2024 UROOSA KHAN SU-92-MSCHW-F22-013 FOS

Synthesis And Characterization Of Bio-Adsorbent Based Mixed Matrix Nanocomposite Membranes For Water Desalination

SUPERIOR UNIVERSITY

Thesis Submitted to

The Superior University Lahore

In Partial Fulfillment of the

Requirement for the Degree of

M.Phil Chemistry

By

UROOSA KHAN

SU-92-MSCHW-F22-013

Session: 2022-2024

Faculty of Sciences

Synthesis And Characterization Of Bio-Adsorbent Based Mixed Matrix Nanocomposite Membranes For Water Desalination

SUPERIOR UNIVERSITY

Thesis Submitted to

The Superior University Lahore

In Partial Fulfillment of the

Requirement for the Degree of

M.Phil Chemistry

By

UROOSA KHAN

SU-92-MSCHW-F22-013

Session: 2022-2024

Faculty of Sciences

Author's Declaration

I hereby state that my MPhil thesis titled **"Synthesis and Characterization of Bio-adsorbent based Mixed Matrix Nanocomposite Membranes for Water Desalination"** is my work and has not been submitted previously by me for taking any degree from this University,

The Superior University, Lahore

Or anywhere else in the country/world.

At any time if my statement is found to be incorrect even after my graduation, the university has the right to withdraw my M.Phil degree.

Uroosa Khan

Date: _____

Plagiarism Undertaking

I solemnly declare that research work presented in the thesis titled **"Synthesis and Characterization of Bio-adsorbent based Mixed Matrix Nanocomposite Membranes for Water Desalination"** is solely my research work with no significant contribution from any other person. Small contribution/help wherever taken has been duly acknowledged and that complete thesis has been written by me.

I understand the zero-tolerance policy of the HEC and University,

The Superior University, Lahore

towards plagiarism. Therefore, I as author of the above-titled thesis declare that no portion of my thesis has been plagiarized and any material used as a reference is properly referred/cited. I undertake that if I am found guilty of any formal plagiarism in the above-titled thesis, even after awarding of MS/M.Phil. degree, the University reserves the rights to withdraw/revoke my MS/M.Phil. degree and that HEC and the University have the right to publish my name on the HEC/University website on which names of students are placed who submitted a plagiarized thesis.

Student/Author Signature: _____

Name: Uroosa Khan

Research Completion Certificate

This is to certify that the thesis entitled **"Synthesis and Characterization of Bio-adsorbent based Mixed Matrix Nanocomposite Membranes for Water Desalination"** submitted by **"Uroosa Khan"** has been accepted towards the partial fulfillment of the requirement for M.Phil. **"Chemistry"**. The quality of the work contained in this thesis is adequate for the award of degree .

Supervisor Name: Prof. Dr. Uqba Mehmood

Designation: Head of Department

Signature: _____

Certificate of Approval

This is to certify that the research work presented in this thesis, titled **"Synthesis and Characterization of Bio-adsorbent based Mixed Matrix Nanocomposite Membranes for Water Desalination"** was conducted by **"Uroosa Khan"** under the supervision of **"Prof. Dr. Uqba Mehmood"**

No part of this thesis has been submitted anywhere else for any other degree. This thesis is submitted to the Faculty of Sciences, The Superior University, Lahore in partial fulfillment of the requirements for the degree of Master of Philosophy in the field of "**Chemistry"** in Faculty of Sciences at The Superior University, Lahore.

Student Name: Uroosa Khan Signature:_____

Examination Committee:

Session Chair: Signature:_____

a) External Examiner: Signature:_____

b) Internal Examiner: Signature:_____

c) Supervisor Name: Prof. Dr: Uqba Mehmood Signature:_____

d) Name of HOD: Prof. Dr. Uqba Mehmood Signature:_____

e) Name of Dean: Prof. Dr. Mohammad Naveed Babur Signature:_____

f) Controller Examination: Dr. Muhammad Haris Signature:_____

Dedication

This is dedicated:

To my loving father Malik Muhammad Khan Niazi , mother Shaheen Akbar

To my siblings Malik Zahid, Aneela Kanwal,and Nabeela Niazi

To my sister in law Tania Malik,

I am deeply grateful for their unwavering love, support, motivation, and encouragement throughout my M.Phil studies.

Acknowledgments

I am profoundly thankful to Allah, the Most Gracious and Most Merciful, for granting me the ability to complete my research and blessing me with the exceptional guidance of Dr. Uqba Mehmood (Department of Biological Sciences Superior University Lahore). I sincerely express my deep gratitude for the outstanding C0-supervision of Dr. Mehwish Batool (Chemical Engineering Department, COMSATS University, Lahore). Her expertise, creativity, wisdom, integrity, encouragement, and dedication made it possible for me to complete this work to such a great extent. Her patience, support, and insightful suggestions played a significant role in the success of this work. Her continuous emphasis on developing soft skills and practical knowledge has ignited my passion for ongoing learning throughout this research work. I am truly thankful to her for providing both moral and material support, without which it would have been impossible for me to complete this work in such a meaningful way.

I would like to express my sincere thanks to Dr. Asim Laeeq Khan (Chemical Engineering Department, COMSATS University Lahore) for his valuable suggestions throughout my research. I am deeply grateful to Dr. Zaman Tahir (Polymer Engineering Department, University of Science and Technology Lahore) for his valuable suggestions and unwavering support in various ways.

I would like to extend my heartfelt gratitude to Engr. Tahir Saif (Chemical Engineering Department, COMSATS University Lahore) for his immense support in prioritizing and assisting with the FTIR analysis of my activated carbon and membranes.

I am also deeply thankful to Mr. Nehal Khan for his invaluable assistance during the synthesis and performance evaluation of membrane samples.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

MMN's	Mixed Matrix Nano-composite Membranes
AC	Activated Carbon
UF	Ultra Filtration
MF	Micro Filtration
NF	Nano Filtration
RO	Reverse Osmosis
CA	Cellulose Acetate
DMF	Dimethyle Formamide
PVP	Polyvinyle pyrolodine
PAN	Polyacrilo nitrile
VTES	Vinyltriethoxysilane
SEM	Scanning electron microscopy
FTIR	Fourier- transform infrared spectroscopy
XRD	X-ray diffraction
MB	Methylene blue
CR	Congo red
FRR	Flux recovery ratio
Rt	Total fouling ratio
Rir	Irreversiblr fouling ratio
Rr	Reversiblr fouling ratio

Abstract

Freshwater resources are being depleted quickly in light of human and natural activity. Desalination of brackish and seawater is becoming increasingly popular in producing fresh water. Several factors, such as the energy source, removal efficiency, feed water quality level, energy need, etc. determine the desalination method's applicability. In the present work, Date Seed base activated carbon (AC) is embedded in mixed matrix nanocomposite membranes (MMNM'S). We have created a novel method for purifying water. Activated carbon which has higher mechanical stability, higher thermal stability, and highly porous and crystalline material was modified with). 3-Aminopropyl tri ethoxy silane to increase its hydrophilicity and its ability to remove salts from water. This modification contributed to an increase in the water adsorption capacity of the activated carbon. The modified AC was subsequently used to create MMNMs with various loading (0.5wt%, 1wt%, 2.5wt%, 5wt %) by embedding it in a Cellulose acetate/Polyacrylonitrile matrix.

The influence of the embedded activated carbon on the morphology and functionality of manufactured MMNMs was examined in terms of pure water flux, Salts rejection, dye removal, water uptake, porosity, mean pore radius, and antifouling characteristics. The produced membranes were characterized by using the following techniques: Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), and Contact angle. The 2.5wt% membrane delivered exceptional water permeability of 97.5 $L.^{m-2}.h^{-1}bar^{-1}$ and salts rejection of 99.2%, and 78% for NaCl and $MgSO_4$, respectively.

The dye rejection performance was also remarkably impressive, with results of 94%, 96%, and 99.8% for Methylene blue, Congo red, and Rose Bengal, respectively. This indicates that the modified activated carbon exhibits a strong affinity for salts and can efficiently remove them from water. Moreover, the flux recovery ratio reached 91.4%, demonstrating the membranes' strength and long-term durability. Incorporating modified activated carbon into mixed matrix nanocomposite membranes enhances the efficiency and effectiveness of the desalination process, while also making it more cost-effective and sustainable. This study represents a major advancement in the field of water purification, with the potential to transform how we treat and purify water for both

human consumption and industrial use.

CHAPTER 1
INTRODUCTION

1.1 Water and Pollution

Water stands as the most vital natural resource, essential for the survival of all living organisms, including humans. Its significance extends to food production, serving as a life source. Despite Earth's 2% freshwater availability, with 1.6% locked in glaciers and polar ice, only 0.036% exists in lakes and rivers, and 0.36% is underground. Urban areas worldwide, particularly in Developing Nations like Pakistan, face severe water shortages. A fundamental need emphasized by the United Nations Development Program declaration in 2006 that safe drinking water must always be accessible. Approximately 2.6 billion people globally face a scarcity of clean water, a troubling figure believed to impact a substantial portion of the world population, leading to the deaths of 3900 children daily.

With nearly 40% of global food grown through irrigation, water scarcity impacts agricultural demands. Industries heavily reliant on water face challenges exacerbated by human activities, population growth, urbanization, industrial expansion, and sudden climate changes. Widespread water pollution poses a serious threat to drinking water, compromising groundwater quality due to pollution[1].

In addition to its impact on human other nuisance species[2]. In contrast, moderate levels of nutrients in surface water are typically not a health, water pollution has significantly contributed to the degradation of ecosystems. Excessive levels of impurities such as nitrogen, Sulphur, and phosphorous compounds can promote the growth of bacteria, algae, and cause for concern. These extreme circumstances require the development of techniques to produce purified water.

1.2 Need of Water Desalination

One essential component for human survival is water. Nonetheless, 97% of the water on Earth is oceanic with a salinity level of more than 30,000g/m^3[3]. The water is unfit for human consumption due to its increased salt concentration. The World Health Organization (WHO) sets guidelines for permissible levels of salinity in drinking water. According to these guidelines, the acceptable limit for salinity is 500 parts per million

(ppm), with allowances for special cases of up to 1000 ppm. However, much of the water on Earth exceeds these limits, with salinity levels reaching up to 10,000 ppm. Seawater typically falls within the range of 35,000 to 45,000 ppm in terms of total dissolved salt**s.** Desalination is the process of extracting dissolved salts and minerals from seawater and brackish water (such as river water) to produce water that is safe for human and animal consumption, irrigation, and various industrial applications. This technology is seen as a viable solution to address freshwater shortages and mitigate water stress, which is a widespread issue affecting communities globally [4]. Given that seawater may be an endless supply, scientists are working very hard to develop a large-scale, realistically possible method for removing salt and minerals at a reasonable cost. There are several methods for desalinating water that use membrane-based or traditional mechanisms. Desalination has been growing quickly in recent years to supply water to the municipal and industrial sectors.

1.3 Shortage of Water in Pakistan

Pakistan suffers from annual water shortages that claim the lives of hundreds of thousands of people.

Pakistan's water supplies are under emergency, according to numerous studies and assessments from different institutions. Pakistan, whose population is expanding quickly, is threatened by food insecurity and a water problem. From 5260 cubic meters per person in 1951 to 1000 cubic meters per person in 2016, there has been a decline in surface water availability. By 2025, this amount might drop to roughly 860 cubic meters, indicating that Pakistan is transitioning from a nation with "water pressure" to one with "scarce water"[5-7] .Pakistan primarily experiences water crises as a result of pollution, droughts, low rainfall, and poor management.

According to a report by the IMF, Pakistan is listed as the 3rd country with a significant water scarcity. The United Nations Development Program (UNDP) and the Pakistan Council of Research in Water Resources (PCRWR) have warned the government that Pakistan is heading toward severe water scarcity, with the country potentially facing a complete water shortage by 2025.Shah Meer Baloch reports that senior management is displaying neglect in addressing this critical threat to the nation’s stability[8]. According

to researchers, Pakistan is projected to experience the most severe impact among its regional counterparts by the conclusion of 2040. It poses a significant threat to Pakistan's future.

The water scarcity in Pakistan will result in dramatic climate changes. In 2015 Karachi the largest city in Pakistan witnessed a minimum of 1200 heatstroke-related fatalities while in May 2018; at least 65 casualties were reported. Water politics may ensue, leading to a complete violation of the country's peace. To avert Pakistan's descent into this state of scarcity, certain measures must be implemented. Desalination is regarded a viable and practical solution for Pakistan's water scarcity challenge. The government has taken only a few actions regarding desalination, but they have yet to be put into effect.

According to President Arif Alvi's statement in the Associated Press of Pakistan on June 9, 2019, implementing a desalination unit capable of treating 1100-1400 million gallons of water per day is seen as a practical solution to address Karachi's water scarcity issue, given that it is already experiencing challenges with water availability as Pakistan's largest city. Significant investment is necessary, along with careful consideration for revenue generation, to ensure that the essential commodity remains readily accessible and affordable for citizens. At present approximately 1% of the global population relies on desalinated water for their daily necessities as seen in countries like Australia and Kuwait. Kuwait predominantly generates a significant portion of its water supply through desalination methods [9-11].

1.4 Water Purification Techniques in Pakistan

Now a day various methods of water purification are being employed in Pakistan. In large-scale industries reverse osmosis plants are frequently utilized for the purification of water. Water purification methods vary on a small scale depending on the specific area and its requirements. Water purification can be categorized into large-scale, medium-scale, and small-scale methods based on the scale of operation. Water purification on a large scale involves utilizing sources such as rivers, streams, lakes, etc. The methods employed include coagulation, sedimentation, filtration, disinfection, and desalination. Medium-scale purification involves utilizing s techniques along with the addition of chemicals like bleaching powder to purify water. On a small scale, water purification methods include boiling, sun exposure, treating with hot copper or iron, filtration through

cloth sieves, and using gravel filtration. Among these desalination stands out as a viable option for both large and small-scale water purification operations. Various desalination technologies are available, and recent advancements in technology have further enhanced the desalination market for water purification. Established desalination technologies are available for treating both seawater and brackish water. These methods can be grouped into three main categories: membrane-based techniques (including forward osmosis, reverse osmosis, nanotubes, nanocomposites, and graphene-based membranes), thermal techniques (such as desalination, membrane distillation, adsorption, humidification, dehumidification, and pervaporation), and alternative techniques (like ion-concentration polarization, microbial desalination cells, and capacitive deionization).

1.5 Water Desalination Process

Desalination technology makes seawater suitable for use by removing salts and minerals. This process transforms otherwise unsuitable water into purified water that can be used for various purposes, such as irrigation, industrial applications, and drinking. Various technologies have been developed over time to supply clean water[12]. These desalination systems have been designed and are typically categorized into three main groups, as illustrated in the figure.

