart from that one other reason which particularly affects marine environment is oil spills accidents that cause oil pollution in water which is the focus of this study. These all are responsible for discharge of many inorganic and organic pollutants in water [4].

### **1.3 Oil-Water Pollution**

Oil and Organics are common pollutants in wastewater. Many industries e.g., food, mining, textile, leather cement, steel, pharmaceutical and petrochemical industry produce oily wastewater. However, in oceans and seas most significant form of pollution is also oil/water pollution with adverse damages to marine ecosystems. When treating oily wastewater and oil spillage clean-up, oil-water separation becomes crucial. Different industries like petrochemical, metallurgical, food, textile, steel, and leather all produce substantial amounts of industrial oily wastewater [5-10]. In the oil industry, the phases of oil production process and its transport can all experience an oil spill, causing serious economic and environmental effects [11-13]. Effects of oily wastewater are;

- Risking human health
- Causing atmospheric pollution
- Influencing crop growth
- Damaging ground and drinking water supplies, damaging aquatic resources
- destroying natural environment [14].

# EFFECTS OF OILY WASTEWATER INCORRECT DISPOSAL

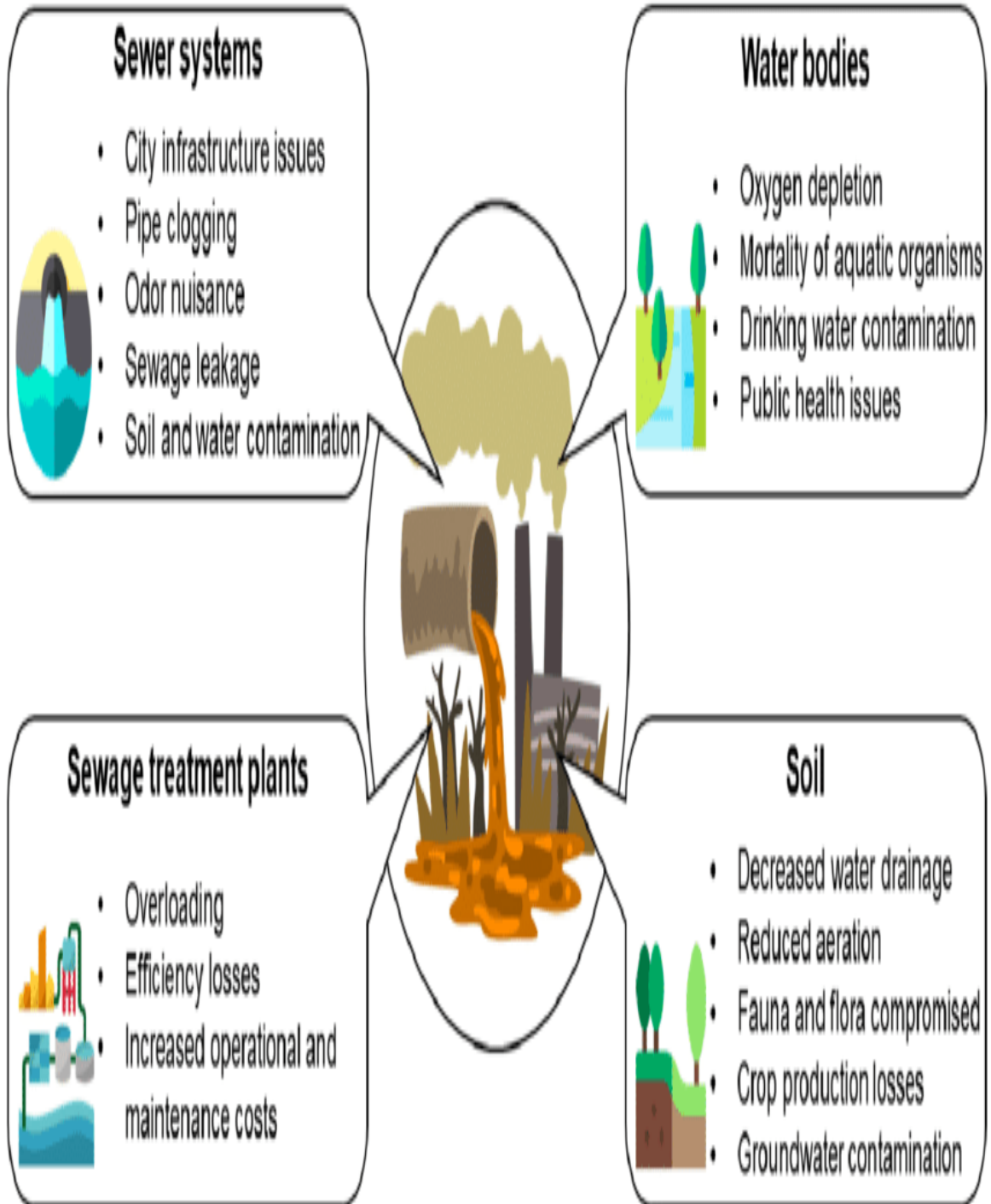


Figure 1.3. Effects of oily-wastewater incorrect disposal

For separation of oily wastewater, several techniques are frequently utilized, including physical, chemical, and biological processes like centrifugation, coagulation, flocculation, gravity separation, membrane separation, and biological technologies. However, the disadvantages of the present oily wastewater separation systems include poor selectivity, an extensive separation time, a large energy input, the requirement for a sizable amount of land, and secondary pollutants production. Membrane filtration under particular wetting circumstances has received a lot of research during the past ten years. Hydrophilic and hydrophobic membranes are designed for aqueous phase filtration. Utilizing membranes that selectively block the water and oil phases, hydrophobic and hydrophilic membranes are utilized in oil-water combinations[15-22].

Oily wastewater resources, physical forms, impact, and treatment advantages are shown in fig.

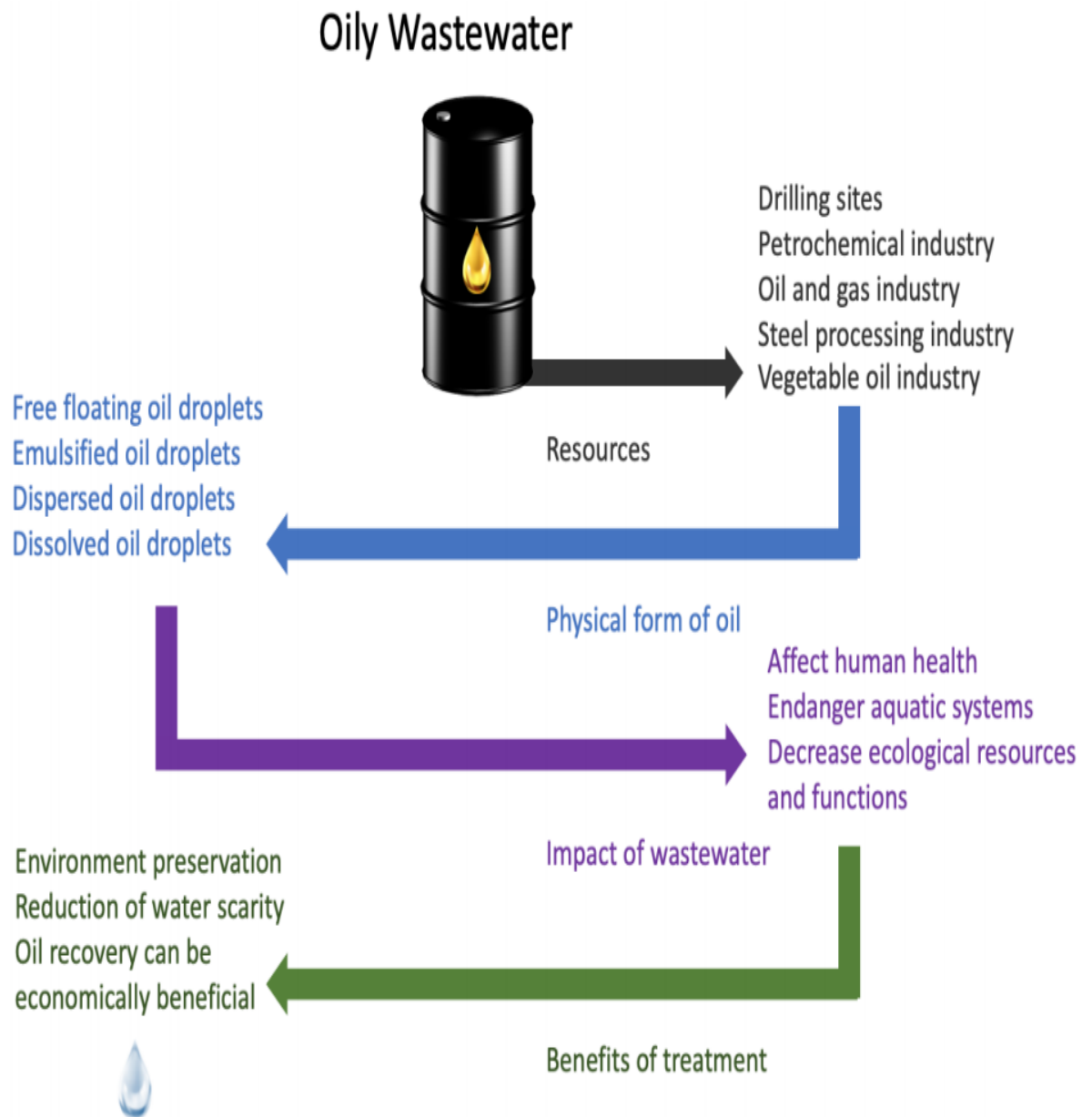


Figure 1.4. Oily Wastewater resources, physical forms of oil, impacts, and benefits of treatment

## 1.4 Membranes

Membrane separation is a wider term used for many different separation processes. The membrane acts as a filter, which removes suspended particles from the water. Membrane processes are dependent on various driving forces like pressure, electrical potential, concentration, etc. To separate a solution into retentate and permeate, a driving force is created around the membrane.

## 1.5 Types of Membranes

Molecule size rejection is the basis of the classification of membranes involved in separation processes. In water treatment processes various types of membranes are used. These membranes include Microfiltration (MF), Ultrafiltration (UF), Nano-filtration (NF) and Reverse osmosis (RO), Gas separation and pervaporation membranes [23]. Some characteristics of different membrane processes are detailed in table 1 [24].

*Table 1. Characteristics of different membrane processes*

<b>Membrane Types</b>	<b>Separation Processes</b>	<b>Pore Size (<math>\mu\text{m}</math>)</b>	<b>Rejections</b>
<b>Microfiltration (MF)</b>	Sieving	100-10000	Particles
<b>Ultrafiltration (UF)</b>	Sieving	2-100	Particles Macromolecules May reject multivalent ions
<b>Nano-filtration (NF)</b>	Sieving Charge	2-0.5	Particles Macromolecules Multivalent ions May or may not reject small organic compounds
<b>Reverse Osmosis (RO)</b>	Sieving Diffusion	<0.5	Particles Macromolecules Multivalent ions Monovalent ions Small-organic compounds

## 1.6 Membrane Fabrication Techniques

Membrane manufacturing techniques are important because the morphology of membranes is affected by fabrication techniques. Techniques that are mostly used are phase inversion, spinning, track etching, and melt spinning combined with cold stretching. In electro-spinning, (ES) pore is simply formed by the evaporation of the diluent. When we discuss the track etching (TE) method the pore formation is based on irradiation, which produces tracks in the foils of selected material and pore, formed via chemical etching. Pore formation in the melt spinning combined with cold stretching (MSCS) mechanical forces operate on the membranes in a cold-stretching step. Some advantages and disadvantages of membrane fabrication methods are listed in table 2 [25].