- Thermal Technology
- Membrane Technology
- Others

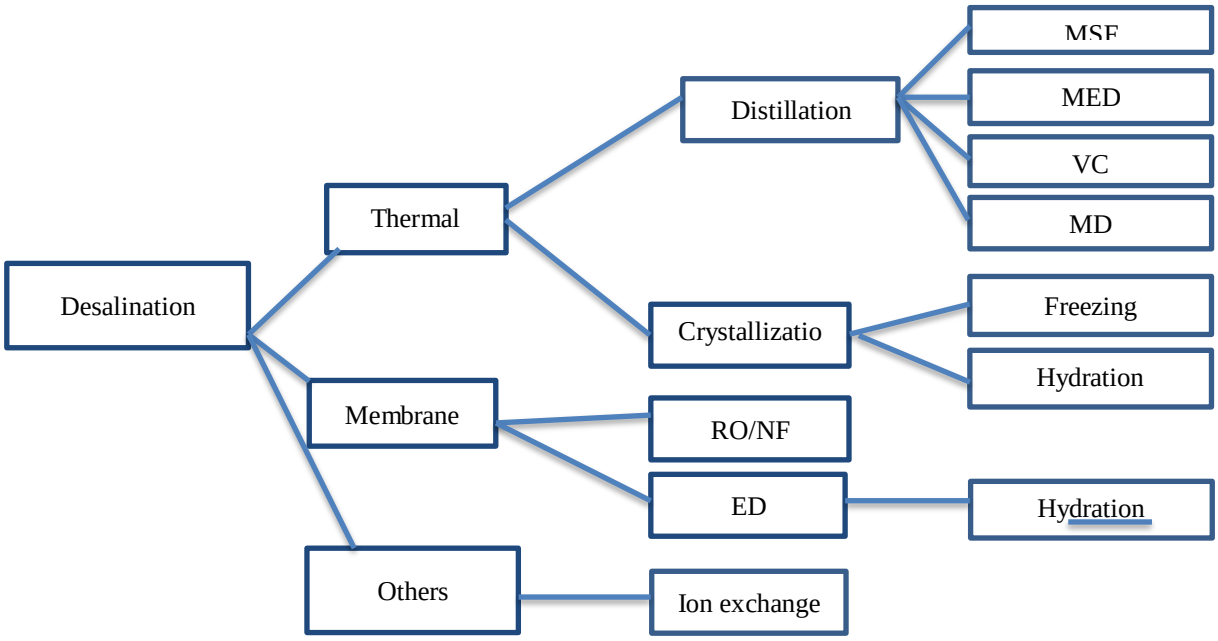

Figure 1.1 Water Desalination Processes

1.5.1 Thermal Technology

One of the most straightforward desalination methods is distillation, where heat is applied to saltwater to generate steam, which is then condensed into distilled water with a significantly reduced salt content. This purified water can be beneficial for industrial, household, and agricultural uses. To minimize the energy needed to evaporate the water, pressure is often reduced during the thermal desalination process. Commercially, thermal desalination can lower total dissolved solids (TDS) in saline water from levels as high as 60,000–70,000 mg/L to less than 10 mg/L[13]. The thermal process can also be referred to as phase change desalination, which includes the following methods[14].

1. Multi-Stage Flash Distillation
2. Multi-Effect Distillation
3. Vapor Compression
4. Freezing
5. Hydration

1.5.1.1 Multi-Stage Flash Distillation

The multi-stage flash distillation process (MSFD) involves moving saline feedwater through a series of chambers. In these chambers, both the temperature and pressure of the water are increased. As the water moves through the chambers, the pressure gradually decreases, causing the water to boil. Vapor is released in each chamber, which is then condensed and collected as purified freshwater[15]. The MSFD distillation process is widely utilized due to its simplicity and large capacity. However, it is currently the least efficient large-scale desalination method due to the considerable energy loss that occurs during the condensation phase[16].

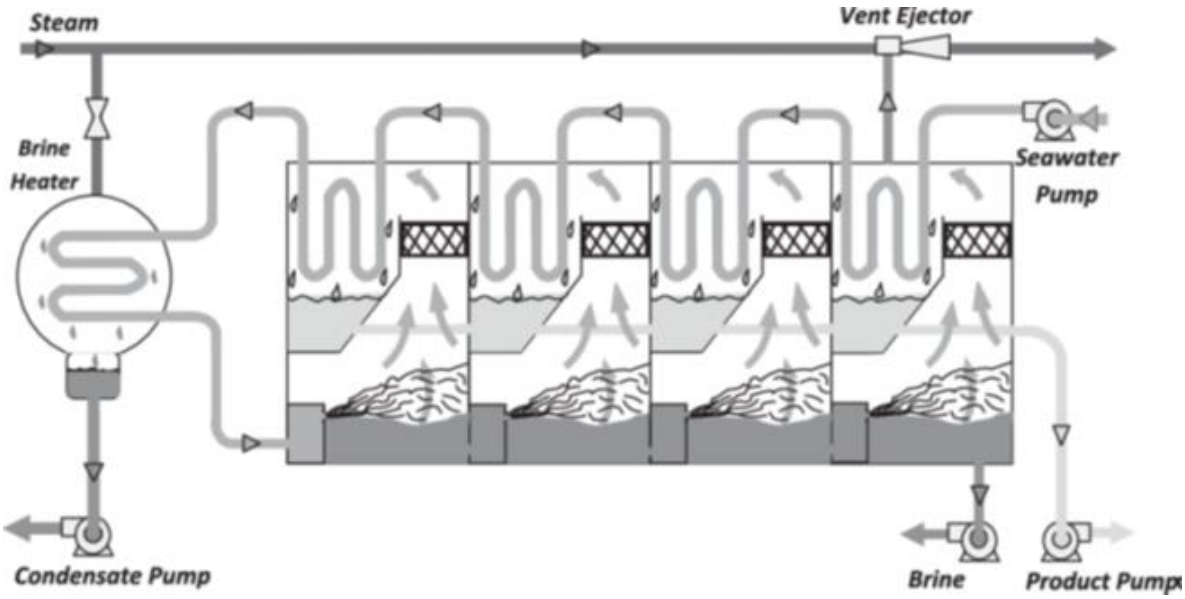

Figure 1.2 Schematic diagram of Multistage Flash Distillation[17].

1.5.1.2 Multi-Effect Distillation

In the MED process, heat is used to evaporate water from the feed solution. Instead of needing excessive heat, the solution is cooled below its saturation temperature, and the pressure in the distillation chamber is lowered beneath the saturation pressure for that temperature.This combination of thermal energy and reduced pressure allows the feed solution to evaporate using less energy compared to the MSFD process. Additionally, multiple stages are used to "recycle" the heated liquids, further improving efficiency[17].

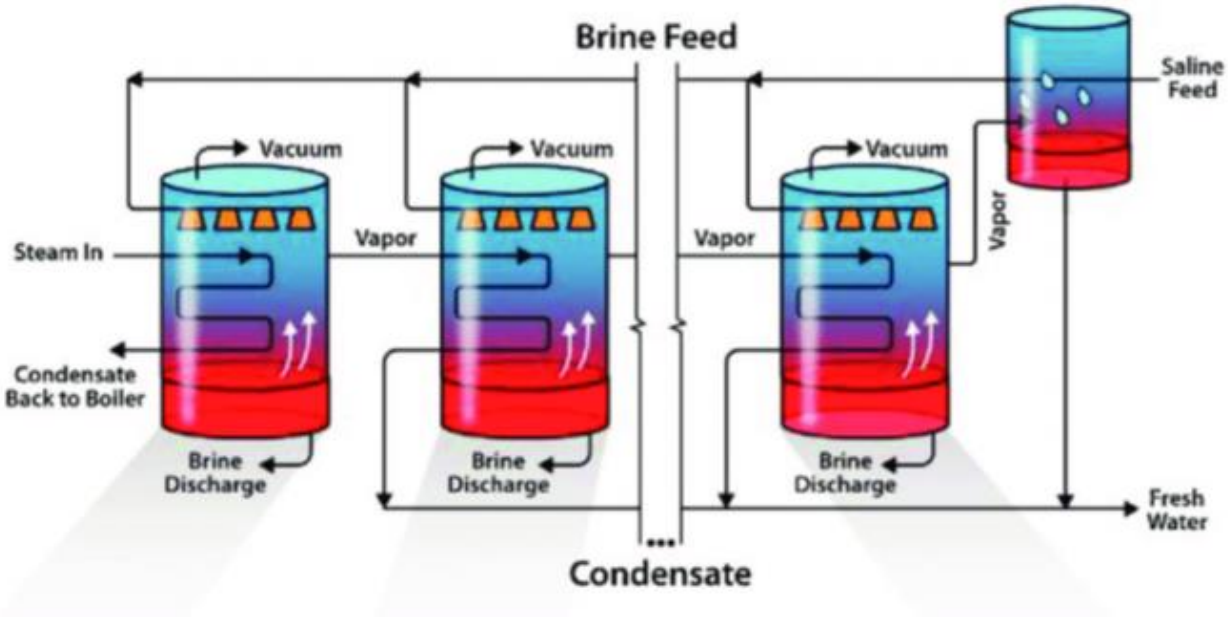

Figure 1.3 Multi- Effect Distillation Unit [19].

1.5.1.3 Vapor Compression Distillation

Vapor compression distillation (VCD) converts saltwater into freshwater by generating heat through vapor compression. Similar to the MSF and MED processes, it lowers the boiling point of saline water by reducing the pressure. This technique can be used on its own or combined with MED. Instead of traditional direct heat exchange, the vapor is compressed to generate the heat required for boiling and evaporation. A mechanical compressor provides the heat for the evaporation process. VCD is primarily used for small-scale distillation in compact units. Figure 1.5 depicts the general diagram of the process[18].

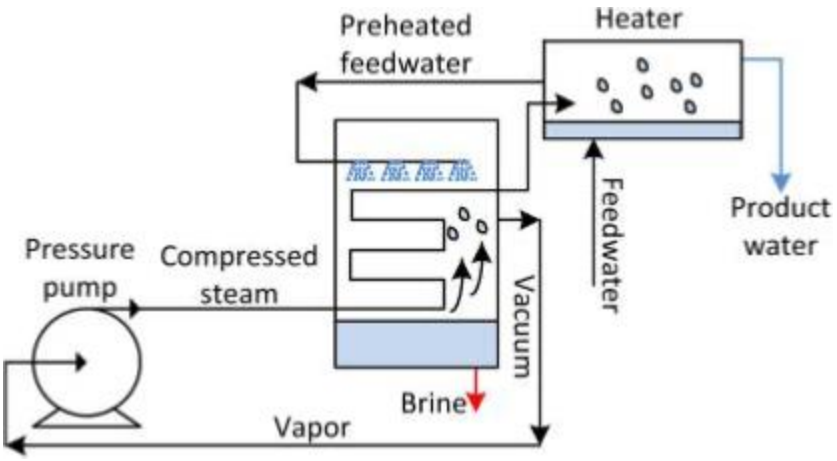

Figure 1.4 VCD Unit [20].

1.5.1.4 Cost Distribution of Thermal Processes

All the common desalination systems mentioned above demand significant energy, whether thermal, electrical, or a combination of both. Figure 1.6 illustrates the overall cost distribution in thermal desalination processes. The main challenge in using these systems is the substantial energy needed for the vaporization phase. Since thermal desalination involves evaporating saltwater, it tends to be costly. Typically, producing 1,000 liters of clean water through thermal desalination requires between 25 and 100 kWh of energy. According to data from the National Research Council, the cost of thermal desalination includes the consumption of thermal energy[19].

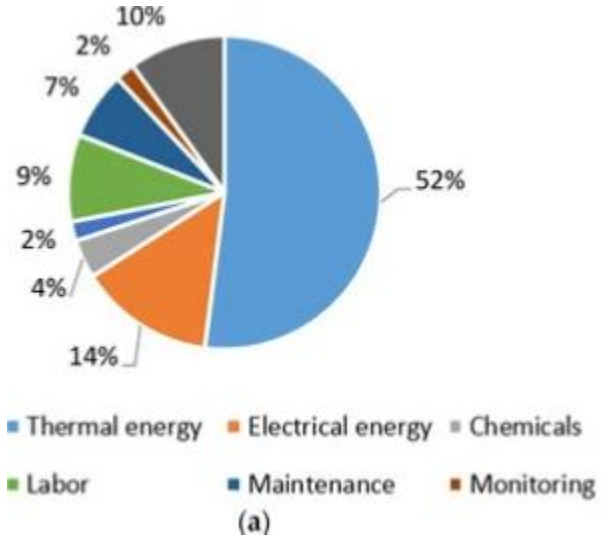

Figure 1.5 Breakdown of costs in Thermal Desalination Processes [22].

1.5.1.5 Disadvantages of Thermal (Conventional) Methods

The main disadvantages of thermal desalination processes are:

1. They are highly energy-intensive, requiring large amounts of electricity or heat to evaporate and condense water[20]. This makes them costly to operate and contributes to greenhouse gas emissions if the energy comes from fossil fuels.

2. Thermal desalination plants produce large volumes of brine, a highly concentrated and salty waste product. Disposing of this brine can harm marine environments if not managed properly. The brine can increase salinity and decrease oxygen levels, suffocating ocean life.

3. Thermal processes are less energy efficient compared to membrane desalination technologies like reverse osmosis. More energy is lost in the evaporation and condensation steps[21].

4. Thermal desalination plants require extensive infrastructure and are capital-intensive to build. This makes them less feasible for small-scale applications.

5. The chemicals used in thermal processes, such as chlorine and hydrochloric acid, can be harmful if discharged into the ocean[22]. They can poison marine plants and animals.

   However, thermal desalination does have some advantages. The waste heat can potentially be recovered to improve efficiency. And in some cases, the brine concentrate can be solidified and reused . But overall, the high energy demands and environmental impacts remain significant drawbacks compared to membrane desalination[4].

6. The chemicals used in thermal processes, such as chlorine and hydrochloric acid, can be harmful if discharged into the ocean[22]. They can poison marine plants and animals.

   However, thermal desalination does have some advantages. The waste heat can potentially be recovered to improve efficiency. And in some cases, the brine concentrate can be solidified and reused. But overall, the high energy demands and environmental impacts remain significant drawbacks compared to membrane desalination[4].

1.5.2 Membrane Technology

Membrane technology is essential in various industrial separation processes. Its benefits, including low energy usage, ease of operation, high selectivity, flexibility in adjusting material properties, and cost efficiency, have led to substantial progress over time, improving membrane performance and efficiency. The various separation challenges that membrane technology can solve are categorized based on the driving forces and chemicals involved in the separation process[23, 24]. Membrane desalination relies on the ability of semi-permeable membranes to selectively allow water molecules to pass through. Various processes are utilized in membrane technology, such as reverse osmosis, nanofiltration, electrodialysis, forward osmosis, and pervaporation. While these processes involve different methods, principles, and mechanisms, the core components of membrane separation remain consistent[25].

Following is the list of membrane technologies available:

- Nano-filtration (NF)
- Ultra-filtration (UF)
- Reverse-Osmosis (RO)
- Forward Osmosis (FO)
- Electrodialysis (ED)
- Pervaporation

1.5.2.1 Nano-Filtration

Nanofiltration (NF) is a membrane-based separation technique that operates at pressures between 5 and 20 bar, effectively separating molecules with molecular weights ranging from 200 to 2000 g/mol. NF offers several advantages over traditional thermal methods like vacuum and steam distillation, particularly because it operates at room temperature and avoids the high energy and heat levels that can damage heat-sensitive materials. NF membranes are highly effective at separating small organic molecules and inorganic ions. Compared to reverse osmosis (RO) membranes, NF membranes have lower rejection rates for monovalent ions, higher permeability, and strong rejection of divalent ions.

These properties make NF useful in various applications, including biotechnology, food processing, pharmaceuticals, and wastewater treatment[26].

1.5.2.2 Ultra-Filtration

Ultrafiltration (UF) is a membrane-based separation technique similar to nanofiltration, but it operates at lower pressures, typically between 1 and 5 bar, to separate molecules. UF membranes are often called molecular filters because they are designed to filter suspended molecules rather than dissolved contaminants[27].

1.5.2.3 Electrodialysis

Electrodialysis was the first commercially successful membrane desalination method. This process uses ion-exchange membranes that selectively allow anions and cations from the feedwater to pass through. When an electric current is applied to the electrodialysis stack, anions move through the anion-selective membrane, while cations pass through the cation-selective membrane. However, due to its lower efficiency compared to other membrane separation methods, electrodialysis is not commonly used for seawater desalination[27].

1.5.2.4 Pervaporation

Pervaporation works by partially vaporizing liquid mixtures across a membrane, which can be either porous or nonporous. This leads to the accumulation of vapor from the permeating components, which can be removed by applying low pressure or allowing a benign liquid to pass through the permeate side. The process is driven by the difference in chemical potential between the phases on either side of the membrane. Unlike distillation, which relies on volatility, pervaporation uses the sorption-diffusion model to describe transport based on molecular size differences. This makes it an effective and cost-efficient alternative for azeotropic separations. Additional benefits include the removal of a third component and lower energy requirements due to energy integration[28].

1.5.2.5 Reverse Osmosis

In this process, the pressure applied is higher than the natural osmotic pressure of seawater, driving the separation. A semi-permeable membrane is utilized to perform the separation[12]. After reverse osmosis (RO) removes approximately 99% of the dissolved contaminants, the purified water is used for drinking and various other purposes[29]. This

process is completed in two stages. In the first stage, physical and chemical treatments are performed, where solid particles, colloids, and bacteria are removed, and chemical treatment is achieved through chlorination. After this, seawater is passed through the RO semi-permeable membrane, and the permeate is collected from different sides. Various types of membranes can be used for this step, with the applied pressure influencing the membrane's strength, permeability, and the removal of contaminants from the feed water. Following the RO process, the permeate undergoes electrolysis to further reduce salt content[30]. Reverse osmosis operates by applying pressure to one side of a solution, typically higher than the osmotic pressure, forcing the solution through a semipermeable membrane. This membrane can remove contaminants as small as 0.1 microns, which are often referred to as reverse osmosis concentrations[31]. The membrane's function simplifies the process by blocking larger solute molecules, keeping them on the pressurized side, and preventing their passage. Conversely, the membrane allows the pure solvent to pass through. As a result, one side of the membrane becomes concentrated with solute molecules, while the other side is diluted. In theory, reverse osmosis occurs when the solvent moves through the membrane against a concentration gradient, essentially flowing from an area of lower concentration to one of higher concentration[32].

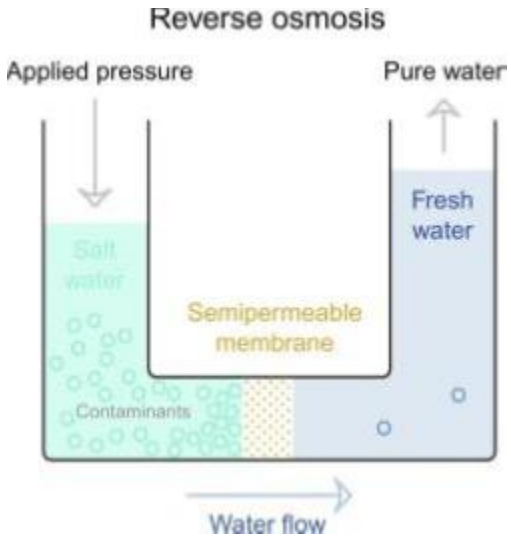

Figure 1.6 Schematic of Reverse Osmosis [36].

1.5.2.6 Forward-Osmosis

Forward osmosis (FO), a membrane technology recognized for its high water recovery and low cost, has attracted considerable interest as a promising method for desalination,

renewable energy generation, and wastewater treatment[23, 33]. Unlike pressure-driven membrane systems, forward osmosis (FO) offers an advantage as it operates without the application of hydraulic pressure[34]. Forward osmosis is a separation process that uses a selective semipermeable membrane to separate a feed solution with lower osmotic pressure from a draw solution with higher osmotic pressure[35]. The difference in osmotic pressure between the feed solution and the draw solution causes water to move across the semipermeable membrane from the feed side to the draw side. Compared to traditional pressure-driven membrane processes, forward osmosis (FO) uses less energy, extends membrane lifespan with better resistance to fouling, and sustains a high water flux[36]. The forward osmosis (FO) method creates a natural driving force by leveraging the concentration difference between the feed solution and the draw solution as they pass through a semipermeable membrane. Rather than depending on hydraulic pressure, FO utilizes the osmotic pressure gradient to transport clean water through the selective membrane. The FO membrane mainly blocks organic molecules while allowing water and dissolved ions to pass through. As freshwater moves from the feed water into the draw solution, it dilutes the draw solution and concentrates the feed solution, producing a highly salty brine[37]. The membrane used in the forward osmosis (FO) desalination process is crucial, as it directly impacts the system's overall efficiency. Highly efficient FO membranes are commonly utilized, offering potentially better performance and selectivity compared to traditional membranes. Osmosis can be reversed by applying additional pressure in areas with higher solute concentrations, opposing the natural movement of water. This pressure is referred to as the fluid's osmotic pressure. The osmotic pressure gradient is what drives water across the membrane, moving from a lower solute concentration to a higher solute concentration[38]. The driving force for the osmosis process can be estimated, and the equation governing water movement in FO is:

$$J_{aw} = A.\ (\Delta\Pi - \Delta P)$$

When P is greater than or equal to zero, the direction of water transport in the FO process is determined, flowing either from the feed solution to the draw solution or vice versa. Lee et al. established the flow directions and driving force for this process in the 1980s[39].

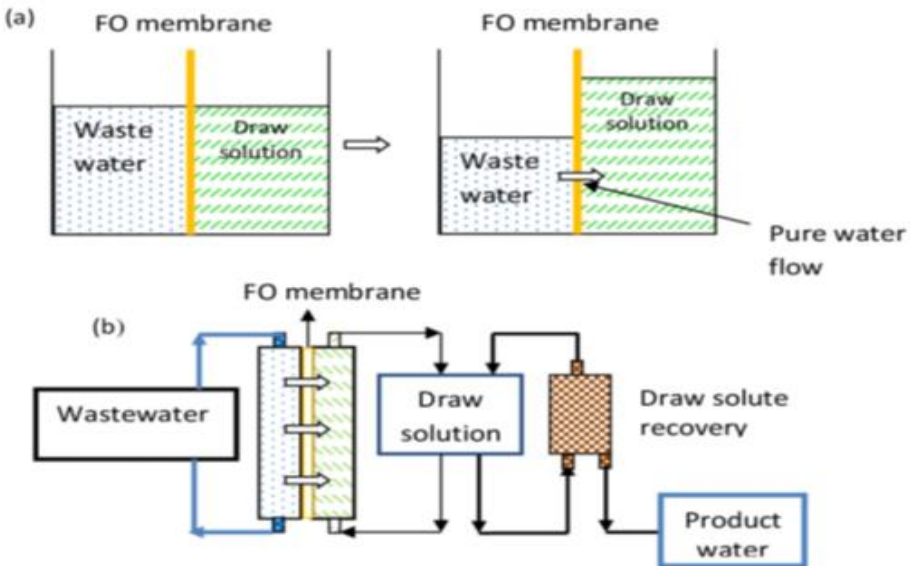

Figure 1.7 Schematic of Forward Osmosis [44].

This research focuses on the synthesis of MMNMs to address issues related to cost and efficiency. In this study, activated carbon was extracted from the date seeds via pyrolysis treatment and incorporated into the Cellulose acetate/ PAN matrix using the phase inversion process. The study aims to achieve improved flexibility, enhanced processability, reduced cost, increased pure water permeability, high salt selectivity, high dye rejection, and excellent anti-fouling properties. This approach provides a new pathway for utilizing biological waste more efficiently, thereby reducing solid waste and making the process more environmentally friendly.

CHAPTER 2
LITERATURE REVIEW

This chapter provides an overview of the advancements made in the field over the past decades, with a focus on polymeric nanocomposite membranes. This primary focus of this section is to develop a desalination system using mixed matrix membranes that combine Nanofiltration (NF) technology. The goal is to create a water treatment method that is clean, efficient, stable, environmentally friendly, and high performing.

2.1 Membranes

A semi permeable membrane serves as a selective barrier between neighboring stages, permitting the passage of certain materials while restricting others(40). Membrane technology is used as a separation method to improve water quality and boost energy efficiency. Membranes serve as barriers in water treatment, removing impurities like viruses, salts, bacteria, and other particles. They can be driven by gradients in temperature (ΔT), pressure (ΔP), concentration (ΔC), or electrical potential (ΔE). The efficiency of membrane separation depends on the specific application, the driving force applied, the size of the particles being filtered, and the type of membrane utilized.In contrast to traditional separation methods, membrane separation is recognized as a clean and exceptionally efficient technology for separating substances. The membrane separation process has garnered significant attention from an industrial standpoint as an alternative to evaporation, freeze concentration, and distillation methods. The efficiency of a membrane relies on factors such as permeability, coefficient, separation factor, and permeation rate. To achieve optimal performance, membranes should be cost-effective to manufacture, highly resistant to harsh environmental conditions, and demonstrate superior permeance and selectivity. Since the 1960s membrane technology has been employed as a separation method in various industries including food and beverages, as well as petrochemical, textile, water treatment, chemical, pulp and paper, and natural gas treatment sectors[41, 42]. The effectiveness of the membrane separation process relies on the existence of a semi-permeable membrane.

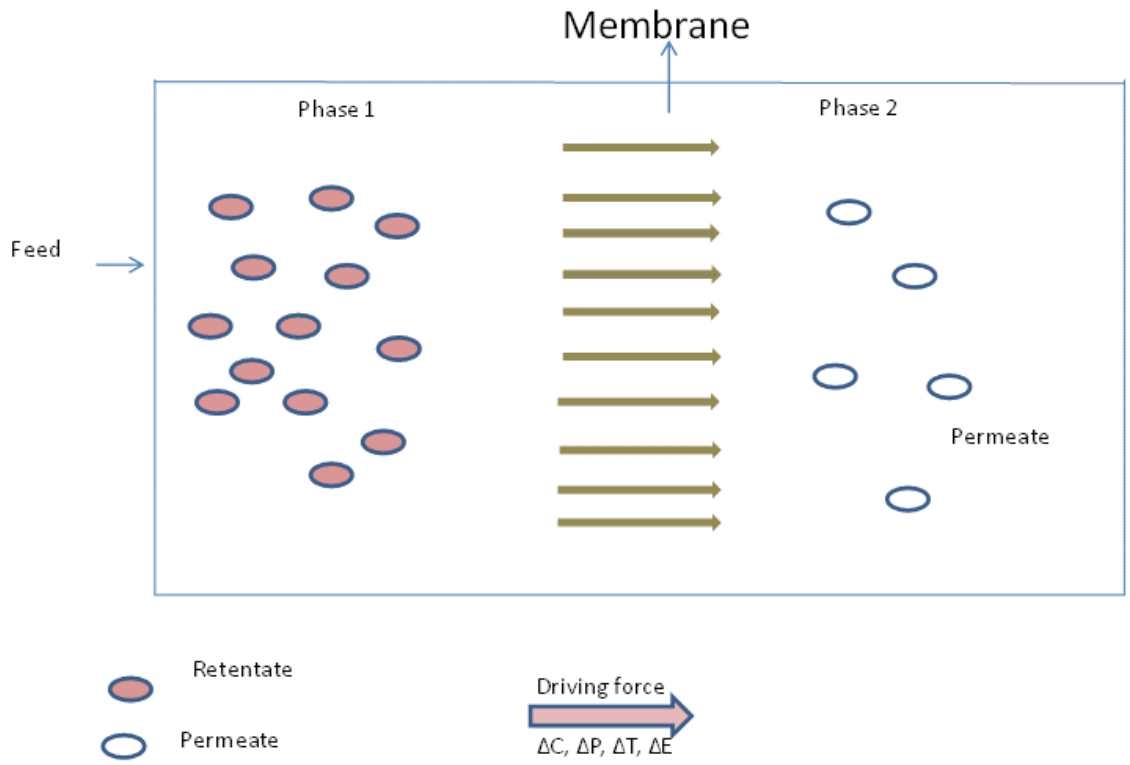

Figure 2.1 Membrane based separation process

2.2 Classification of Membrane

Membranes can be categorized in various ways based on factors such as their origin, composition, and morphology. They can be classified as organic or synthetic, and further divided into inorganic, organic, hybrid, composite, or mixed matrix materials. Morphologically, membranes may be symmetric or asymmetric. Therefore, their classification depends on multiple criteria. Typically, membranes are broadly categorized into two main types—organic and inorganic—based on the materials used for their synthesis.