*Table 2. Advantages and disadvantages of membrane fabrication methods*

Method	Advantages	Disadvantages
TIPS	Compatible with semi-crystalline polymers that are difficult for ordinary solvents to dissolve. Intrinsically reproducible and less prone to errors.	Costly and organic solvents are not environment friendly
NIPS	Additives addition controls surface characteristics and pore size	Difficulty in controlling process
VIPS	It allows the morphologies of both flat-sheet and hollow-fiber polymer membranes to be modified and tailored.	Commercial membranes development is limited.
MSCS	The method is easy and cheap, making it appropriate for large scale production. There is no solvent in the procedure. Outstanding mechanical strength	The minimal transverse tear resistance is the result of high orientation in the membrane structure.



TE	Accurate measure of Pore shape, size, and density	Limited to specific use and large-scale productions. Highly expensive
ES	Produce highly hydrophobic polymer membranes directly. Low-cost and high productivity.	Production capacity is limited with less reproducibility.

The phase inversion method is further classified into sub-categories. In thermally induced phase separation (TIPS) pores are formed by the sites that are occupied by diluent and they convert into micro pores when they are removed. While pore formation in non-solvent induced phase separation (NIPS) appeared when de-mixing results in the liquid-liquid phase. Besides these two-phase inversion membrane fabrication methods vapor-induced phase inversion (VIPS) pore formation is due to transfer of non-solvent as a vapor or gas with the solvent [25].

### 1.7 Problem Statement

All conventional techniques are efficient for oil-water separation, but they have certain limitations too. Membrane technology is experiencing a period of rapid expansion in chemical industry. Recently, membrane technology has gained a lot of interest in treating oily wastewater, a green alternative to conventional separation methods. Membrane technology is most competent process as it is highly efficient in separation, simpler process, low energy consumption and no addition of chemicals[5, 26-43].

### 1.8 Objectives of Study

The aim of this project is fabrication of 2D nano material-based cellulose acetate membranes for efficient treatment of oily wastewater.

- To fabricate 2D Nanomaterial based membranes
- To characterize the membranes in terms of morphology
- To evaluate and analyze the performance of prepared membrane in terms of oil rejection

## **1.9 Scope of Study**

Wastewater from domestic units and industries is varied based on the various types of inputs and involving different processes. The possible implication of this research may be that treated water can be reused for agricultural purposes, treated water can be sent to water bodies as it will not affect marine environment. Ground and drinking water resources can also remain un-affected by this treated water.

# Chapter 2

## Literature Review

### 2.1 Conventional Oil-Water Separation Techniques

Different industries including petrochemical, metallurgical, food and beverage, textile, steel, pharmaceutical, petroleum refinery and food are increasing at an unprecedented pace which also causes global problems. During processing, water encounters a number of pollutants, for instance hydrocarbons, hazardous chemicals, cooling towers and heat exchangers. Wastewater produced by these industries cannot be reused and has effects on living species in many ways. This discharged oily water severely damages aquatic life as well as pollutes ground water which is the biggest dilemma of the present time. With the increase in population, demand for clean water is also increasing, particularly in areas having shortage of this precious resource. If the water pollution increases at 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 at hand. Treatment of polluted water to reduce the pollutants to an acceptable range is the way out in this situation. Conventional separation techniques such as coagulation, gravity settling, skimming, flocculation, and biological procedures are used for oil-water separation. A number of chemical and biological solvents are required in these processes to treat wastewater which could have disastrous consequences for humanity. Limitations of these techniques for oil-water treatment are:

- Costly
- Usage of toxic compounds
- Large area required for installation
- Generate polluted components

These drawbacks insist to search for suitable treatment processes which produce less hazardous pollutants[5, 44].

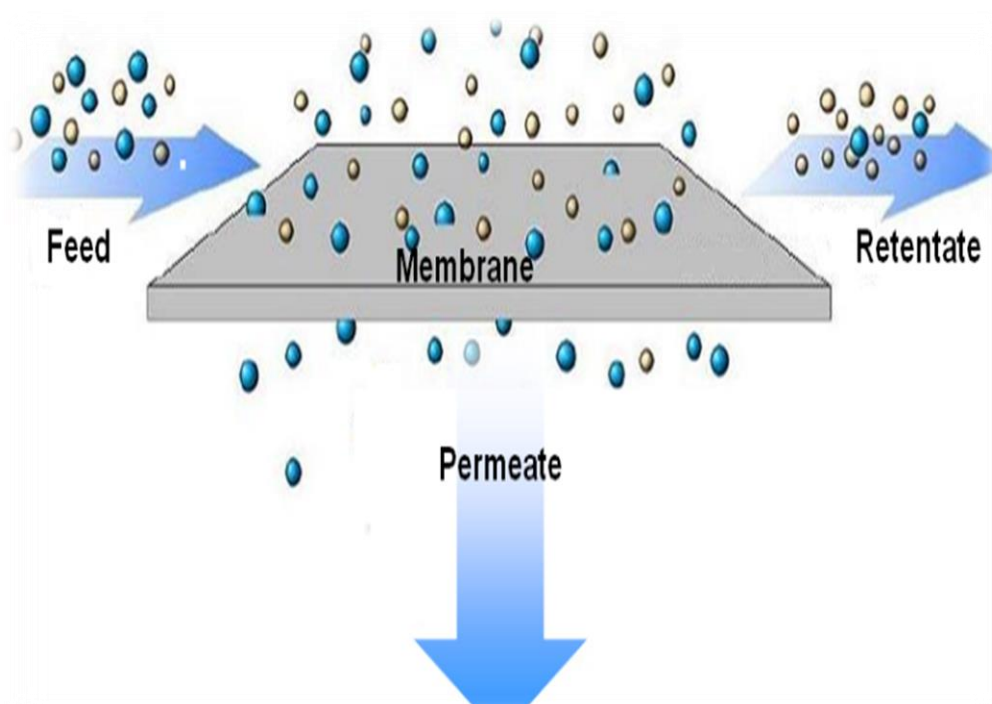
Different conventional techniques advantages and disadvantages are listed in table 3 below [45-54];

*Table 3. Advantages and Disadvantages of conventional techniques for oil water separation*

<b>Conventional Techniques</b>	<b>Advantages</b>	<b>Disadvantages</b>
<b>Centrifugation</b>	Easy to process Environment friendly	Large energy requirements Not environment friendly process
<b>Forth Floatation</b>	Easy Process Low energy requirement	It cannot treat highly viscous oily wastewater
<b>Solvent Extraction</b>	Efficient process	Costly process No heavy metals treatment Not environment friendly process
<b>Microwave Irradiation</b>	Fast and efficient process	High cost Specific design of equipment
<b>Ultrasonic Irradiation</b>	No need of any chemicals Fast and efficient process	High equipment cost Heavy metals cannot be treated
<b>Pyrolysis</b>	Fast and effective process Large capacity for treatment	Costly process
<b>Landfill</b>	Large treatment capacity Less cost	More place requirement Slowest process
<b>Oxidation</b>	Complete and fast removal of petroleum hydrocarbons (PHCs) in oily sludge	High cost Extensive quantity of chemical required Environmentally unfit
<b>Bio-slurry</b>	Great PHC removal Fastest degradation approach	Applicable to small scale High cost
<b>Solidification</b>	Low cost PHC stabilized compounds can be produced quickly and efficiently	Recyclable energy loss Less efficient process

## 2.2 Membrane Technology

Membranes are considered as the strong participant in the treatment of polluted water. The membrane acts as a filter, which removes suspended particles from the water. Membrane separation technology is being used in a number of processes for wastewater treatment. The membrane technology is overtaking the conventional treatment process as it does not offer any chemical exposure during and after its processing. Generally, membrane separation can be understood by a process shown in figure 2.1.



*Figure 2.1. Simple membrane separation process*

Normally, pure water acts as permeate; the concentrated solution is retentate, which should be disposed of. Pressure driven membrane filtration techniques differ depending upon pore sizes, which can be dense or porous membranes. Different molecules such as salts, organic molecules, macromolecules can be separated by depending on membrane filtration techniques. Different pressure-driven membranes are microfiltration (MF), ultrafiltration (UF), nano-filtration (NF) and reverse osmosis (RO). MF and UF use a sieving mechanism for removing colloidal and suspended particulates. NF and RO are used for softening or desalination processes as they remove the dissolved solids[24, 55, 56].

Rapid growth has been witnessed in membrane technology both at academic and industrial level. In the case of treatment of oily wastewater membrane gives high efficiency due to their capacity of separating oil from water [14]. Porous membranes are commonly used for oil water separation treatment. There are several techniques through which porous membranes could be synthesized.

### **2.3 Classification of Membranes Material**

Membrane materials that are selected for membrane fabrication are important because of their chemical and mechanical stability as well as strength. Membrane materials are majorly divided into natural, synthetic, and biological materials. Natural and biological materials are easily fabricated but because of limited operating conditions (pH range and temperature range below 100<sup>0</sup>C) and cleaning requirement (microbial attacks), synthetic materials are mostly used. Besides the conditions, the stability of synthetic materials is high. Therefore, they are used for the manufacturing of membranes. Synthetic membranes are further subdivided into inorganic, organic, liquid, composite (mixed matrix) and nanomaterial-polymeric membranes. Organic membranes are easy to manufacture, for low-temperature range and chemically inert mixture separation while inorganic is difficult to manufacture, for high-temperature sustainability and chemically active mixture separation. Composites combine properties of both organic and inorganic materials while nanomaterial-polymeric combine and exhibit new properties of both inorganic nanomaterial and polymer [57].

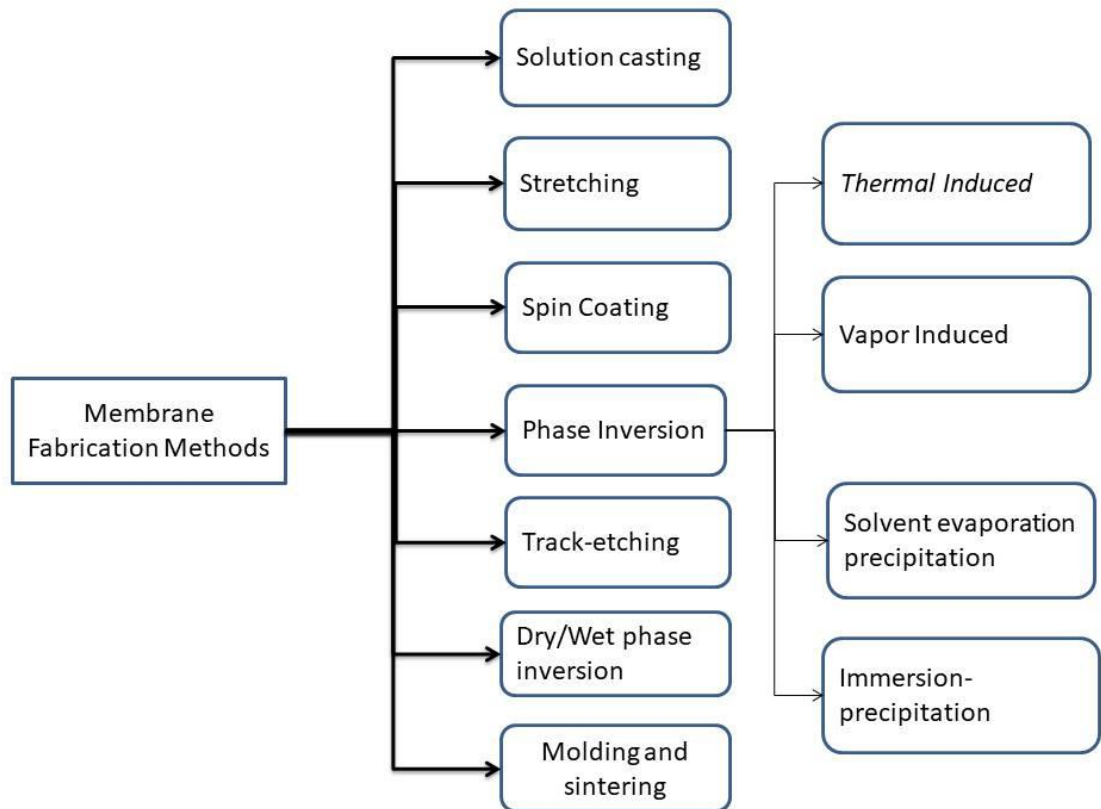
Number of the polymers named as polyvinyl alcohol (PVA), polysulfone (PS), polyurethane (PU), polyacrylonitrile (PAN), and polyacrylonitrile (PAN) have been explored for mixed matrix membranes in water purification [58].