2.2.1 Types of Membranes Based On Material

There are three types of membranes based on materials

- Organic membranes
- Inorganic membranes
- Mixed Matrix Membranes (hybrid membranes)

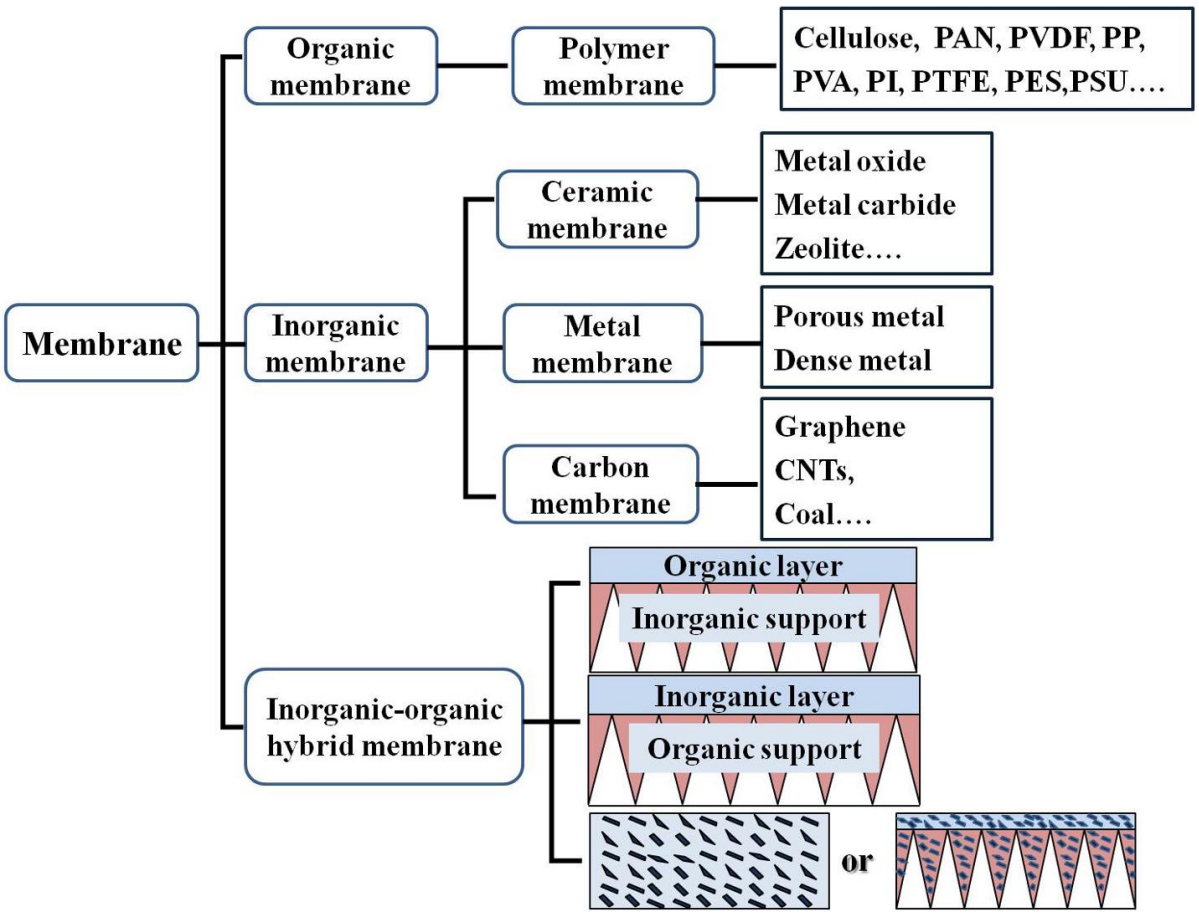

Figure 2.2 Types of membranes [48].

2.2.1.1 Inorganic Membranes

Inorganic membranes include materials such as liquid, ceramic, zeolite, carbon, and hybrid organic membranes. Various fabrication techniques are employed to produce these membranes, such as the sol-gel method, chemical vapor deposition, and slip casting. In recent times, inorganic membranes have found applications in desalination, with Titania, zirconia, alumina, and carbon membranes being predominantly used for water purification purposes.

i. Ceramic Membranes

Ceramic membranes can be made from various metal oxides or their combinations, including silicon carbide, glass, zirconia, and alumina. In addition to metal oxides, non-oxides can also be utilized in the production of ceramic membranes. These membranes typically consist of three layers: a non-porous layer, an intermediate layer, and a

microporous layer, each differing in pore size and thickness[43].

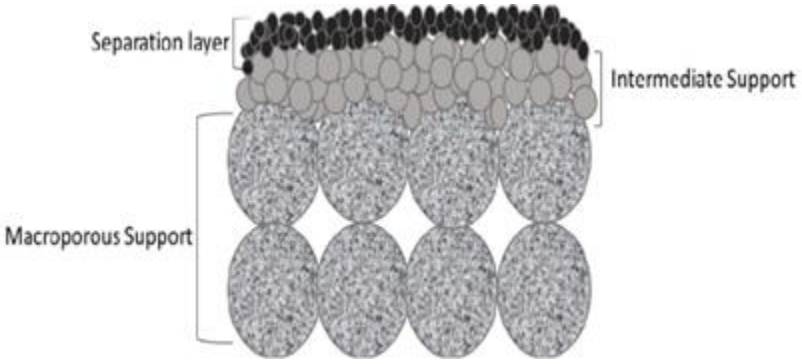

Figure 2.3 Ceramic Membrane Structure

ii. Silica Membranes

Silica membranes are widely utilized for hydrogen separation and real-time reactions on an industrial scale. These membranes are highly valued in membrane reactors due to their ability to produce the highest yields(43).

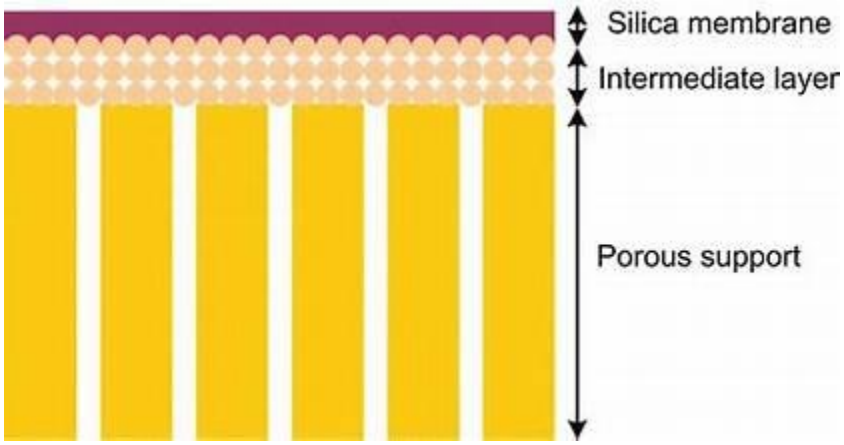

Figure 2.4 Silica membranes [49].

iii. Zeolite Membranes

Hydrated aluminum silicates, referred to as zeolites, exist in both natural and synthetic forms and contain cations from groups 1 and 2 of the periodic table, such as sodium, calcium, potassium, magnesium, barium, and strontium. The selection of rings in the

zeolite framework is determined by the number of oxygen atoms. The wettability and surface charge of the membrane is influenced by the concentration of silicon and aluminum in the zeolite structure. The water affinity and hydrophilicity of the membranes are governed by the aluminum content within the zeolite.

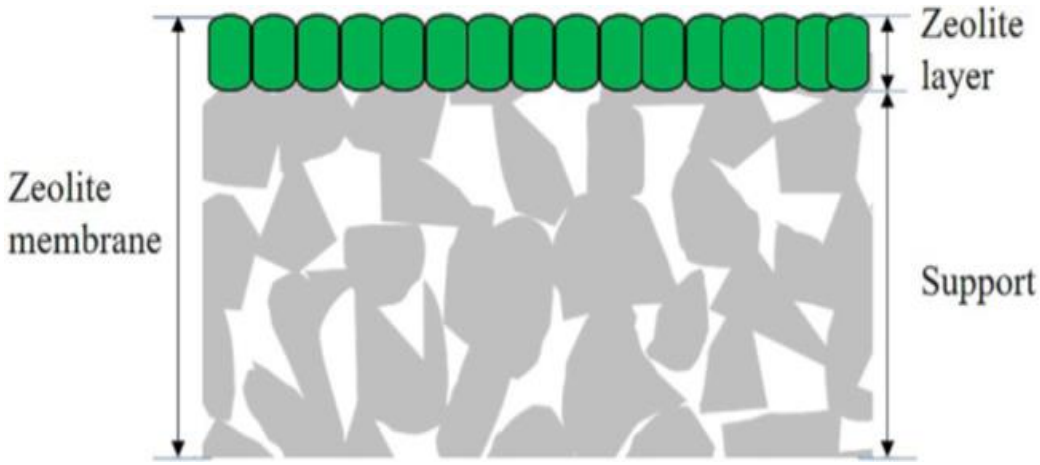

Figure 2.5 Structure of Zeolite Membrane [50].

2.2.1.2 Organic Membranes

Polymeric membranes have garnered considerable interest due to their excellent chemical durability, mechanical properties, and ease of processing, making them both cost-effective and widely applicable across various industries. Commonly used polymers for membrane filtration include polyether sulfone (PES), polyurethane (PU), polyethylene terephthalate (PET), polyamide (PA, also known as nylon), and polypropylene (PP), among others[44]. These membranes are favored for their cost-effectiveness, user-friendliness, and scalability. However, they come with certain drawbacks. Polymeric membranes tend to have lower resistance to solvents and are vulnerable to harsh environmental conditions, such as high temperatures, pressure, and exposure to corrosive organic solvents. Over time, they may suffer from decreased permeance and water flux due to aging and the increased rigidity of the membrane following cross-linking[45]. Figure 1 depicts the structural composition of a polymeric membrane.

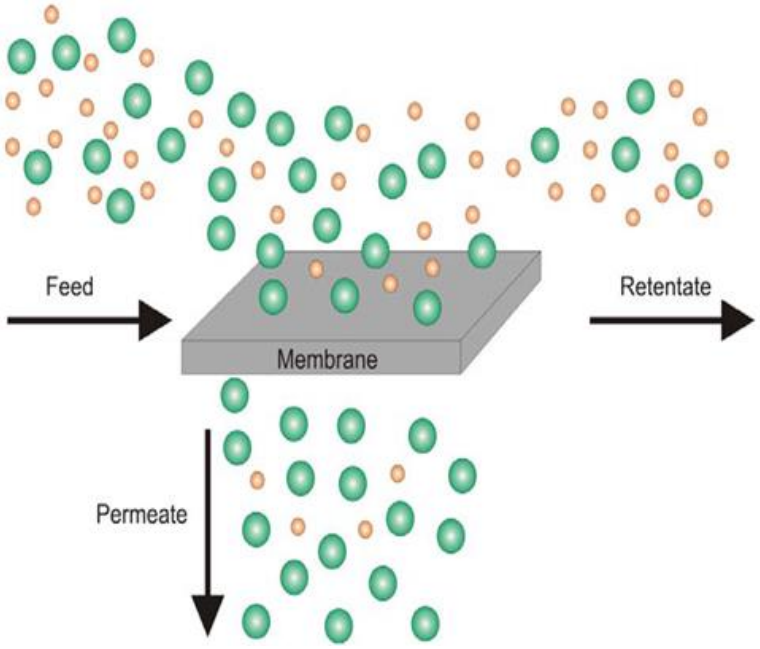

Figure 2.6 Polymer based membrane

2.2.1.3 Polymer Matrix Nanocomposite (PMNC)

In order to get around problems with traditional polymeric membranes in water purification, nanocomposite membranes have garnered a lot of attention due to their hydrophilicity, mechanical, and thermal stability, and antifouling qualities. The amount of articles produced in this discipline is rising daily at a considerable rate[46]. Various methods have been recorded for preparation, some of which are covered here. Both polymer- and non-polymer-based nanocomposites exist. The documented techniques for creating polymer Nanocomposites included melt intercalation, template synthesis, in situ polymerization, and intercalative polymerization. Among them, combining monomer or polymer with reinforcing elements and incorporating inorganic material into organic polymer are the most often utilized techniques. The membrane's life span, strength, stiffness, and surface area all increase as a result[2].

Various techniques, such as reverse osmosis, ion exchange, gravity, and adsorption, have been described for water. An assortment of adsorbents, including nanoparticles, has been employed to remove toxins from water at a reduced cost. These adsorbents are effective at removing water pollutants and heavy metals.

These adsorbents are inexpensively available in the commercial market. These days, membrane technology is an effective method based on the fundamentals of adsorption, electrostatic phenomena, and sieving[47].

Two well-established filtration methods are cross-flow and dead-end filtration processes. In dead-end filtration, water flow perpendicular to the membrane surface under applied pressure, making it ideal for solvent and water-based feed solutions. In cross-flow filtration, turbulence is generated on the membrane surface, and the feed and filtration flow directions are at a 90° angle to each other.

Thin film composites, which support an ultra-thin barrier layer over porous polymeric membranes by the use of various polymers such polyurea, polyamide PA, polyamide PA, polyuria-polyamide, PSF, polyvinyl alcohol, Chitosan, P123, P127, and pollster amide, were the main drawback in PM. In terms of water rejection and permeability, these kinds of polymers have demonstrated encouraging outcomes. TiO2 and GO composites, two types of PM, are showing promise in desalination and water filtration. However, the low yield and problems in GO synthesis continue to pose a hurdle in the development of GO-based membranes. GO membranes are a viable option for desalination processes despite these drawbacks because of their increased stability, improved salt rejection, and antifouling qualities[48, 49].

The creation of polymeric membranes requires the fabrication of TFNs (thin film nanocomposite) or MMMSs (mixed matrix membranes). NPs are employed in the production of these membranes. Several kinds of nanomaterials or nanofillers are used, such as silicate minerals, zeolites, metal oxides, carbon nanotubes, graphene oxide, and activated carbon. The integration of nanomaterial flux leads to an enhancement in salt rejection and separation. Membranes made of nanomaterials are employed in a variety of processes, including adsorption, gas separation, and water treatment[50, 51].

Water treatment applications also use inorganic membranes, although their production is challenging and costly. They do, however, provide excellent pore structure stability, long life, and great chemical stability. Washing can be done using various solvents and anti-scaling agents.

Since the temperature in water treatment is high (between 500 and 800), greater mechanical strength is needed to withstand the applied forces. The selection of membranes is contingent upon various aspects, such as the composition of the membrane, ambient temperature, and material structure stability[42]. Washing can be done using various solvents and anti-scaling agents.

Since the temperature in water treatment is high (between 500 and 800), greater mechanical strength is needed to withstand the applied forces. The selection of membranes is contingent upon various aspects, such as the composition of the membrane, ambient temperature, and material structure[42].

2.2.1.4 Mixed Matrix Nanocomposite Membranes (MMNMs)

The application of mixed matrix is an important way to manufacture high-performance membranes. A polymer phase combined with inorganic filler makes up MMNMs. The idea behind developing an MMNM was to combine the permeability of polymeric materials with the selectivity of inorganic materials to produce a cutting-edge hybrid membrane.

MMNMs can have both symmetric and asymmetric morphology. Dense thin-layer membranes are referred to be symmetric, while inorganic filler and continuous polymer layers are referred to as asymmetric [52].

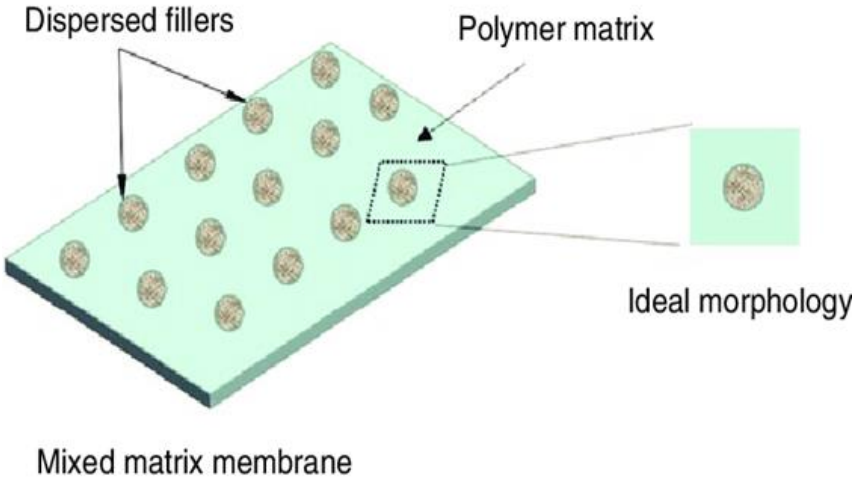

Figure 2.7 Mixed matrix membrane

Mixed matrix membranes are used in water purification to increase hydrophilicity,

decrease fouling, improve mechanical and thermal stability, and enhance antibacterial characteristics. It is still challenging to make MMNMs devoid of defects and to achieve a homogeneous dispersion of the inorganic and organic phases. Nanoparticles are included in the polymer solution to get around this problem.

The solvent is mixed with a dissolved polymer. In a different reagent container, NPs are dissolved in a solvent and mixed. After that, the filler solution is mixed with the homogenous polymeric solution and left overnight to stir. The membrane is then cast after that.

Understanding the separation efficiency of MMNMs can be challenging due to the significant influence of multiple parameters. However, reproducing dependable and efficient MMMs is challenging, and this is a need for commercialization. Historically, the main challenge in developing dense membranes was addressing the issue of insufficient interfacial bonding between the polymer and filler. MMNMs are fabricated using various techniques, including phase inversion, track etching, stretching, and electrospinning.(53).The most promising technology is PI, and these days, phase inversion is also used to create commercial membranes[54]. Dense polymeric membranes typically exhibit lower flux, so the phase inversion method is employed to enhance flux and control membrane thickness. In this process, the polymer transitions from a liquid to a solid state. Several techniques are used in phase inversion, including solvent evaporation, precipitation through controlled evaporation, and thermal precipitation. Precipitation can occur either through vapor phase or immersion, with immersion precipitation being the most common method for fabricating phase inversion membranes. The phase inversion process is influenced by a number of important variables, such as the casting solution's composition, humidity, evaporation time, and polymer concentration. The flow, selectivity, and general appropriateness of the membrane for its intended use are all directly impacted by these factors. Mixed matrix nanocomposite membranes (MMNMs) are used extensively in water purification to enhance permeability and selectivity, remove impurities, reduce fouling, and offer remarkable mechanical, chemical, and thermal durability. Different nanomaterials, either liquid, solid, or a combination of both, are incorporated into the polymer matrix via MMNMs.

These nanomaterials typically include porous or nanoporous substances such as zeolite, activated carbon, graphene oxide, and carbon nanotubes, as well as nonporous materials like silica, TiO_2, SiO_2, and Al_2O_3[55-57]. The inorganic fillers significantly influence

membrane morphology by potentially blocking pores and causing aggregation. Choosing appropriate polymers and fillers can enhance both selectivity and permeability. Based on a literature review, this study centers on the incorporation of nanoparticles (fillers) on polymeric membranes for desalination applications[58].

2.3 Membrane Synthesis Techniques

There are numerous techniques for synthesizing membranes, as well as various types of membranes and their applications. Given the diversity of materials, a broad array of preparation methods is available. However, some of the most significant approaches are outlined below, which enable the fabrication of both organic and inorganic membranes, as well as self-supporting and composite membranes.

2.3.1 Dip-Coating

This is one of the simplest and most commonly used techniques in industry. In this method, a support material is immersed or dipped into a coating solution for a specific period and then dried. This process deposits a membrane layer from the casting solution onto the support. It is widely employed for producing composite membranes. Through this technique, thin layers as small as 1 am can be achieved, and multiple coatings can also be applied if needed[59]. Figure 1.9 illustrates the dip-coating process.

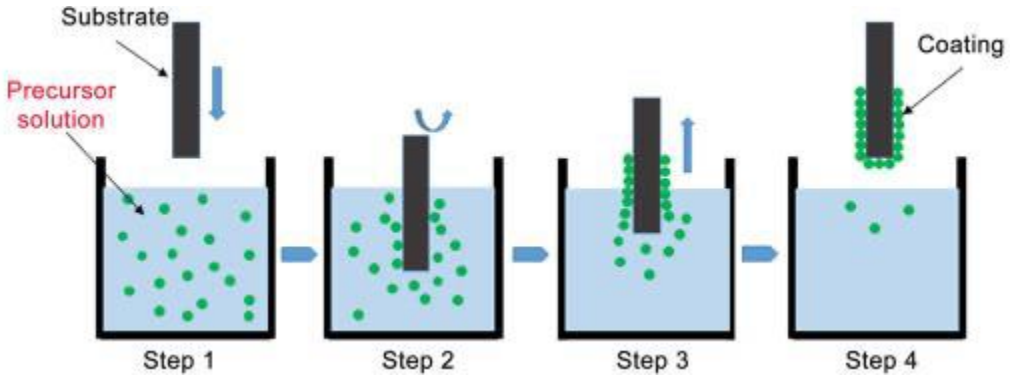

Figure 2.8 Dip-Coating [54].

2.3.2 Spin-Coater

This process is similar to the dip-coating method, but differs in that, instead of immersing the support into the solution, the layer is applied to the support using centrifugal force. This approach allows for greater uniformity and the production of extremely thin layers with very low thickness[60]. Figure 2.3.2 illustrates the operation of the spin-coating process.

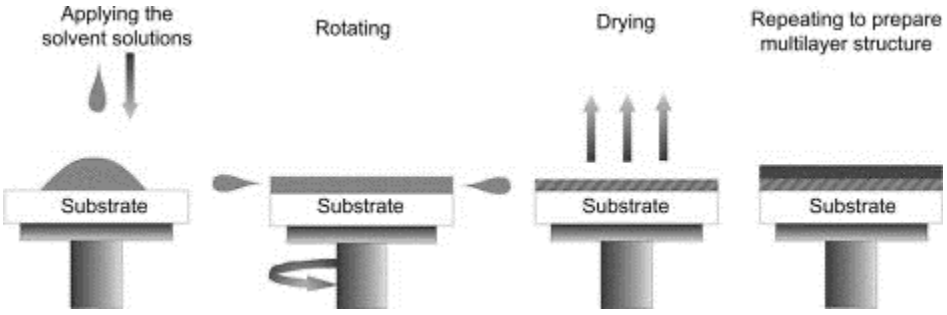

Figure 2.9 Spin-Coater [56].

2.3.3 Phase Inversion

Phase inversion is a technique that transforms a polymer from a liquid to a solid state, also referred to as phase conversion. The most commonly used method is Non-Solvent Induced Phase Inversion, widely known as Wet Phase Inversion. This process allows for the synthesis of almost all types of membranes, especially hollow fiber and flat sheet membranes. Membranes can be classified as either porous or dense. Certain key factors should be considered during the formation of porous or non-porous membranes[61]. Porous membranes are formed if the following conditions are met:

- Polymer concentration is low
- No volatile solvent is added, and no evaporation time is given
- High solvent and non-solvent affinity are achieved
- Addition of non-solvent to a polymer solution or a second polymer to solution

Formation of the dense membrane is achieved if:

- Polymer concentration is high (density increases with polymer concentration)

- A volatile solvent is added to the casting solution (density increases with solvent concentration)
- Evaporation time is given before coagulation (density increases with Eva [oration time)
- No affinity between solute/solvents
- Feed solution is pure also no addition of non-solvent or other polymer is done.

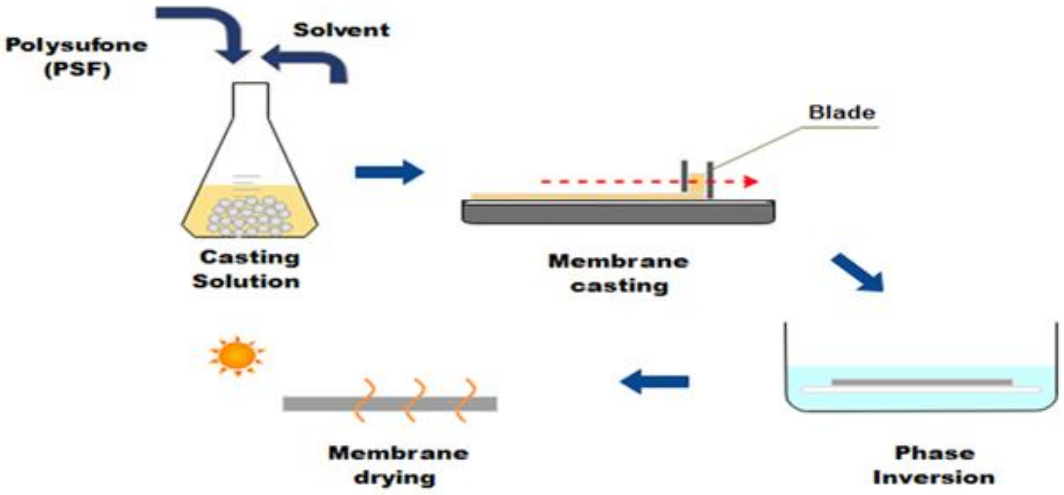

Figure 2.10 Phase inversion [58].

2.3.4 Interfacial Polymerization

This method involves precisely controlling the polymerization of a thin layer applied over support at the interface between the two layers. Commonly used monomers for this process include:

- MPD (M- phenylene-diamine)
- TMC (trimethyl chloride)

This process involves three stages, where the product undergoes thermal treatment to complete the crosslinking and reaction process. Initially, the product is coated with an aqueous amine solution, followed by a coating with an organic TMC solution in the second stage. The following factors influence the membrane's morphology and performance during this process:

- Monomer concentration
- Post- Treatment
- Characteristics of support
- Reaction time

Creating interfacial polymerized membranes presents several challenges. One issue is the uneven and non-uniform polymerization, which can lead to increased film thickness and the internal-concentration polarization effect. Numerous studies are being conducted to develop ultra-thin, defect-free interfacial polymerized membranes to achieve both high performances, in terms of high flux and high rejection rates.

free interfacial polymerized membranes to achieve both high performances, in terms of high flux and high rejection rates.

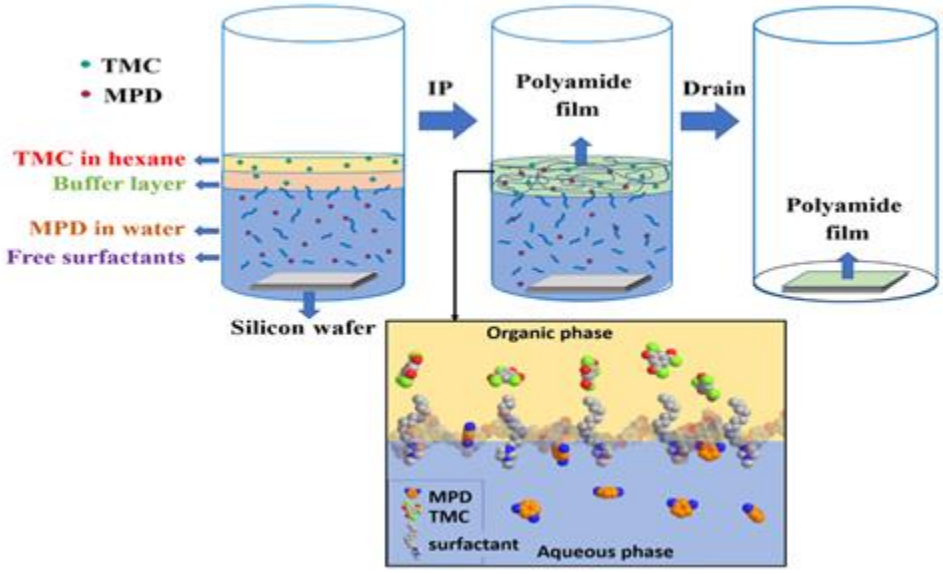

Figure 2.11 Interfacial polymerization [59].

2.4 Description of Fillers Used in Mixed Matrix Membrane (MMM)

For MMM, several filler kinds are utilized. The following describes some of the most popular and useful nanoparticles for MMM preparation.

2.4.1 Zeolites

Zeolites are porous minerals made of silicon, aluminum, and oxygen; they are also

referred to as molecular sieves. They are crystalline in structure, with internal channels and voids. These cavities and channels may hold cations, such as phosphate, sodium, magnesium, and calcium ions, water, and/or tiny molecules[62]. They have exceptional chemical and physical properties, such as sorption and diffusion capacities, due to their distinct pore sizes and channels. Since the last few decays, zeolites have been used as inorganic filler in MMM. Zeolites can be added to membranes to improve their surface characteristics, including contact angle, solid-liquid interfacial free energy, film thickness, water flux, and pore size[63].

2.4.2 Silica

The non-porous inorganic filler is silica. High surface area, chemically and thermally durable, and comparatively innocuous to the environment are silica nanoparticles[64]. It has been demonstrated that adding silica increases the membrane's water permeability, contact angle, and surface roughness. By strengthening the bond between the functional group and the polymer matrix, the amount of water transported over the membrane increases. The ideal conditions for the sol-gel synthesis process are employed to incorporate silica into the membrane [65-67].

2.4.3 TiO_2

TiO2 nanoparticles have a photocatalytic activity that kills bacteria and breaks down organic compounds(68). The membrane's hydrophilicity and fouling resistance have both enhanced with the addition of TiO2[69-72]. Because of the large specific area and nanosized diameter of TiO2, non-selected voids are avoided during the manufacture of MMM incorporating TiO2 as nanofillers.TiO2 addition causes the membrane's porosity to decrease, which lowers flow.TiO2-impregnated membranes exhibit improved mechanical strength and hydrophilicity[73].

2.4.4 Carbon nano-Tubes (CNTS)

Graphite sheets are molded into nanotubes to create carbon nanotubes. Water is transported via a membrane without friction thanks to the impregnation of CNTs. Based on their pore diameter, water permeates CNT-based materials but MMM salts are repelled. CNTs are hollow cylinders that are one-dimensional and have a large length-to-diameter ratio[74].

2.4.5 Metal Organic Frameworks (MOFS)

Metal-organic frameworks (MOFs) are porous hybrid materials made of a central metal bonded by coordinating bonds to organic linkers [75-79]. Their exceptional adsorption affinities, great thermal stability, and changeable pore diameters are all present[80]. High surface area regulated porosity is one of the other features. They have strong sorption ability because of their large surface area. Because of their greater affinity for the polymer matrix than inorganic fillers, MOFs in membranes have demonstrated superior benefits and performance over porous materials with rigid frameworks, such as zeolites. In addition, MOFs in membranes reject specific molecules based on their size, shape, polarity, and conformation, while also preventing non-selected voids[81].