Cellulose acetate (CA) is used for membrane synthesis as an organic cellulosic polymer. The base polymer is significant in membrane selection. For organic membrane casting, derivatives of CA are popular polymers. CA is advantageous over other polymers as it shows good mechanical strength, biocompatibility, and high fluxes. Anti-fouling property is also enhanced due to hydrophilic nature of CA [59]. This material is an interesting polymer regarding its biodegradability, environmental stability, cost effectiveness and commercial availability [60]. It can be used as a

filtration medium. The hydrophilic structure makes them good membranes for microfiltration and ultrafiltration [57].

## **2.4 Membrane Fabrication Techniques**

In membrane separation, the most important part is membrane itself. Structure, function, transport properties, and mechanism of each membrane are different because these parameters are based on material and preparation techniques as shown in figure. Normally, permeate flow across the membrane is very low and thin membrane is required which also has mechanical strength. The membrane fabrication with specified morphological structure is comprised of several methods that are minimal tricky and have simple principles [61]. Methods are specific for a variety of polymers and result in unique porosity and ultra-structures. Some examples are involved in these methods such as track-etched membranes usually have low porosity with narrow size distribution. On the contrary, asymmetric skin structure and higher porosity than usual are achieved by the phase-inversion process. Therefore, selection of material and fabrication technique is chosen by the application of membrane. In some applications, the only barrier layer is important such as gas separation and pervaporation applications. While in other applications separation is prime importance to check the performance of membrane such as water treatment [62, 63].



*Figure 2.2 Membrane fabrication methods*

## **2.5 Phase Inversion**

Phase inversion is the most commonly used process for membrane synthesis. This method covers the area of both polymeric as well as inorganic membranes. In this technique, a mixture of any polymer and solvent that can form a homogenous solution under some condition of composition and temperature and can be separated into two phases by specific conditions. Some different ways are used for the precipitation of polymer in which heating, water vapors, solvent evaporation, and immersion precipitation are included.

### **2.5.1 Thermal Induced**

In this technique, the solution is thermally induced, and the film is casted with the hot polymer solution. When the solution is induced, the de-mixing is done and then the solvent is removed by freeze-drying or evaporation. Normally, when the temperature decreases at the same time solvent also decreases. When cooling is done then membrane form with the polymer pore phase [64].



### **2.5.2 Vapor Induced**

It is a process in which separation of solvent from solution is done by vapors or humid air. Vapors with high temperatures are passed through the film for casting and polymer concentration is increased by the exposure to vapors within a specific time period after that membrane is fractured because of the excessive solvent evaporation. This method is usually followed when it is difficult to contact film to non-solvent bath [65].

### **2.5.3 Solvent Evaporation Precipitation**

It is a simple technique of phase inversion for the preparation of membrane. In this process, simple mixing of polymer and solvent leads to dope solution preparation. Dope solution is solidified by the evaporation of the solvent. It is a slow process because evaporation takes place at room temperature. This method is mostly used for coating or the fabrication of membrane with support for mechanical strength [66].

### **2.5.4 Immersion Precipitation**

Probably immersion is the most widespread methodology for the preparation of micro as well as ultra-filtration membranes. Dope solution is prepared by a simple method and then dipped in a non-solvent coagulant bath. In this technique, diffusional interchange takes place between the solvent and non-solvent. A combination of mass transfer and phase separation prepares the membrane structure [67].

## **2.6 Membranes for oil-water treatment**

Yang et al. (2011) successfully synthesized dynamic membranes having high efficiency for the oily wastewater separation. They deposited  $\text{MnO}_2$  particles on surface of the Kaolin layer leading to a Kaolin/ $\text{MnO}_2$  dual layer composite membrane. The Kaolin layer composed of  $\text{KMnO}_4$  and Kaolin having concentrations of 0.1 and 0.4 g/l. Results reveal that as the oil concentrations rise the flux of the permeate decreases but oil rejection increases. These membranes become stable in neutral or alkaline system having oil retention of 99% [68].

Abadi et al. (2011) engineered ceramic Microfiltration membrane comprises of ( $\alpha\text{Al}_2\text{O}_3$ ) having tubular shape for the treatment of oil emulsions. Permeates collected after the membrane separated the oil from water have oil and grease (OG) content about 4 mg/l. Microfiltration process reduces the total suspended solids, turbidity and OG contents to about 100%, 98.6% and 85%. Total organic components of the

wastewater reduced to 95% after being passed through ceramic membrane. Microfiltration was also compared with conventional techniques like biological methods and results showed that microfiltration can replace conventional techniques. Moreover, the effects on flux and total oil contents are also studied in terms of transmembrane pressure, temperature, and cross flow velocity. 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].

Sarfraz et al. (2012) worked on the hybrid system of the NPM-PAC to control membrane fouling. Results demonstrated that the membrane fouling comprising of NPM (Nano Porous Membrane) decreases as the amount of PAC (Powdered Activated Carbon) increases. The 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 reduces the flux of membrane because the resistance of cake layer will increase. Organic removal of wastewater was also increased when NPM membrane coupled with PAC concentrations. The incorporation of PAC in NPM membranes increased the removal efficiencies 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/m<sup>2</sup>h [69].

Salahi et al. (2013) worked in nano-porous membranes fabricated in the form of sheets. These nano-porous membranes were made up of polyacrylonitrile (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 [70].

Amir et al. (2014) synthesized a membrane using polyethersulfone and cellulose acetate. PEG-400 was introduced as a pore former. To increase overall hydrophilicity of the membrane CA was added into PES. In this research two membranes were compared Made up of Polyethersulfone and PES/CA/PEG400. These membranes were compared based on 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 to investigate oil 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<sup>2</sup>h and oil rejection of 88% [71].

Hu et. Al (2015) synthesized GO modified ceramic membrane by vacuum method. XPS measurements indicated homogeneous coating of GO on membrane pore surface. Comparing the modified membrane with non-modified membranes showed that modified membranes exhibit better separation efficiency. The prepared membrane exhibited high flux and high oil-water separation efficiency indicating GO membranes can surely be used to treat oily wastewater [72].

Zhao et. Al (2016) fabricated free standing GOP nanohybrid membranes. Prepared GOP membranes showed proper channel structures and great anti-fouling property. An extreme increase in permeate flux was observed from GO membrane (267 Lm<sup>-2</sup>h<sup>-1</sup>) to GOP membrane (1867 Lm<sup>-2</sup>h<sup>-1</sup>) due to intercalation of palygorskite (PGS) nanorods within interlayers of GO nanosheets. The prepared membranes showed excellent anti-fouling property [73].

Li et. Al (2017), on CA membrane a hierarchical structure was made by layering process using SeP (1D material) and GO+LDH (2D material). Underwater superoleophobicity was observed in the case of hierarchical structure of both SeP with GO and LDH. SeP+GO showed best anti-fouling property and oil rejection compared to other membranes in the study. Permeation and anti-fouling abilities of membranes were enhanced by the addition of 2D materials [74].

Shoba et. Al (2018), membranes were prepared by using different concentrations of CA with DMF as a solvent. Increase in CA concentration increased crystallinity due to increase in pore size. CA membranes cannot be prepared with higher concentration than 17.5% due to the highly viscous nature of CA. Water flux increases first then it shows decline due to addition of certain concentrations of CA. increase in CA concentrations also affects oil rejection, permeate flux and roughness [75].

Nazarian et al. (2019) used Cellulose Acetate (CA) in polyetherimide (PEI) solution to enhance membranes structure for oil water treatment. Characterization of membranes was done by SEM, water flux, contact angle and oil rejection tests. The

addition of CA showed thick outer layer with finger-like morphology. Membranes showed high water flux due to high hydrophilicity and finger-like morphology. Maximum oil rejection of 98% was observed [76].

Shen et al. (2019) prepared membranes from CA and polymer additive (PA). These blended membranes had improved surface hydrophilicity and oleophobicity. Mechanical strength of these blended membranes was better as compared to pure CA membrane. Addition of PEG 600 increased pure water flux from 0 to 33 or 34 L/m<sup>2</sup>h bar. 92.5% of oil rejection was shown by the membrane. Membrane also showed good antifouling performance [77].

Ang et al. (2020) incorporated polydopamine (PDA) particles into CA and studied its effects on membrane properties and its performance. Addition of PDA particles changed membranes morphology into macro voids structure. Hydrophilicity and porosity of membrane was also enhanced. This also gave high permeation flux. Membrane with PDA 0.2 wt% gave best results as water flux of 771.98 L/m<sup>2</sup>h and oil rejection (93-99%), while greater PDA concentrations showed decrease in permeation [78].

Chen et al. (2020) used an adapted electrostatic technique to construct ultrathin TiO<sub>2</sub> coating on various 2D and 3D substrates including stainless steel mesh, metal felt and GF membrane. TiO<sub>2</sub> coatings enhanced morphological structure of substrates in terms of surface and presented super oleophobic and super hydrophilic properties. While the pore size of substrate showed a slight increase. GF membrane coated with TiO<sub>2</sub> separated surfactant-free and surfactant stabilized emulsion with 98% efficiency [79].

He et al. (2021) used different concentrations of porous boron nitride nanosheets (BNNS) with polyacrylonitrile (PAN) to prepare membranes by one step electrospinning method. Mechanical and chemical properties along with physical structure, contact angle and oil separation efficiency were studied. BN/PAN nanofibrous membrane surface was changed from smooth to rough by decrease in diameter of BN/PAN nanofiber. Successful incorporation of BN in nanofibrous membranes was showed by FTIR results. Underwater superoleophobicity properties were found on BN/PAN nanofibrous membrane surfaces. For pump/oil water

emulsions 4wt% porous BNNS loading showed highest oil rejection of 99%. Membranes can be reused more than 25 times to separate oil water emulsions [80].

G.N. et al. (2021) developed PEI/PF127/GO composite membrane by using phase inversion process for oil water separation. Incorporation of GO nanoparticles and co-polymer PF127 increased surface hydrophilicity and membrane separation performance. SEM images revealed a large number of pores are present in membrane. While FTIR results confirmed the presence of GO nanoparticles and co-polymer. Membranes showed great thermal and mechanical stability. Better results were obtained by PG-2 membrane which showed 95% oil rejection and excellent anti fouling ability [80].

Al Ansari et al. (2022) incorporated hydrophobic MoS<sub>2</sub> in hydrophilic networks of CA. SEM images confirmed that membrane was highly porous with uniform distribution of MoS<sub>2</sub> Nano spheres in the polymer frame. Amphiphilic membrane showed contact angle of 54° confirming its hydrophilic nature. 97-99% oil rejection was observed at various toluene concentrations. Membrane also showed anti-fouling ability [81].

Zhao et. Al (2022) fabricated a hybrid membrane by electrospinning method containing special characteristics of superhydrophobicity and super-oleophilicity. The highest rejection efficiency achieved was >99.5%. chemical stability of PH-CNT membrane showed that it can be used in practical applications. Membranes synthesized by electrospinning process can be produced at a large scale, indicating the use of this membrane for treatment of large wastewater quantities [82].