2.4.6 Activated Carbon (AC)

Activated carbon is regarded as an effective type of filler material for MMNMs. Activated carbon, also known as activated charcoal, is a highly porous form of carbon with a large surface area that is widely used for various applications such as water treatment and adsorption of chemicals and pollutants. It is produced from different carbonaceous materials like agricultural waste, olive stones, walnut shells, and peanut hulls through processes involving physical or chemical activation with agents like KOH or H3PO4. The preparation of activated carbon involves carbonizing and activating the original material to enhance its adsorptive properties, with factors like activating agent concentration and particle size influencing its effectiveness. Activated carbon's adsorption capabilities are attributed to its microporosity, allowing for strong physical adsorption forces, making it a valuable tool for purification and recovery processes in various industries.

AIMS AND OBJECTIVES

1- To synthesized bio-adsorbent through pyrolysis method.

2- To synthesize pristine membranes by the phase inversion method.

3- To synthesize Mixed matrix nanocomposite membranes (MMNMs) via the phase inversion method, incorporating the filler (bio-adsorbent).

4- The synthesized mixed matrix nanocomposite membrane was characterized to analyze, functional groups, contact angle, porosity, and water uptake.

5- To investigate the desalination process by using the bio-adsorbent.

CHAPTER 3

METHODOLOGY

3.1 Material

High purity research grade chemicals were used in this study. Date seeds (Phoenix dactyliferous) were purchased from the Asia food international (Khairpur Mirs Pakistan). Acetone (CH_3 $COCH_3$), Ethanol (C_2H_5OH) ,Hydrochloric acid, Polyvinylpyrrolidone (PVP)(C_6H_9NOn), Sodium Chloride (NaCl), Magnesium Sulfate monohydrate ($MgSO4.H_2O$), and vinyltriethoxysilane(($(C_2H_5O)_3SICH=CH_2$)was purchased from Sigma Aldrich® (Steinem Germany. Potassium hydroxide (KOH) was purchased from Merck. Cellulose acetate ($C_{14}H_{16}N_4$) was purchased from Across Organics (Belgium).

3.2 Synthesis of Biochar via Pyrolysis Technique

The biochar was prepared from date seeds via pyrolysis is shown in figure 3.1. Initially the seeds were manually separated from the fruit by hand. The seeds were cleaned by washing them with deionized water and rinsing them with acetone to remove any impurities. Subsequently, they were washed again with deionized water to ensure no dust particles remained[82]. The cleaned date seeds were then dried in an oven at 180℃ for 24 hours to eliminate any related contaminants and moisture content[83]. After drying, the seeds were crushed twice using a German jaw crusher and further refined using a Disc ball mill. Additional refinement was carried out using a lab scale grinder. Finally, the crushed seeds underwent sieve analysis to produce bio-mass at a desired particle size of less than 200mm[83]. To create the biochar, the powdered date seeds of uniform size was subjected a single-step slow pyrolysis procedure. 100g of the biomass sample was paralyzed in a muffle furnace at 500℃ for 4 hours in a nitrogen environment as a part of the pyrolysis technique to produce biochar [84]. The biochar was cooled in a muffle furnace until it reached room temperature and subsequently transferred into a desiccator for 15 minutes. Concurrently the biochar was collected from the muffle furnace and stored for future utilization in carbon activation processes. The mass yield was determined based on the final weight of the biochar.

$$\text{Mass yield\%} = \frac{mb}{mf} \times 100$$

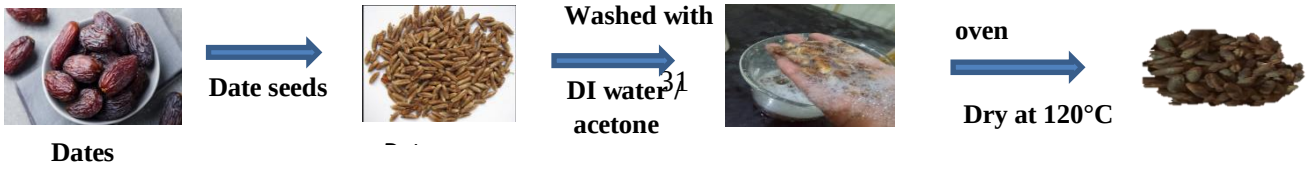

Figure 3.1: Synthesis of Biochar from Date Seeds.

3.3 Synthesis of Activated Carbon from Biochar

In the production of activated carbon, the thermochemical activation process was employed to enhance the porosity and surface area of the activated carbon. The process is shown in figure 3.2. A wet impregnation was conducted the biochar underwent impregnation with concentrated KOH at a weight-to-volume ratio of 1:1 dispersing in an aqueous solution of ethanol followed by stirring for 2 hours and subsequent filtration(83). Following the filtration process, the impregnated biochar was subjected to overnight drying in an oven set at 120℃[85]. This step was essential to remove excess moisture and prepare the material for subsequent processing steps[86]. After the drying process, the biochar underwent a high-temperature treatment to produce activated carbon for 4 hours in a muffle furnace within an inert nitrogen atmosphere, with a flow rate of 150cm^3/min at a temperature of 950°C[87]. The activated carbon obtained was subjected to a purification procedure involving treatment with hydrochloric acid (HCL) followed by rinsing with deionized water to adjust the pH to neutral levels. The washed product was subsequently dried in an air oven at 110℃ overnight to ensure it was thoroughly dried[88].

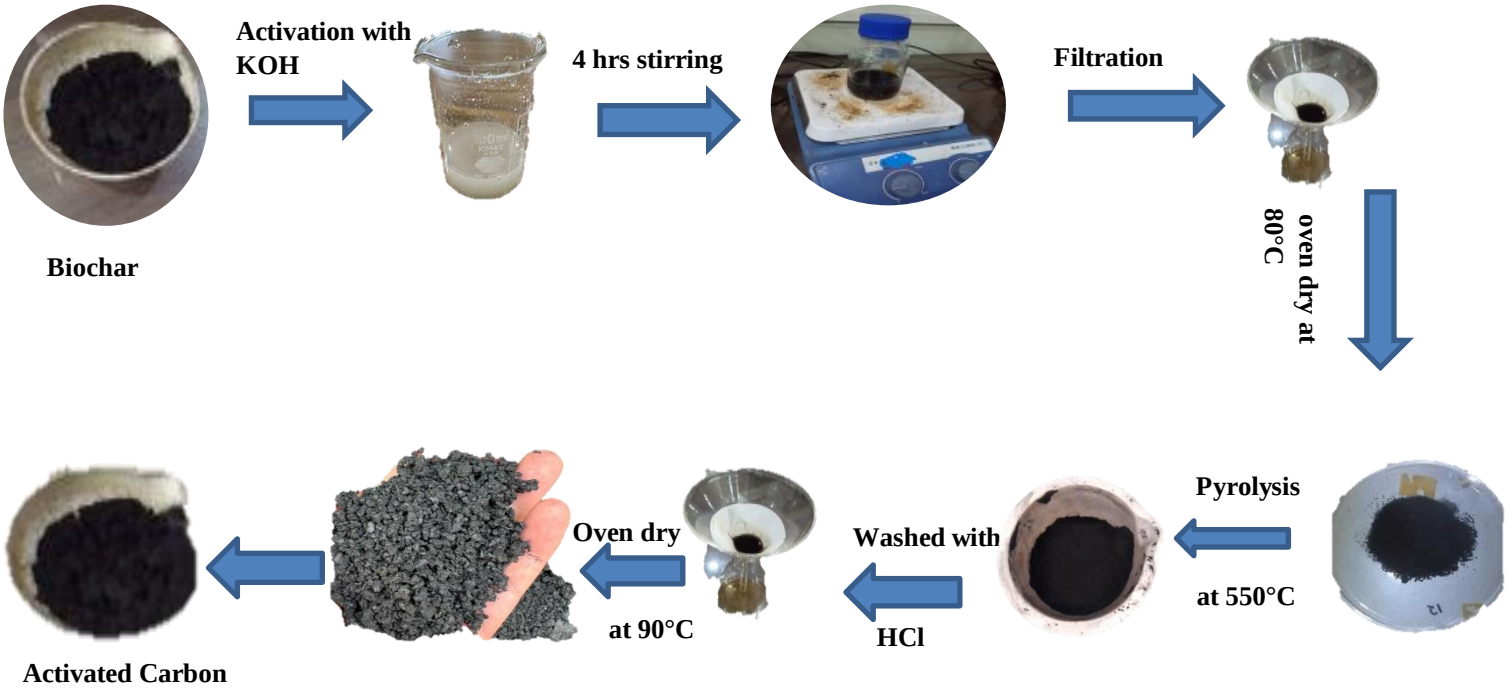

Figure 3.2 Synthesis of activated carbon from Date Seeds Biochar.

3.4 Modification of Activated Carbon

To enhance the stability of synthesized activated carbon nanoparticles and prevent agglomeration, surface modification was performed using polyvinyle triethoxysilane as a silane group attachment. 3 grams of activated carbon were transferred in a three-neck flask containing 175 mL of toluene and subjected to sonication for 45 minutes. Subsequently, 175 µL of the cross-link vinyltriethoxysilane was added dropwise under a nitrogen (N_2) atmosphere and stirred for 6 hours at a temperature of 65-70°C. After the reaction was complete, 45 mL of ethanol was added to dilute any unreacted pol vinyltriethoxysilane molecules. The particles were then separated from the solution by centrifugation at 12,000 rpm, washed with ethanol, and further washed with ultrapure water. Finally, the modified activated carbon was oven-dried at 80-90°C for 14 hours.

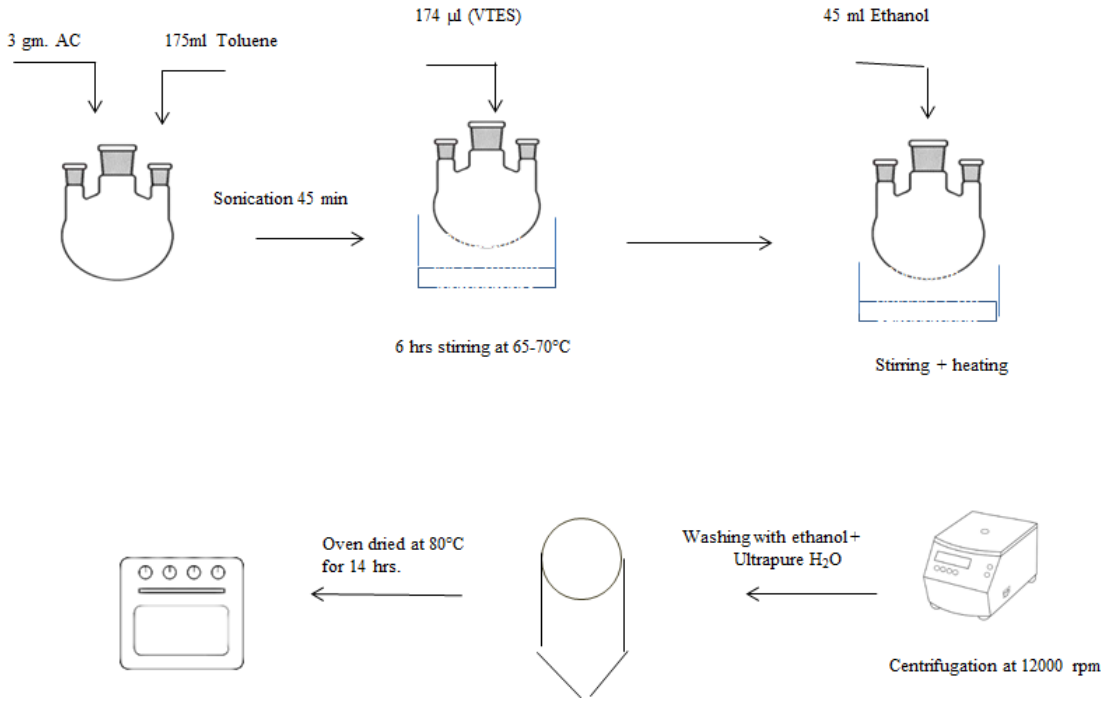

Figure 3.3 Modification of Date Seeds Activated Carbon

3.5 Synthesis of Pristine Membrane

The pristine CA/PAN membrane without filler was prepared by the Phase inversion method. To prepare a 23 weight percent dope solution, the polymer was dissolved in a DMF solvent. The compositions of the polymer and solvent r were carefully adjusted. To ensure uniform dispersion, the polymer was gradually dissolved in the solvent while being vigorously stirred for five hours at a temperature of 70 ℃. Once a homogeneous polymer solution was obtained, the casting solution was left at room temperature for 24 hours to remove any trapped air bubbles. As depicted in the figure, the membrane was fabricated by casting the dope solution onto a non-woven polypropylene support at a speed of 50 mm per second at room temperature, using an automatic film applicator (Electromer 4340). After casting, the membrane was allowed to dissipate for ten seconds. Phase inversion takes place when the fabricated membrane is immersed in a water bath, using water as a non-solvent, for 15 seconds while maintaining the bath temperature at 19℃. Following this process, the membrane was soaked in a 70/30 water and isopropanol mixture for 19 hours. To maintain the pore structure and integrity, it was then immersed in a glycerol solution for four hours. In the final stage, the membrane was completely dried at ambient temperature for 24 hours between two filter sheets [53,89].

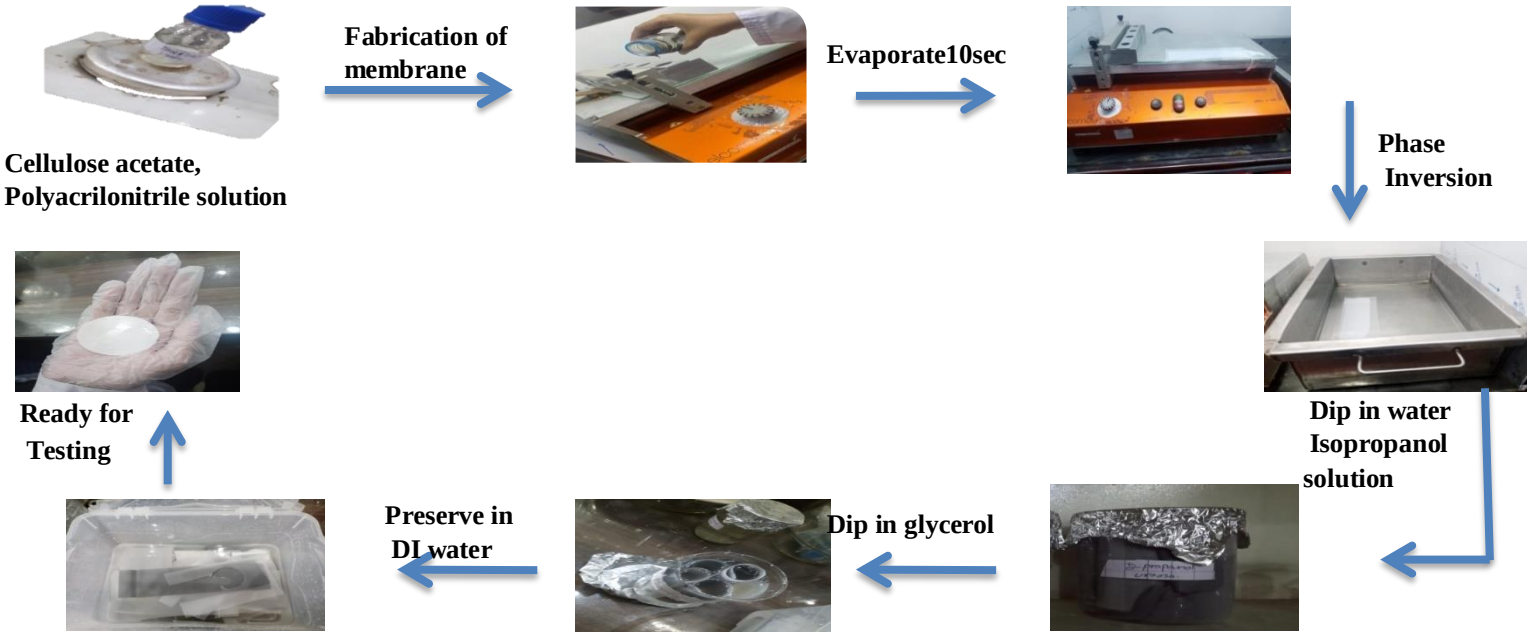

Figure 3.4 Fabrication of CA/PAN Pristine Membrane

3.6 Fabrication of mixed matrix nanocomposite membrane (MMNM's)

By adding particular concentrations of AC (0.5 weight percent, 1 weight percent, 2.5 weight percent, and 5 weight percent), AC-filled MMNMs were also created utilizing the phase inversion approach. The polymer was dissolved in a DMF solvent, with the solvent and polymer compositions adjusted, to create the final solution, which had a weight percentage of 23. To create a uniformly dispersed solution, the polymer was dissolved gradually in the solvent while being vigorously agitated for four to five hours at 65 to 70°C. AC nanoparticles were introduced separately to a brand-new reagent container that contained DMF solvent. To ensure an even dispersion, the nanoparticles were then continuously vigorously stirred into the solvent about four to five hours at 65 to 70°C. The nanoparticle solution and the polymer dope solution were then mixed together, and 2.5 weight percent of the pore former (PVP) was added. To ensure complete mixing, the entire solution was agitated throughout the night. After achieving a homogeneous polymer/nanoparticle solution, all trapped air bubbles were removed by letting the casting solution sit at room temperature for a full day. As shown in the figure, the membranes were subsequently created by casting the dope solution onto a non-woven polypropylene support at a rate of 40–60 mm per second using an automatic film applicator (Electrometer 4340). The membranes were left to evaporate for ten seconds after casting.

Using water as a non-solvent, the manufactured membranes were immersed in a water bath for 10–15 seconds to achieve phase inversion, while the bath temperature was kept at 18–19°C. Following this procedure, the membranes were submerged for 19 hours in a 70/30 water and isopropanol mixture. They were then submerged in a glycerol solution for four hours to preserve the integrity of the pore structure. The membranes were finally allowed to dry completely by being placed between two filter sheets and left at room temperature for a full day.

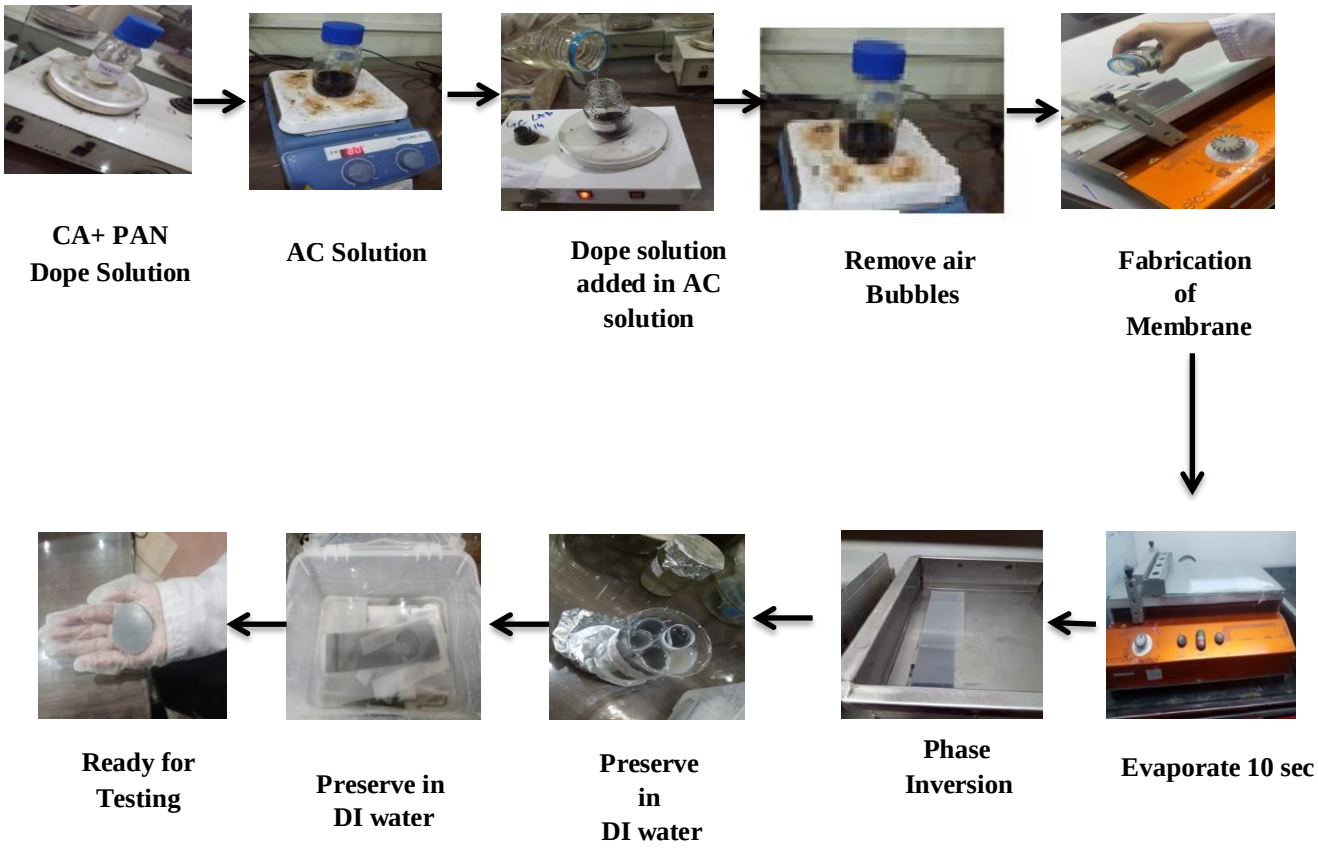

Figure 3.5 Fabrications of Mixed Matrix Nanocomposite Membranes

Table 3.1 Composition of Prepared Membranes.

Membrane	CA/PAN (w %)	PVP (w %)	AC (w %)	DMF (w %)
M	30/10	10	0	50
MAC1	30/10	10	0.5	49.5
MAC2	30/10	10	1	49
MAC3	30/10	10	2.5	47.5
MAC4	30/10	10	5	45

3.7 Testing of Membranes:

The membranes were subsequently evaluated using a dead-end filtration system. The schematic diagram of the testing setup is given below.

3.7.1 Working of Dead-End Filtration System

A dead-end filtration cell was employed to assess the membrane's performance under the appropriate pressure conditions. The key performance indicators for the membrane included water flux and salt rejection, along with tests for anti-fouling and dye rejection.

To determine the pure water flux across the membrane at the designated pressures, distilled water was used as the feed solution. The membrane's salt rejection capability was evaluated using NaCl and $MgSO_4$ solutions. These solutions were prepared by dissolving 1 g of each salt in 1000 ml of distilled water before initiating the salt rejection test. For the anti-fouling test, a standard Bovine serum abumin (BSA) solution was prepared by dissolving 1 g of BSA in 1000 ml of distilled water, The procedure for testing membranes using the dead-end filtration method involved the following steps:

1. The membrane was cut into a circular shape to fit the membrane coupon of the dead-end filtration cell.
2. The circular membrane was then placed inside the dead-end filtration cell (Sterlitech HP 4950, USA).
3. The cell was filled with 250–300 ml of the feed solution, and the assembly was securely fastened. Nitrogen gas was introduced into the cell by opening the valve and adjusting the pressure using a pressure gauge until dropwise permeation was achieved. The stirring speed was set to 500 rpm. To ensure stability, the membrane was allowed to compact under the specified pressure condition, and any collected permeate during this stabilization phase was discarded.
4. For the dye rejection test, the permeate was collected in UV spectroscopy tubes for analysis using UV spectroscopy.

Once the system reached a steady state, a glass vial was attached to the setup to collect the permeate, and the time taken to fill the vial was recorded. The pure water flux, fouling indexes, and salt rejection were calculated using the relevant formulas.

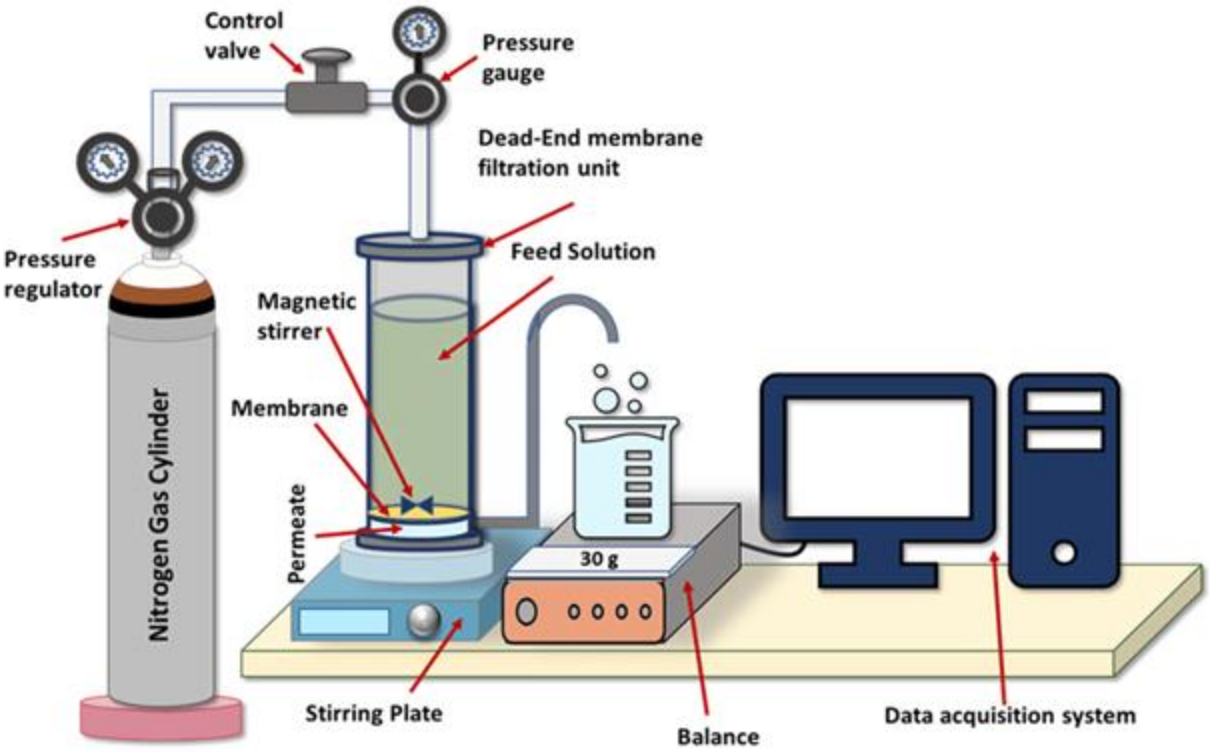

Figure 3.6 Working of Dead end cell

3.7.2 The Pure Water Flux (PWF)

The pure water flux was measured at room temperature following membrane compaction. Water permeance was calculated using the formula provided in Equation 1, as described in the literature [92].

$$J = \frac{v}{\Delta t . A_{eff} . \Delta P} \text{ ------ eq 1}$$

Where,

J = PWF ($LMHbar^{-1)}$

V= volume of permeate (L)

Δt = Time (hrs)

A_{eff} = active area of membrane ($m^{2)}$

Δp = applies pressure (bar)

3.7.3 Porosity and Mean Pore Radius

The porosity of the fabricated membranes was determined using the gravimetric method, as described in the literature.

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times l \times d_w} \text{ ---- eq 2}$$

Where,

ε = porosity and mean pore radius of the membrane

ω_1 = weight of wet membrane

ω_2 = weight of dry membrane

A = area of membrane (m_2)

d_w = water density (998 kg/m^3)

l = thickness of membrane

The mean pore radius was calculated using Equation 3, based on pure water flux and porosity data, as reported in the literature [93].

$$r_m = \sqrt{(2.9 - 1.75\varepsilon) 8\eta Q / \varepsilon \times A \times \Delta p} \text{ ----- eq3}$$

Where,

η = viscosity of water

Q = volume of permeated pure water per unit time (m3/s)

Δp = pressure

3.7.4 Salt Rejection

To evaluate the membrane's selectivity, different salts such as NaCl and $Ni(NO_3)_2 \cdot 6H_2O$ were used as feed solutions. Salt rejection was tested using 4000 ppm solutions of the aforementioned salts, which was passed through the synthesized membranes at a pressure of 6 bars. A conductivity meter was employed to measure the salt concentrations in both the feed and permeate solutions. Rejection was calculated using Equation 4, as reported

in the literature[94].

$$R\ (\%) = \left(1 - \frac{Cp}{Cf}\right) \times 100 \text{ ----- eq4}$$

Where,

Cp = concentration of salt in permeate

Cf = concentration of salt in fee

R = salt rejection

3.7.5 Dye rejection

Membrane dye rejection tests were conducted using methylene blue, Congo red, and rose Bengal. Each dye was prepared in a 30-ppm solution and used as the feed solution. These solutions were passed through the membranes at a pressure of 6 bars and room temperature. The concentrations of the dyes in both the feed and permeate solutions were analyzed using a UV spectrophotometer. The flux and rejection rates were calculated using Equations 1 and 4, respectively. The dye that showed the highest rejection was then used to test the stability of the best-performing membrane, as identified in the literature[95]. This stability test involved running the filtration process for 36 continuous hours, during which the dye solution flux and dye rejection were measured every 2 hours.