Yan et. Al (2023) synthesized dual-functional nanocomposite hydrogel-coated membranes. These hydrogel-coated membranes showed high oil-water separation and anti-fouling property. The highest flux recovery rate achieved was 96.7%. in the synthesized membranes, excellent Pb<sup>2+</sup> adsorption capacity was observed. Membranes showed good chemical stability and super-oleophobicity properties under some conditions [83].

Liu et. Al (2023) fabricated NUS-8-NH<sub>2</sub> coated mesh membranes. Membranes prepared with vertically grown NUS-8-NH<sub>2</sub> nanosheets were capable of high

efficiency oil rejection. Anti-corrosive properties were also exhibited by the prepared mesh membranes. Stainless steel mesh was used for a proper coating of NUS-8-NH<sub>2</sub>. For practical application, usage of NUS-8-NH<sub>2</sub> is suggested as it shows better rejection efficiency and anti-corrosive properties [84].

# Chapter 3

## Material and Method

### 3.1 Materials

Cellulose acetate (CA) ( $M_w = 30,000$  g/mol, powder form) as a polymer, Polyethylene glycol (PEG-400) as a pore forming agent and Dimethylformamide (DMF) solvent were purchased from Sigma Aldrich. Lab scale high purity Nitrogen gas was supplied by Paradise Company, Pakistan.

For the synthesis of h-BN nanosheets, hexagonal boron nitride (h-BN) powder ( $M_w = 24.82$  g mol<sup>-1</sup>) was provided by Shanghai Macklin Biochemical Co. Ltd. N-methyl-2-pyrrolidone (NMP) solvent was purchased from RCI Labscan Limited.

Sodium dodecyl sulphate (SDS), a surfactant used to prepare emulsions De-ionized (DI) water was used throughout the experiment. All chemicals and solvents utilized in this research study were of analytical grade and used directly without any prior treatment unless stated.

### 3.2 Synthesis of h-BN Nanosheets

Hexagonal boron nitride (h-BN) nanosheets were prepared by following procedure; 3g of bulk h-BN powder was first added to 60 ml of N-methyl-2-pyrrolidone (NMP) in a flat-bottomed stainless-steel beaker. This dispersion was then subjected to liquid-phase exfoliation using ultrasonic processor. The sonication process was carried out for 48 hours in an ice bath to properly regulate the temperature. Moreover, sonication was performed in pulsed mode with two second on and one second off pulse with sonication power of 130 W and at a frequency of 20 kHz, while keeping the amplitude at 60%. On completion of liquid-phase exfoliation, the exfoliated solution was then transferred to 10 ml round-bottomed centrifuge tubes for size-selected separation of nanosheets using high-speed centrifuge. The centrifugation was performed at a rotational speed of 1500 rpm for 45 minutes. Afterwards, the supernatant was collected in a petri dish and placed in vacuum drying oven. The supernatant dispersion was then heated to a temperature of 80°C for 24 hours to allow the solvent to evaporate, leaving behind dried h-BN nanosheets. The nanosheets were then scraped off using a stainless-

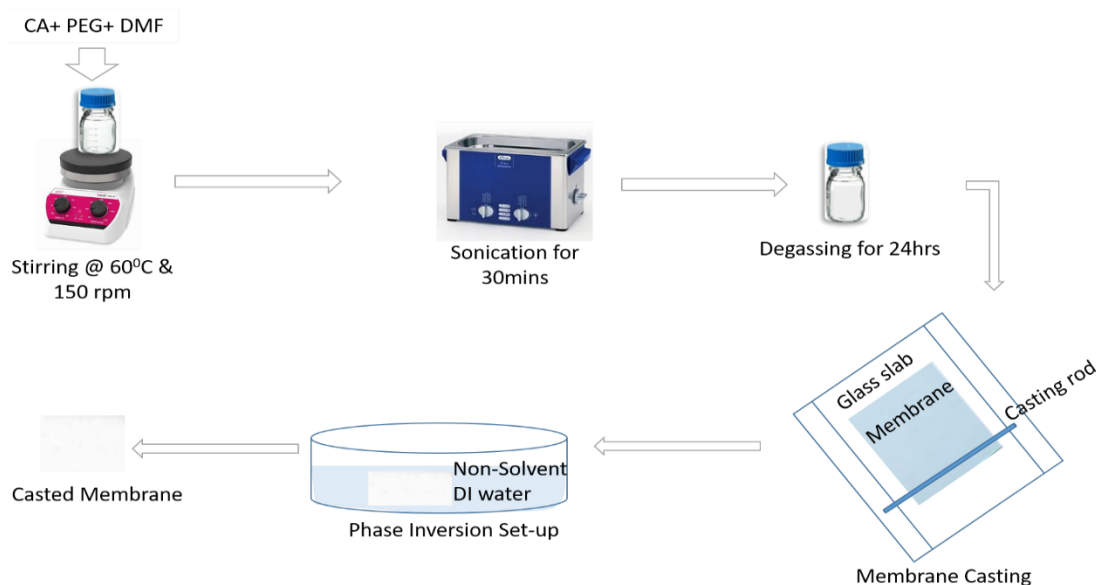
steel spatula and weighed to determine the yield of h-BN nanosheets. The dried nanosheets were then transferred to a sample bottle to prepare BNNS-DMF dispersions for mixed matrix membrane synthesis.

### 3.2 Preparation of Pristine Membrane

The Non-Solvent Induced Phase Separation (NIPS) method was used to prepare membranes. CA used as a polymer, PEG as a pore forming agent and DMF as a solvent and DI water as a non-solvent in coagulation bath. Dope solution was prepared by dissolving 15 wt% CA and 12 wt% PEG in DMF at 150rpm and 60<sup>0</sup>C temperature for overnight.

Solution was sonicated for half an hour and then solution was degassed for 24hrs to remove any bubbles formed during the above process.

Membrane was casted on glass slab manually. Casted membrane was then left for 30s and then immersed in non-solvent (i.e; DI water) for 24hrs. Membrane was placed in DI water until further usage.



*Figure 3.1 Fabrication of Pristine CA membrane*

### 3.3 Fabrication of Mixed Matrix Membranes (MMMs)

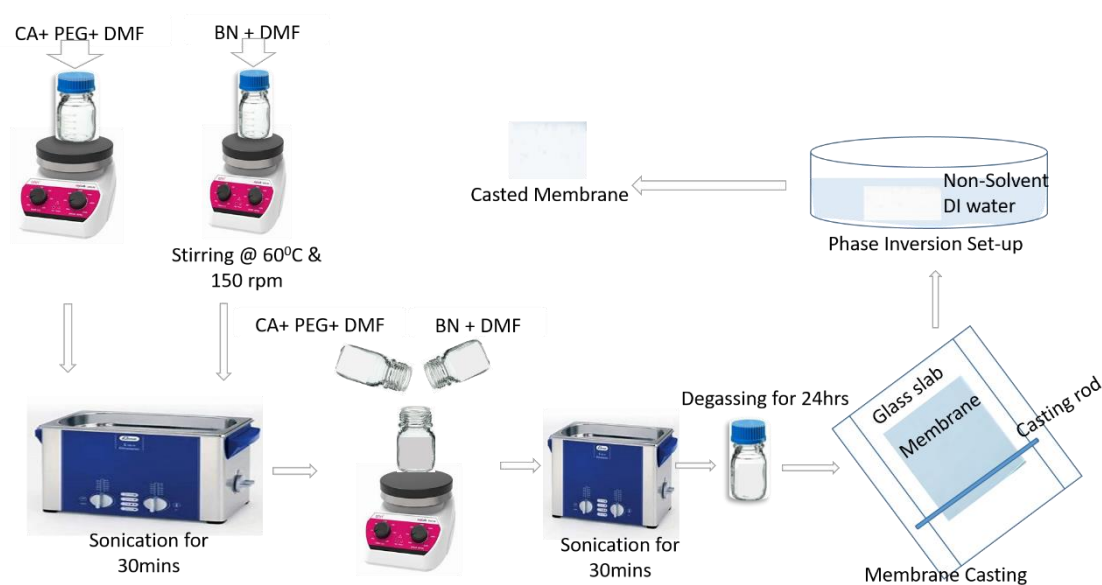
The same NIPS method was used to prepare 2D Nanomaterial based membranes. BN-Nano-sheets with varying concentrations were used as 2D-nano material.



15wt% CA and 12 wt% PEG were added in two-third of DMF's total quantity at 150 rpm and 60°C temperature. The rest one-third DMF was used for dispersion of BN Nano-sheets at same conditions and then sonicated for half an hour. BN Nano-sheets concentration varied from 1wt% to 3wt% (based on polymer concentration).

Then both solutions were combined and stirred overnight for complete dissolution. This dope solution was once again sonicated for half an hour to achieve complete dispersion of Nano-sheets. Dope solution was then degassed for 24hrs to remove excessive air bubbles.

Membranes were casted on glass slab manually. Casted membranes were then left for 30s and then immersed in non-solvent (i.e; DI water) for 24hrs. Membranes were placed in DI water until further usage.



*Figure 3.2 Fabrication of MMMs membrane*

The composition of the prepared membranes is presented in Table 4.

Table 4. List of synthesized membranes in this study

<b>Sample Nomenclature</b>	<b>Cellulose Acetate (CA) (wt%)</b>	<b>Polyethylene Glycol (PEG) (wt%)</b>	<b>Boron-Nitride (BN) Nano-sheets (wt% of polymer)</b>
<b>M1</b>	15	12	0
<b>M2</b>	15	12	0.1
<b>M3</b>	15	12	0.15
<b>M4</b>	15	12	0.2
<b>M5</b>	15	12	0.25
<b>M6</b>	15	12	0.3

### **3.4 Characterization Techniques**

#### **3.4.1 Scanning Electron Microscopy**

Scanning Electron Microscopy (SEM) analyzes the physical properties by observing the morphology of membranes. To obtain the morphology of a membrane SEM is widely used. In this project, SEM was used to investigate the surface and cross-sectional images, the thickness of membranes, the presence of pores as well as the existence of defects on the surface of the membranes. Random samples of the membranes were cut to examine surface morphology. To get a clear cut of cross-section, samples were cryogenically fractured in liquid nitrogen. The membrane was then sputtered with gold. Membrane morphology of cross section and surface was then studied with the help of JEOL JSM-6490A scanning electron microscopy.

#### **3.4.2 Fourier Transform Infrared Spectroscopy (FTIR)**

An analytical technique known as infrared spectroscopy is used to confirm the presence of functional groups and chemical bonds in the molecular arrangement of materials. This is a spectroscopic method used because of its high sensitivity, simple mechanism with only one moving part, and shorter analysis time than traditional infrared spectroscopy. In this, an interferometer is used instead of monochromatic

interferometer by which the material is exposed to all infrared wavelengths. The range of wavelength used in IR-spectroscopy is  $4000\text{cm}^{-1}$  -  $400\text{cm}^{-1}$ . When an organic molecule absorbs infrared radiation in this region, this radiation is converted into vibrational, bending, stretching, or rotational energy. There are two areas: 1) fingerprint regions corresponding to the individual molecules and allowing unique identification. 2) the region of range of functional groups. This is same for molecules with same functional groups thus similar reactivity. The produced membranes were spectrally analyzed using a Perkin Elmer-100 FTIR spectrometer. The powder was hydraulically pressurized before being thinly coated with the sample membranes to create potassium bromide (KBr) pellets. The samples were then tested in transmittance mode in the  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  wavelength range.

### **3.4.3 Contact Angle Measurement**

Contact angle is an important parameter to estimate the wettability of the surface for incident liquid since it is generally considered a direct measurement of hydrophilicity or hydrophobicity of membrane surface. Hydrophilic surfaces are preferred because of their ability to improve the overall membrane performance. The sessile drop method was used in order to measure the contact angle for all the synthesized membranes in this work. The sample was cut and placed in a sample holder. As a liquid droplet, distilled water was dropped through an upright syringe placed above membrane sample. After 40 seconds, static contact angle measurements were obtained. Generally, contact angle ( $\theta$ ) greater than  $90^\circ$  represents the hydrophobic nature of incident surface while contact angle ( $\theta$ ) lesser than  $90^\circ$  is indication of hydrophilic nature of the incident surface.

### **3.4.4 Porosity and Mean Pore Radius Analysis**

Membrane porosity and mean pore radius are essential factors for membranes performance. Overall performance of membranes in respect of flux and rejection is greatly dependent on these two parameters. Gravimetric method and Gueroutt-Elford-Ferry equation were used respectively to measure mean pore radius ( $r_m$ ) and Porosity ( $\phi$ ) of all the synthesized membranes. [206]. Porosity was measured by following formula

$$\varphi = \frac{W_w - W_d}{\rho_w A l} \quad \text{Eq. 3.1}$$

Here;

‘W<sub>w</sub>’ is wet weight of membrane sample,

‘W<sub>d</sub>’ is dry weight of membrane sample,

‘ρ<sub>w</sub>’ is density of pure water,

‘A’ and ‘l’ are area and thickness of membrane sample.

Mean pore radius is measured by following equation;

$$r_m = \sqrt{\frac{8(2.9 - 1.75\varphi)\eta L Q}{\varphi A \Delta P}} \quad \text{Eq 3.2}$$

Where;

“φ” is porosity from eq 3.1,

“l” is thickness of membrane sample (m),

“η” is viscosity of water (i.e., 8.94 × 10<sup>-4</sup> Pa.s),

“Q” is pure water flux (m<sup>3</sup>/s),

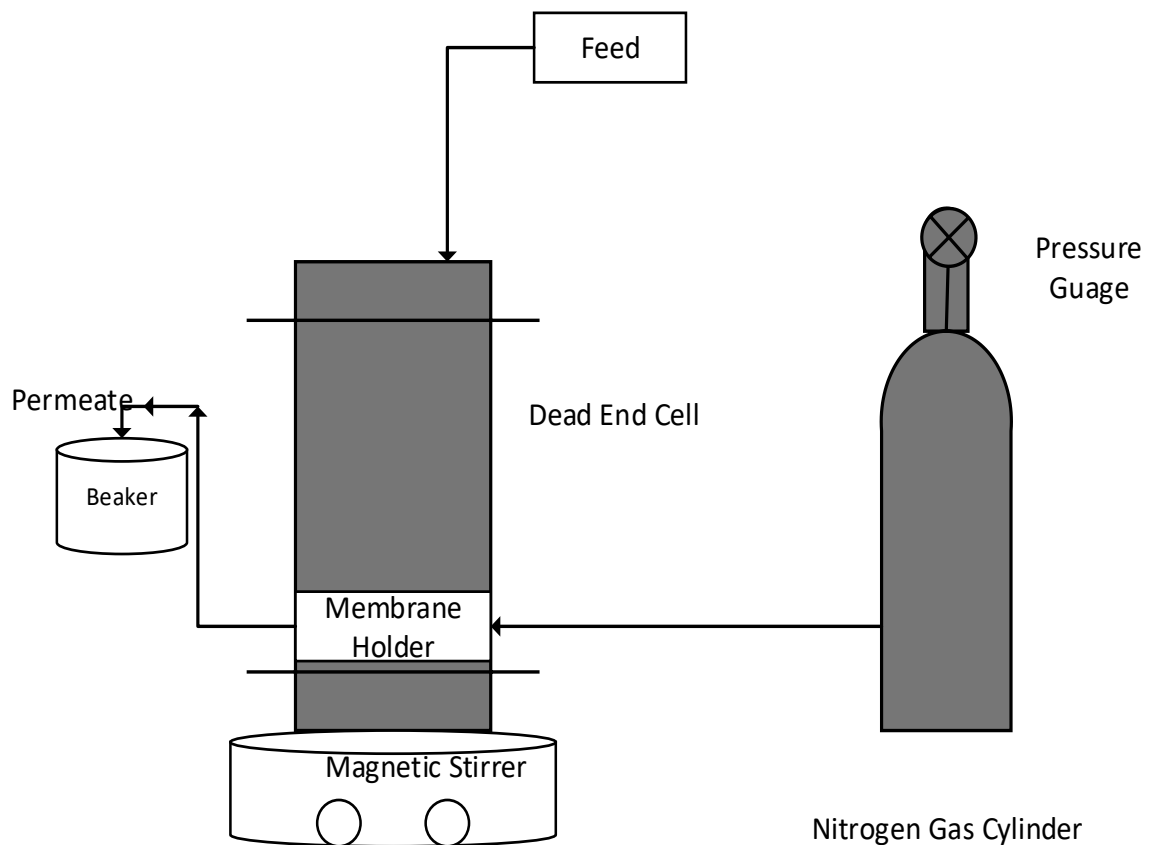
“A” is area of membrane sample (m<sup>2</sup>) and “ΔP” is operating pressure (1 MPa).

### 3.5 Performance Studies

Membranes performance was assessed based on pure water flux and oil rejection using STERLITECH stirred dead-end filtration cell (Model-HP4750, USA). Operating pressure of 2 bars was used to determine the pure water flux (L/m<sup>2</sup>h) of all the synthesized membranes. Moreover, rejection studies were accomplished using oil-water solution. Kerosene-oil water (O/W) emulsion was made by adding same volume of oil and Sodium dodecyl sulphate (SDS) (used as surfactant) in one liter of DI water.

All membranes were tested three times and average values were taken. Figure presents a schematic of membrane testing unit.

Stainless stirred cell (Maximum working capacity: 300 ml) was used for performance analysis. The active area of membranes was  $14.6 \text{ cm}^2$ . This unit consists of a magnetic stirrer and pressure regulatory assembly. Gasket seal was fitted to stirred cell to avoid any pressure leakages. Mechanical stirrer was inserted into a cell to lessen the fouling effect. Nitrogen-an inert gas was used to pressurize the cell with 2 bar as operating pressure. A beaker was used to collect permeates.



*Figure 3.3 Dead end cell assembly*

### **3.5.1 Pure Water Flux**

At first, pure water flux of each membrane was determined. A 150 ml distilled water sample was filled in pressurized stirring cell and sample collected at 2 bar pressure. Water flux was calculated by gravimetric method. Stirring is not required in this

measurement. Pure Water flux ( $J_w$ ) of a membrane can be estimated through noting the time to collect fixed volume of water. Formula used to calculate pure water flux is shown below;

$$J_w = \frac{V}{A \cdot \Delta t} \quad \text{Eq 3.3}$$

‘V’ is volume collected of pure water,

‘A’ shows effective membrane area,

‘t’ represents the time in which volume is collected.

Generally, pure water flux is given in L/m<sup>2</sup>h or m/s.

### 3.5.2 Oil-Water (O/W) Emulsion Flux

O/W emulsion flux or permeate flux was obtained by using same dead-end filtration set-up. Prepared kerosene oil-water solution was used as feed. Permeate volume was collected at 2 bar operating pressure, time was noted for permeate volume collected. Permeate flux was calculated using following formula;

$$J_o = \frac{V}{A \cdot \Delta t} \quad \text{Eq 3.4}$$

‘V’ is volume collected of permeate,

‘A’ shows effective membrane area,

‘t’ represents the time in which permeate volume is collected.

Generally, permeate flux is given in L/m<sup>2</sup>h.

### 5.2.3 Oil Rejection

Dead end filtration cell used for water flux calculations was also used for oil rejection experiments. Stock solution for kerosene oil-water was made by process listed in literature. Permeate volume was collected at set conditions of 2 bar pressure and 200rpm stirring speed.

Percentage rejection of oil was calculated by following equation;

$$Rejection (\%) = \frac{C_f - C_p}{C_f} \times 100 \quad Eq\ 3.5$$

Where  $C_f$  and  $C_p$  is the concentration of oil in the feed and permeate solution respectively (mg/L), which was measured by calculating total organic carbon (TOC) content in feed and permeate solutions.

#### **3.5.4 Anti-fouling Performance**

Dead end filtration unit was used to determine the anti-fouling ability of all the prepared membranes. For obtaining flux recovery ratio (FRR) values this procedure was followed: (a) Pure water flux values ( $J_{w1}$ ) of all the membranes were noted at 2 bar operating pressure. (b) Then membranes were tested for oil-rejection studies. (c) After that all the membranes were washed with DI water and then again tested for pure water flux values ( $J_{w2}$ ). FRR was calculated by using following equation;

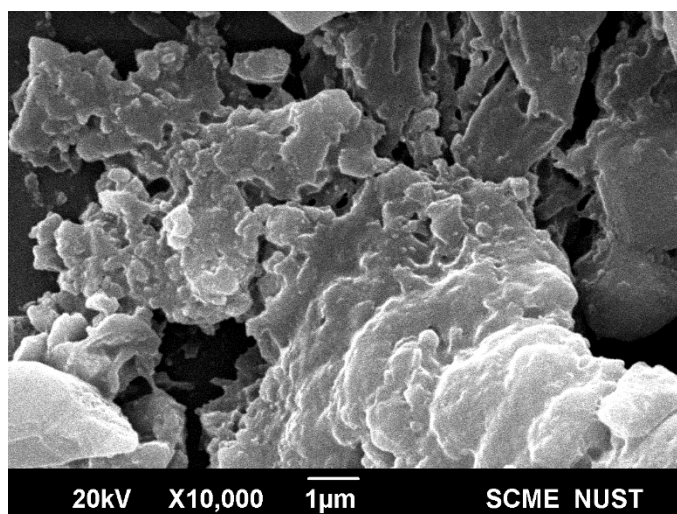
$$FRR (\%) = \frac{J_{w2}}{J_{w1}} \times 100 \quad Eq\ 3.6$$

# Chapter 4

## Results and Discussion

### 4.1 Scanning Electron Microscopy (SEM)

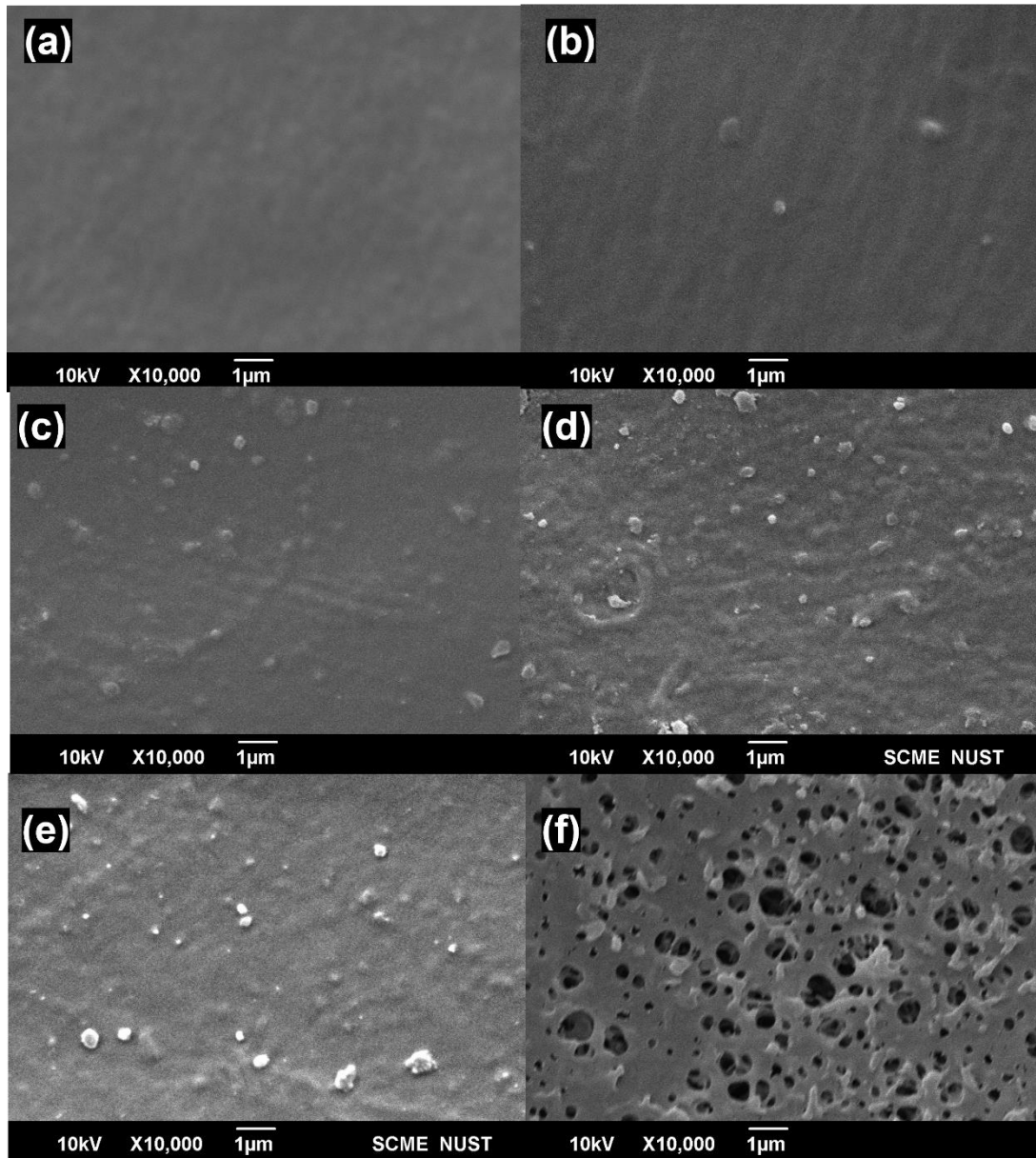
SEM image of hexagonal boron-nitride (h-BN) nanosheets prepared at 1500rpm is shown in fig 4.1. Fig 4.1 shows nanosheet flakes are smaller in size and the flakes are separated appropriately in an arrangement of few-stacked nanosheets.



*Figure 4.1. SEM micrograph of h-BN nanosheets*

Surface SEM images of the prepared membranes with different BN loading are presented in fig 4.2. M1(CA/PEG) was free of BN loading, as BN loading was increased number of spots also increased, which can be indicated as presence of BN nanosheets. As shown in fig 4.2 (b-e) there was no agglomeration of BN nanosheets and were distributed evenly on the surface of the membrane. A noticeable agglomeration of BN nanosheets was observed in M6 as compared to other membranes, it is shown in Fig 4.2 (f). Surface images of all membranes indicated smooth and dense upper layer except for M6. BN agglomeration along with porous surface layer was observed in CA/PEG membrane with 0.3wt% BN loading (M6).

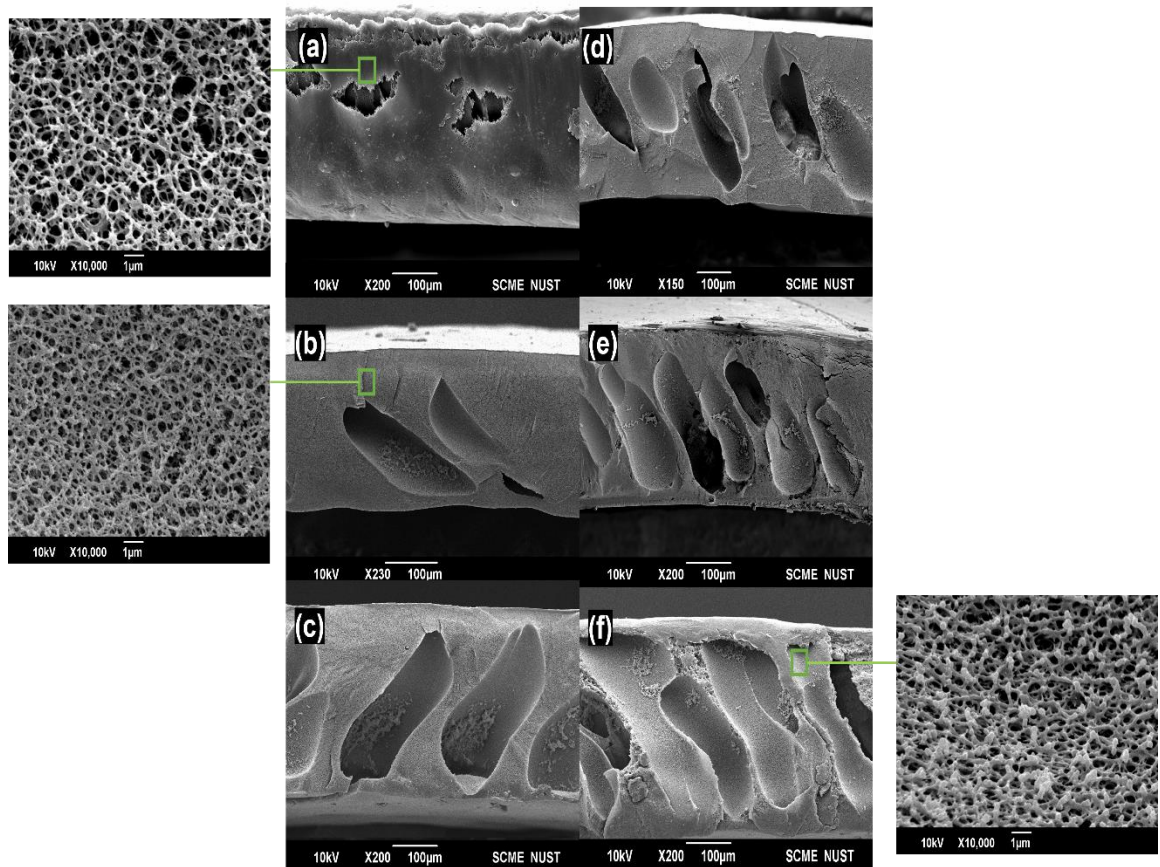




*Figure 4.2 SEM images of surface of membranes*

Cross-sectional images of all the prepared membranes at different BN concentrations ranging from 0.1-0.3 wt% are shown in fig 4.3. From Fig 4.3 (a) it is clearly indicated that CA/PEG membrane with zero BN concentration had smaller macro-voids. With increasing the BN concentration in CA/PEG membrane from 0.1 wt% to 0.3wt%, number and size of macro-voids also increased as represented in Fig 4.3 (b-f). Pure CA/PEG membrane showed cloud shaped macro-voids while with addition of BN,

shape of macro-voids shifted from small clouds to large finger-like structures.



*Figure 4.3 SEM cross-section images of membranes*

## 4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy is performed to confirm the existence of functional groups that we incorporated in polymer membrane. Pure CA membrane ( $M_1$ ), CA membrane with 0.1 wt% BN ( $M_2$ ) and CA membrane with 0.3 wt% BN loading ( $M_6$ ) were studied to check the existence of certain functional groups. Fig 4.4 represents comparison FTIR spectrum of  $M_1$ ,  $M_2$ , and  $M_6$  membrane.

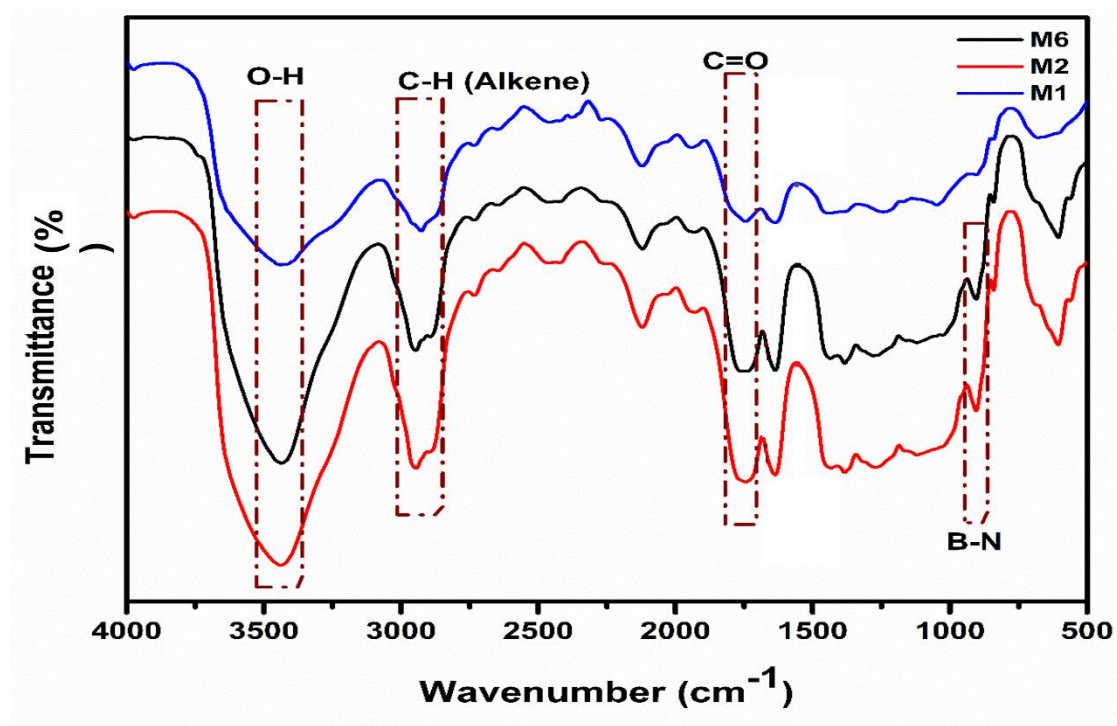


Figure 4.4 FTIR spectrum for membrane samples

Nearly around  $3450\text{ cm}^{-1}$  stretching vibrations due to O-H functional group presence were observed in CA membrane. Similar vibrations were observed at  $3440\text{ cm}^{-1}$  and  $3442\text{ cm}^{-1}$  for  $M_2$  and  $M_6$  respectively, indicating the existence of O-H functional group in all membrane samples, as it is key component of cellulose acetate's structure.

A strong stretching vibration for C-H bond was observed at  $2940\text{ cm}^{-1}$ ,  $2945\text{ cm}^{-1}$ ,  $2942\text{ cm}^{-1}$  for  $M_1$ ,  $M_2$ , and  $M_6$  respectively. The strong bond due to C=O stretching vibrations was observed around  $1750\text{ cm}^{-1}$  for all samples. All these bonds are vital part of structure of cellulose acetate, so presence of CA in all membranes is confirmed.

A strong stretching vibration was also observed at  $889\text{ cm}^{-1}$  and  $886\text{ cm}^{-1}$  for CA membrane with 0.1 wt% BN and CA membrane with 0.3 wt% BN respectively, indicating B-N bond. This ensures that BN is totally incorporated in the CA membranes. This peak also aligns with already published literature [85]. The slight difference between published literature peaks and our sample peaks can be defined by some physical interactions.

#### 4.4 Contact Angle

Results of contact angle of CA/PEG and BN modified membranes as shown in Fig 4.5, indicate that addition of nanomaterials to the CA/PEG membrane increased hydrophilicity. Water flux and anti-fouling capabilities of membranes are influenced by an important characteristic known as surface hydrophilicity. Lower the contact angle value indicates higher the hydrophilic properties. Fig 4.5 shows contact angle values decreased with the addition of BN nanomaterials as compared to CA/PEG(M1) membrane with highest contact angle of  $66.2^{\circ}$ . With the addition of 0.1 wt% BN to CA/PEG membrane contact angle decreased from  $66.2^{\circ}$  to  $52.2^{\circ}$ . Further addition of BN decreased contact angle value lowest to  $38.8^{\circ}$  for M6 membrane.

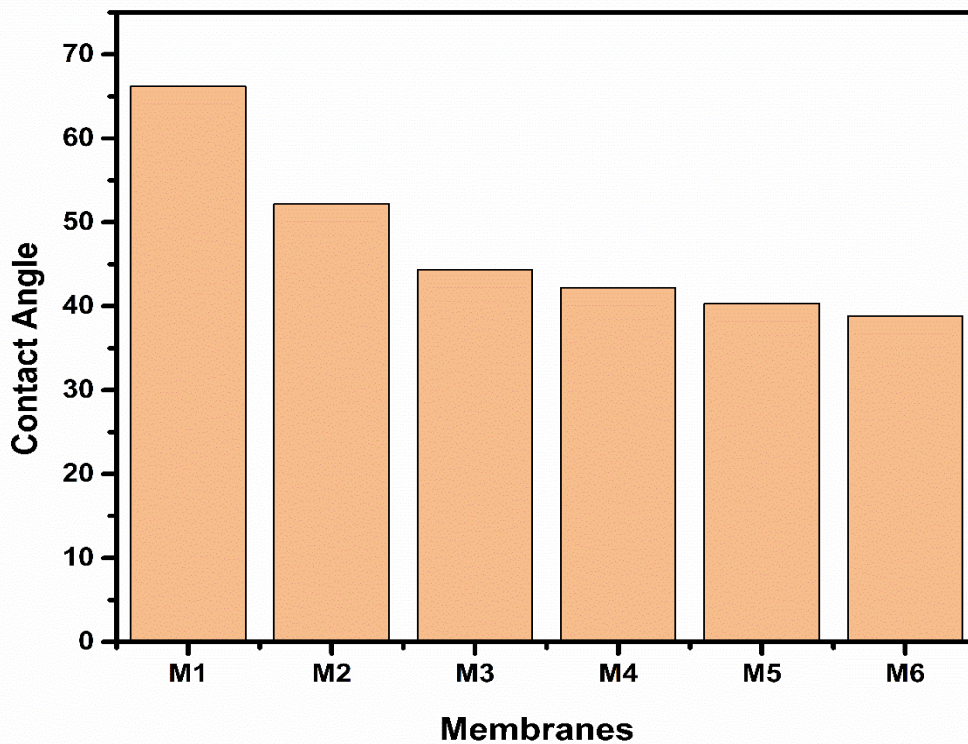


Figure 4.5 Contact angle measurements of prepared membranes

#### 4.5 Porosity and Mean Pore Radius Analysis

Table 5 shows porosity and mean pore radius values of CA/PEG and BN modified membranes. All BN modified membranes had higher porosity values as compared to pristine CA/PEG (M1) membrane with lowest porosity value of 68%. Results clearly



show that with increase in concentration of BN in CA/PEG membranes, porosity of the membranes increased. Porosity values increased from 73% to 82% for 0.1% BN loading to 0.25% BN loading. After 0.25% BN loading a decrease in porosity value was observed at 0.3% BN loading showing porosity of 79%. Reason for this decrease in porosity can be appearance of concentrated BN particles which blocked the pores, limiting the permeation rate. These results also co-relate with SEM results.

As for mean pore radiuses, Pristine CA membrane showed mean pore radius of 34nm. While with addition of BN to CA/PEG membrane an enhancement was observed in mean pore radius values. Mean pore radius increased with increasing content of BN loading in CA/PEG membrane, with highest mean pore radius value obtained for 0.25 wt% BN loading. Mean pore radius value decreased to 45nm for M6 (0.3 wt% BN). Reason for this decrease can be same as for porosity decrease.

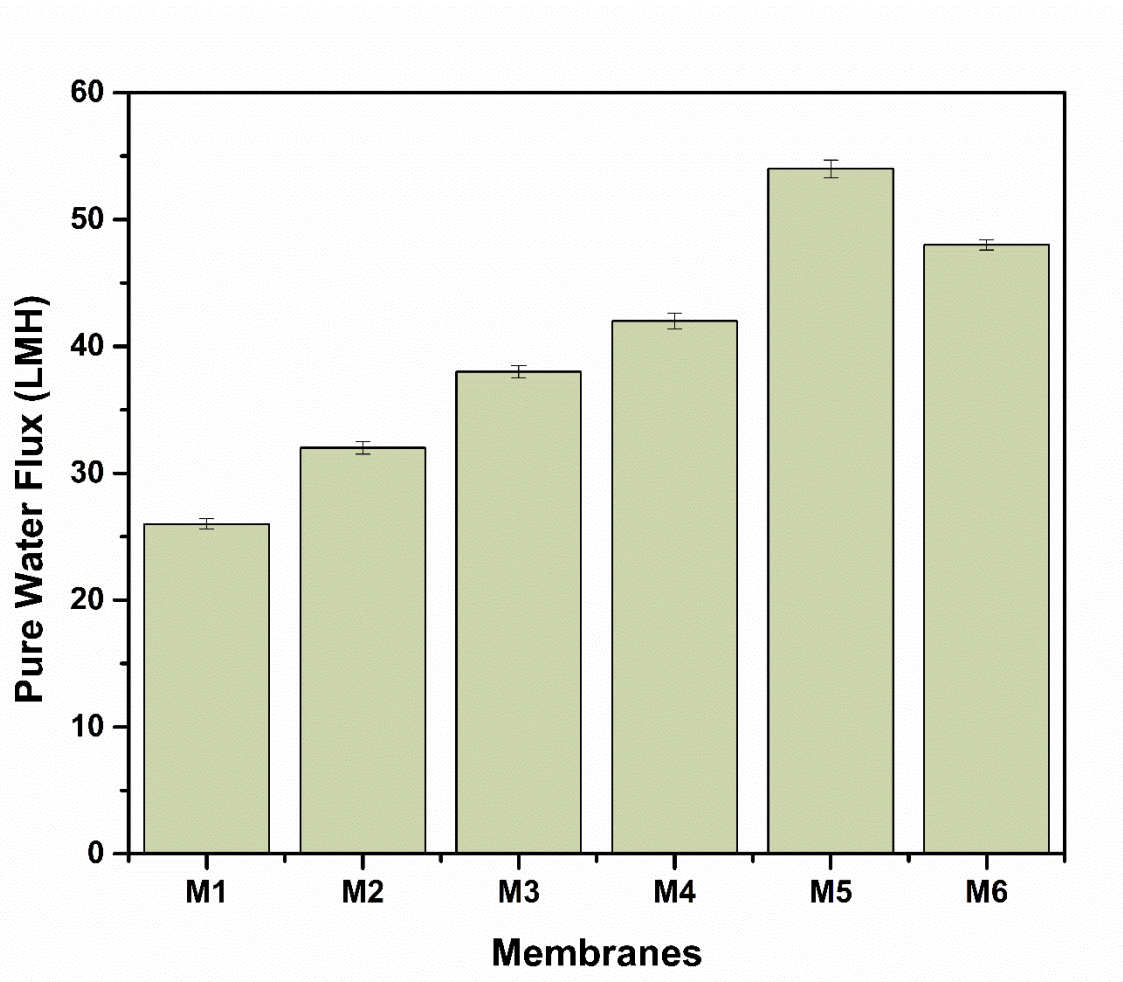
*Table 5. Porosity and mean pore radius measurements of synthesized membranes*

<b>Membrane</b>	<b>Porosity (%)</b>	<b>Mean Pore Radius (nm)</b>
M1	68	34
M2	73	39
M3	75	42
M4	78	44
M5	82	47
M6	79	45

#### **4.5 Performance Studies**

Pure water flux (PWF) of pure and modified membranes is presented in Fig 4.6. For better elucidation of the effect of incorporated BN nanosheets, pure water flux values obtained for CA/PEG and BN loaded membranes at 2 bar operating pressure are shown in Fig 4.6. M1 showed the lowest flux of 26 L/m<sup>2</sup>h. As the lowest flux value stands for CA/PEG membrane with zero BN addition, so it can be stated that addition of BN nanosheets enhanced the pure water flux values because of larger mean pore radiuses of CA/PEG/BN membranes as compared to pure CA/PEG membrane. PWF values increased with the increase in concentration of BN loading. BN loading enhanced porosity and hydrophilicity of membranes as stated in above results, therefore pure

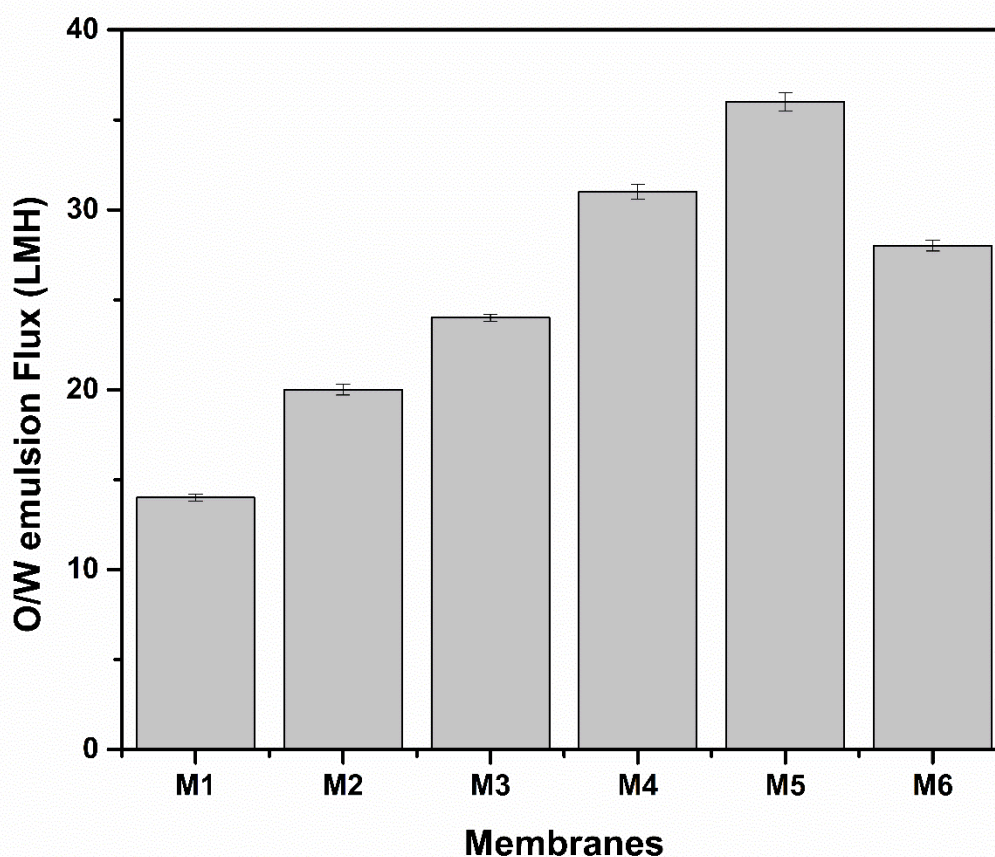
water flux values also increased. Highest PWF value obtained was 54 L/m<sup>2</sup>h for M5 having 0.25 wt% BN loading. There was a slight decrease in PWF for membrane with 0.3 wt% BN. That may be due to smaller mean pore radius and porosity of M6 membrane. Agglomeration of BN can also be stated as one of the reasons for this decrease in PWF.



*Figure 4.6 Pure water flux of prepared membranes*

Fig 4.7 represents oil-water (O/W) emulsion flux measurements of all the prepared membranes. O/W emulsion flux values were greater with addition of BN nanosheets,

as compared to CA/PEG (M1) membrane having O/W emulsion flux value of  $14 \text{ Lm}^{-2}\text{h}^{-1}$ . O/W emulsion flux values increased along with increasing concentration of BN loading, similar to pure water flux values. CA/PEG membrane with 0.25 wt% BN loading showed O/W emulsion flux value of  $36 \text{ Lm}^{-2}\text{h}^{-1}$ , which is the highest O/W emulsion flux value among all the prepared membranes. Large mean pore radius of M5 compared to other membrane accounts for its high O/W emulsion flux value. Porosity, mean pore radius, and hydrophilic properties are key characteristics of membranes, which are ultimately responsible for the differences in permeability between various membranes. Low PWF and O/W emulsion flux of CA/PEG (M1) membrane are result of its lowest mean pore radius and porosity value. While M5 membrane showed highest porosity and larger mean pore radius, that promoted water passage through the membrane. The reason for reduction in PWF and O/W emulsion flux values at higher concentration than 0.25 wt% BN loading can be agglomeration of BN nanosheets on the membrane. Agglomeration of nanosheets blocks the pores of membrane (section 4.4), reduces flux values.

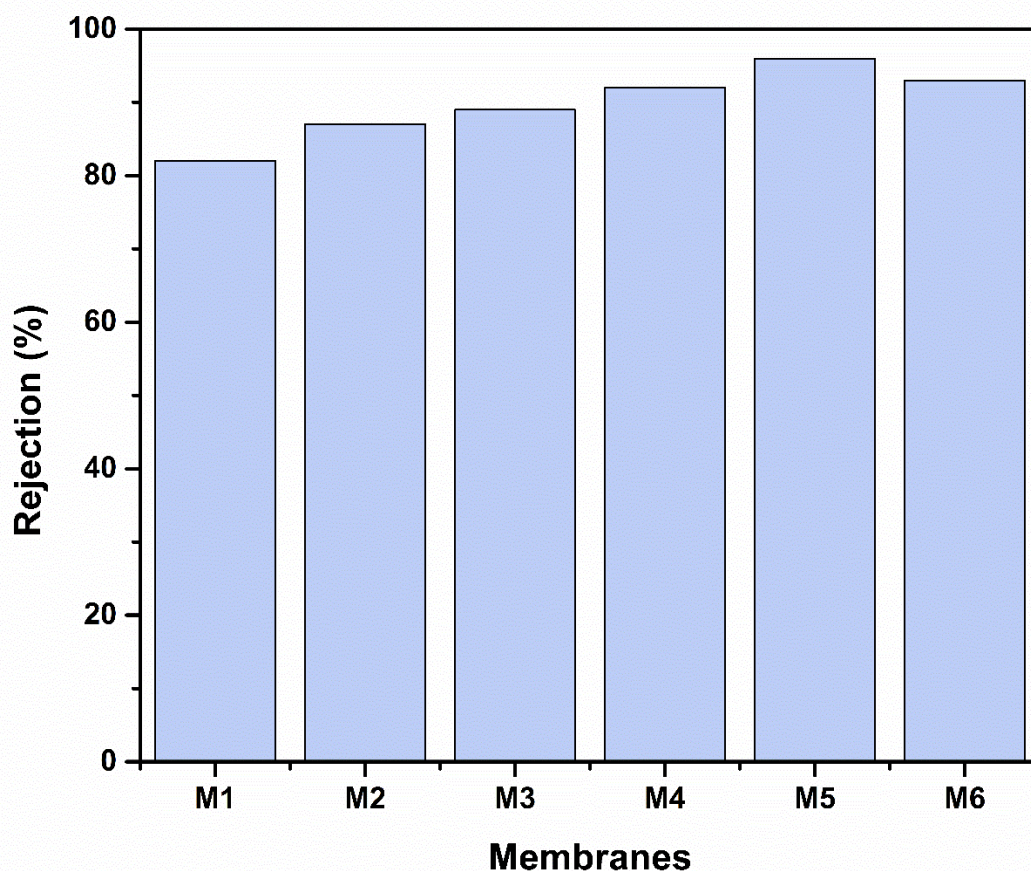


*Figure 4.7 O/W emulsion flux of membranes*

Kerosene oil-water was selected for the evaluation of rejection behaviors of all the prepared membranes. Dead-end filtration unit was used at an operating pressure of 2 bars to test all the prepared membranes. Rejection efficiency of all the membranes is presented in fig 4.8. Separation efficiency of 82% was achieved for CA/PEG (M1) membrane. The removal efficiency of oil from CA/PEG membranes was enhanced by using BN nanosheets, as rejection efficiency for M1(CA/PEG) and M2 (CA/PEG/BN-0.1%) is 82% and 87% respectively. As already explained in Fig 4.5 CA/PEG membrane had highest contact angle indicating lowest hydrophilicity. Hydrophilicity increased with increase in BN concentration, as hydrophilicity increased a tight hydration layer was formed above membrane, improving the oil removal. Increasing BN concentration increased hydrophilicity of the membranes, hence oil removal efficiency increased. Highest rejection efficiency achieved was 96% for CA/PEG membrane with 0.25 wt% BN loading (M5). Although M6 had lowest contact angle value but it showed a little less rejection than M5 membrane. This can be attributed to



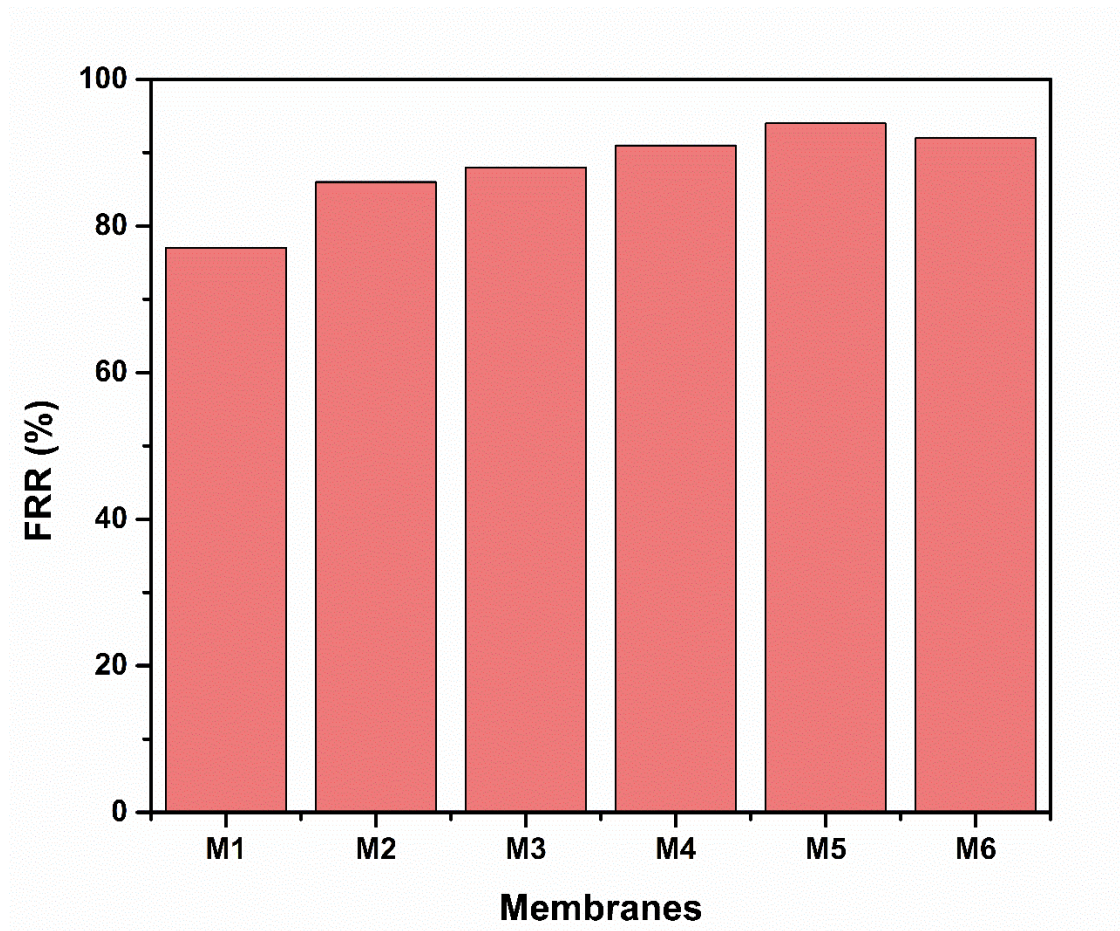
its low porosity and smaller mean pore radius values. Additionally, there was just a slight difference in contact angles of M5(40<sup>0</sup>) and M6 (38.8<sup>0</sup>).



*Figure 4.8 Rejection efficiency of membranes*

Fig 4.9 represents the antifouling ability of all the synthesized membranes. The antifouling property of all the prepared membranes was investigated in terms of flux recovery ratio (FRR). Kerosene oil was considered the foulant in this study. FRR was higher for membranes containing BN nanosheets as 86%, 88%, 91% and 94% for M2, M3, M4, M5 membranes as compared to M1 membrane (CA/PEG) with FRR of 77%. Highest FRR achieved was 94% for 0.25 wt% BN loading CA/PEG membrane. Hydrophilicity of the membranes plays an important role in this increase of FRR values. Membranes having hydrophilic surfaces are less likely to foul. It is commonly known that highly hydrophilic membranes form a tight hydration layer above the surface of the membranes that inhibits the foulant caking on the membrane's surface. There was a slight decrease in FRR value at 0.3 wt% BN concentration in CA/PEG

membrane. The reason for this decrease can be same as for rejection efficiency decrease at certain concentration of BN.



*Figure 4.9 Flux recovery ratio (FRR) of membranes*

# Conclusion and Recommendations

## Conclusion

In this work, Boron nitride nanosheets were impregnated to cellulose acetate/polyethylene glycol casting solution to synthesize mixed matrix membranes using phase inversion technique for oil-water separation application. All the membranes were characterized in terms of SEM images, FTIR analysis, contact angle measurements, porosity, and mean pore size measurements. The inclusion of BN nanosheets in CA/PEG membrane has a significant effect on membrane's property and performance. According to SEM results, BN nanosheets incorporation showed large macro-void structures, suitable for better water transport. Membranes porosity and hydrophilicity were also enhanced. These enhanced properties are attributed to better flux values and significant reduction in fouling on membrane surface. Optimum BN concentration in this study is 0.25 wt% (M5) as a significant decline in PWF and O/W emulsion flux values was observed at 0.3 wt% BN membrane. M5 showed largest mean pore radius and highest porosity. M5 provided highest PWF of  $54 \text{ Lm}^{-2}\text{h}^{-1}$ , highest O/W emulsion flux of  $36 \text{ Lm}^{-2}\text{h}^{-1}$ , highest oil rejection (96%) and best anti-fouling performance (FRR=94%). 0.3wt % BN membrane (M6) had lowest contact angle value obtained of  $38.8^{\circ}$ , it also showed oil rejection of 93% and FRR value of 92%. There is a slight difference in oil rejection and anti-fouling property of M5 and M6 but due to smaller mean pore radius and agglomeration of BN nanosheets in M6 membrane it cannot be considered as optimum membrane.

## Recommendations

- i. Prepared CA/PEG/BN membranes can be used to separate different oil-water emulsions or heavy metals.
- ii. Membrane's morphology can be enhanced by using different nanomaterials and by varying immersion-precipitation conditions.
- iii. A combination of hydrophilic additives can be used to increase hydrophilicity and separation efficiency of membranes.

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## Fabrication and Analysis of BoronNitride Nanosheets based Membranes for Water Treatment

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