3.7.6 Anti- Fouling Property

The anti-fouling properties of the fabricated membranes were evaluated using bovine serum albumin (BSA) as the fouling agent at a concentration of 1000 ppm. The experiments were conducted at room temperature under a pressure of 8 bars[96]. For this test, the pure water flux (PWF) was initially determined by passing distilled water through the membrane to stabilize the system. Five cycles of PWF measurements were then conducted over 100 minutes, with each cycle lasting 20 minutes. Subsequently, five cycles of bovine serum albumin (BSA) solution flux were measured over the next 100 minutes, also at 20-minute intervals. The membranes were then washed with deionized (DI) water for 30 minutes to facilitate recovery. Finally, an additional five cycles of PWF measurements were performed over the subsequent 100 minutes the flux recovery ratio was calculated by equation 5. For reversible, irreversible, and total fouling EQ. 7,8,6 were used as reported in [92, 97].

$$F.R.R\ (\%) = \frac{JW.2}{JW.1)} \times 100 \text{------- eq5}$$

$$T.F.R = \left(1-\frac{JP}{JW.1}\right) \times 100 \text{ ------ eq6}$$

$$R.F.R = \left(\frac{jw-jw12}{jw1}\right) \times 100 \text{ ----- eq7}$$

$$IR.F.\ R = (T.F.R-R.F.\ R)\text{----} \quad \text{eq8}$$

Where

JW1 = Pure Water Flux

Jw2 = Flux of BSA

Up = Pure Water Flux after 30 minutes of washing

F.R.R = Flux Recovery Ratio

T.F.R or Rt = Total Fouling Ratio

R.F.R or Rr = Reversible Fouling Ratio

IR.F. R or Rir = Irreversible Fouling Ratio

3.8 Characterization Techniques

Various characterization methods were employed to determine and validate the properties of the samples. The specific characterization techniques used are as follows:

3.8.1 Fourier Transform Infrared Spectroscopy

The study aimed to examine the interactions and reactions between polymer chains and chemical bonds that are compatible with the polymers, pore formers, and fillers [98]. The analysis was conducted using a Thermo Scientific Nicolet 6700 (Thermo Fisher, USA). FTIR spectra for both neat and mixed matrix nanocomposite membranes were recorded with 128 scans, covering a wavelength range of 4000 to 650 cm^{-1}, and a resolution of 8 cm^{-1}.This analysis verifies the presence of impurities, such as solvents and nonsolvent. The sample dimensions are 1 × 1 cm^2. FTIR was employed to identify the various functional groups present in activated carbon (AC), pristine samples, and mixed matrix nanocomposite membranes (MMNMs).

3.8.2 X-Ray Diffraction Spectroscopy (XRD)

The crystallinity of the samples was analyzed using X-ray diffraction (XRD) techniques[99]. This approach is essential, as the performance of the synthesized particles is heavily influenced by XRD results. The crystalline structure significantly affects properties such as the electronic band structure, which is associated with the catalyst surface characteristics. The peaks obtained were closely matched with documented literature, confirming the purity of the samples. In this study, activated carbon (AC), pristine, and fabricated mixed matrix nanocomposite membranes (MMNMs) were characterized using XRD.

3.8.3 Scanning Electron Microscopy

SEM analysis was used to investigate the morphology, as well as the cross-sectional and surface structures of both neat and composite membranes with varying nanoparticle concentrations [100]. SEM images were obtained using a Scanning Electron Microscope (Inspect S-50, Thermo Fisher Scientific, USA) operating at 12.5 kV. The flat-sheet nanocomposite membranes were cut into 0.25 × 0.25 cm^2 pieces, frozen in liquid nitrogen, carefully fractured to expose the cross-sectional structures, mounted on blocks, and then coated with a thin gold layer via sputtering before analysis.

3.8.4 Contact Angle Measurement (CA)

The sessile drop method was used to measure the membrane surface contact angle in order to assess the hydrophilicity of composite membranes as well as the effects of pore formers and nanoparticles (NPs). Deionized (DI) water droplet measurements at three different sites on each sample are averaged to provide the stated contact angle results. Over time, lateral images of the droplet profile were captured by a camera with a high resolution system[53].

CHAPTER 4

RESULTS

In this chapter, the experimental results obtained from various analyses of the composite membranes are presented and discussed. The primary aim of these investigations was to evaluate the structural, chemical, and performance characteristics of the membranes in relation to their composition, including the incorporation of nanoparticles and pore former.

4.1 Fourier Transform Infrared Spectroscopy Result of Date Seed Activated Carbon:

An FTIR spectrum was collected to analyze the surface chemistry of the activated carbon (AC) particles. The infrared (IR) spectrum (Figure 4.1) reveals the presence of various functional groups in the AC. The characteristic absorption peaks were identified and compared with existing literature to confirm the associated functional groups. The FTIR spectra showed broad absorption bands, indicating the presence of oxygen-containing functional groups, such as hydroxyl, carboxyl, and carbonyl groups, on the sample surfaces. These include the C-O stretching of carboxyl or carbonyl groups at 1727 cm^{-1}, C-O-(C) stretching at 1264 cm^{-1}, and C-O-(H) stretching at 1020 cm^{-1}. The absorption peak at 3359 cm^{-1} is associated with hydroxyl groups, reflecting O-H stretching vibrations from intermolecular hydrogen bonding in compounds like alcohols, phenols, and carboxylic acids. Additionally, alkyl C-H stretching vibrations are observed at 2959 cm^{-1}[86].

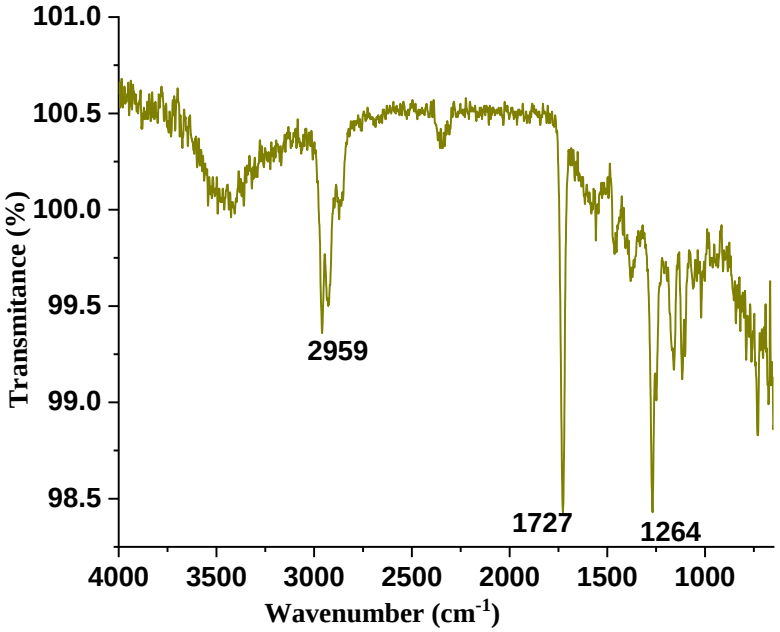

Fig 4.1 Fourier Transform Infrared Spectra of Date Seed Activated Carbon

4.2 X-ray Diffraction Analysis of Date Seed Activated Carbon:

The XRD patterns of the activated carbon (DSAC) shown in Figure 1 reveal distinct diffraction peaks at 25° and a subtle peak at 45°, corresponding to the (002) and (100) crystal planes, respectively, indicative of a graphitic structure. The crystallinity of DSAC is measured at 14.4%, suggesting that the KOH-treated activated carbons (ACs) exhibit an amorphous or semi-crystalline nature. Consistent with previous studies [47,48], activated carbon generally displays an amorphous structure. According to Mohammad et al., activated carbon comprises a disordered microcrystalline structure with randomly oriented graphitic microcrystals [49]. Many researchers also describe activated carbon as an amorphous material with a high surface area and significant porosity [9,10,11].

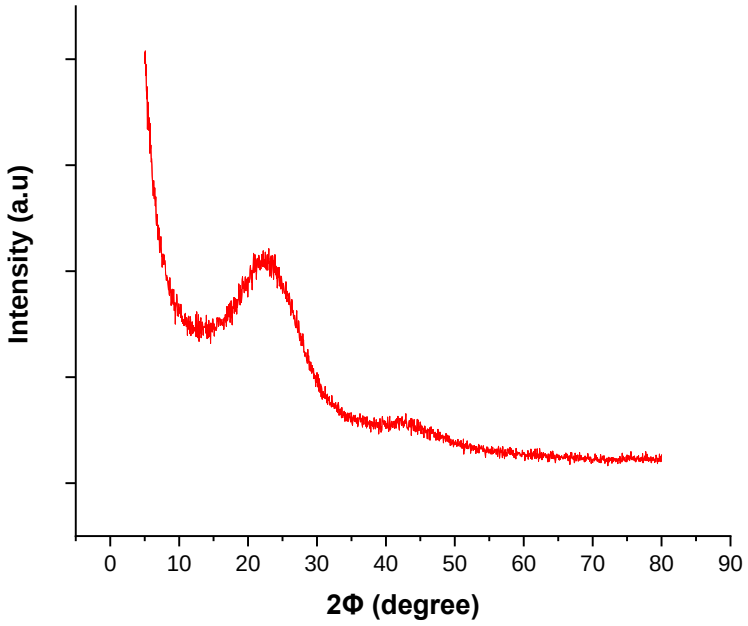

Fig 4.2 X-ray Diffraction Spectra of Date Seed Activated Carbon

4.3 Fourier Transform Infrared Spectroscopy Results of Membranes:

FTIR Spectrum for neat and activated carbon-filled mixed matrix Nano composite membranes (Figure 4.2). The spectra indicate the presence of activated carbon, cellulose acetate, polyacrylonitrile, and PVP within the membrane structures. The peak observed at 1036 cm^{-1} is characteristic of the C-O-C stretching, which is indicative of the presence of activated carbon. The spectrum reveals a strong peak at 1233 cm^{-1}, associated with the cyclic C-O-C and ether group stretching vibrations found in both cellulose acetate and activated carbon [102]. The peak at 1632 cm^{-1} is clearly linked to the C=C stretching of mono-substituted alkenes in cellulose acetate. A peak at 1742 cm^{-1} corresponds to the carbonyl (C=O) group present in both cellulose acetate and activated carbon. For all membranes, the characteristic peaks for O-H and C-H stretching vibrations were observed at 3356 cm^{-1} and 2945 cm^{-1}, respectively [103].

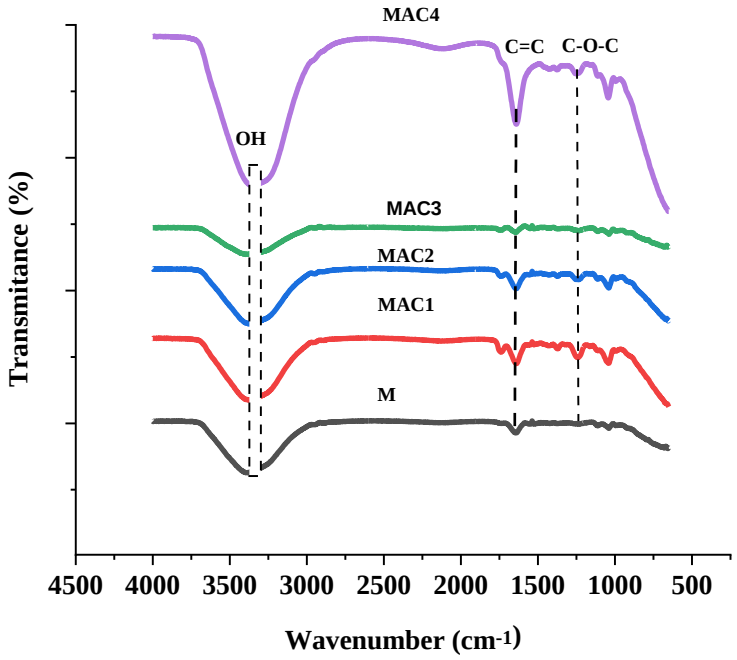

Figure 4.3 Fourier transform infra-red spectrum of CA/PAN Mixed Matrix Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5% AC),MAC4 (5%AC) .

4.4 Contact Angle Measurement:

The contact angles of the membranes were measured to assess their hydrophilicity. This serves as an indirect assessment and a key parameter. The hydrophilicity of the M-MAC4 composite membranes was determined using the sessile drop method. The contact angles were measured five times, and the average values for the synthesized membranes (Figure 4.4). The highest contact angle was observed for M, indicating the membrane's lowest hydrophilic properties. The composite membrane exhibited a lower contact angle compared to the M membranes. Furthermore, the contact angle decreased from 54° to 19° as the activated carbon content increased from 0.5 wt.% to 5 wt.%, indicating an enhancement in hydrophilicity[107]. Surface hydrophilicity is a crucial factor in achieving higher flux and permeation rates in nanocomposite membranes, as it can significantly influence flux[108]. A lower contact angle signifies a more hydrophilic membrane surface. The M membrane exhibited the highest water contact angle, measured at 54 ± 3.2 degrees. Increasing the activated carbon content beyond 2.5 wt.% did not improve hydrophilicity, as this led to the aggregation of activated carbon[109].

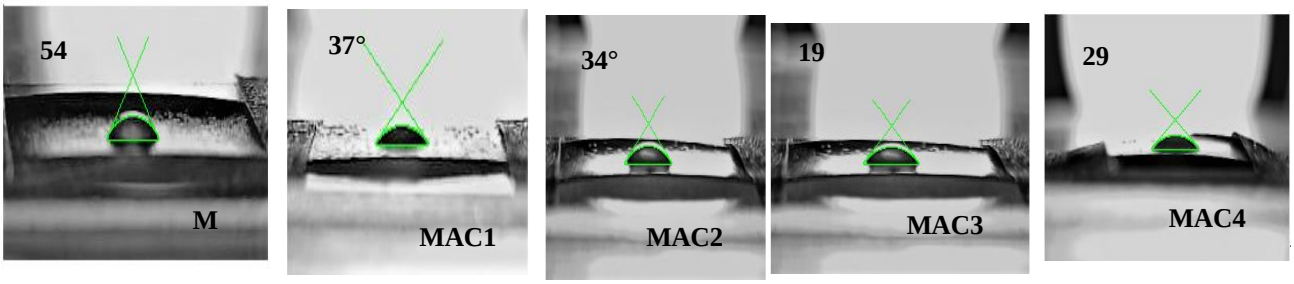

Figure 4.5 Contact angles Of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

4.5 Water Flux:

The water flux of pristine as well as activated carbon filled Nano filtration membranes (Figure 4.5). The M membrane exhibits the lowest pure water flux (PWF) at 62.8. While the membranes of 0.5wt%, 1wt%, 2.5wt%, and 5wt% of activated carbon show the PWF of 75.4, 89.6, 97.5, and 78$Lm^{-2}h^{-1}$ respectively. The water flux progressively increases as the activated carbon content rises up to 2.5wt%. The hydrophobicity of activated carbon facilitates the absorption of water molecules onto the membrane's surface, leading to the formation of a water layer. This preferential absorption of water molecules over other substances decreases the membrane's mass transfer resistance and consequently enhances the water flux [110]. However, the pure water flux significantly decreased when the activated carbon content in the membrane exceeded 5wt%. This reduction in flux can be attributed to the increased viscosity of the casting solution, which leads to a slower phase inversion process. In other words, a high filler loading obstructs the membrane pores, reduces the roughness of membranes, and reduces the average pore size[111].

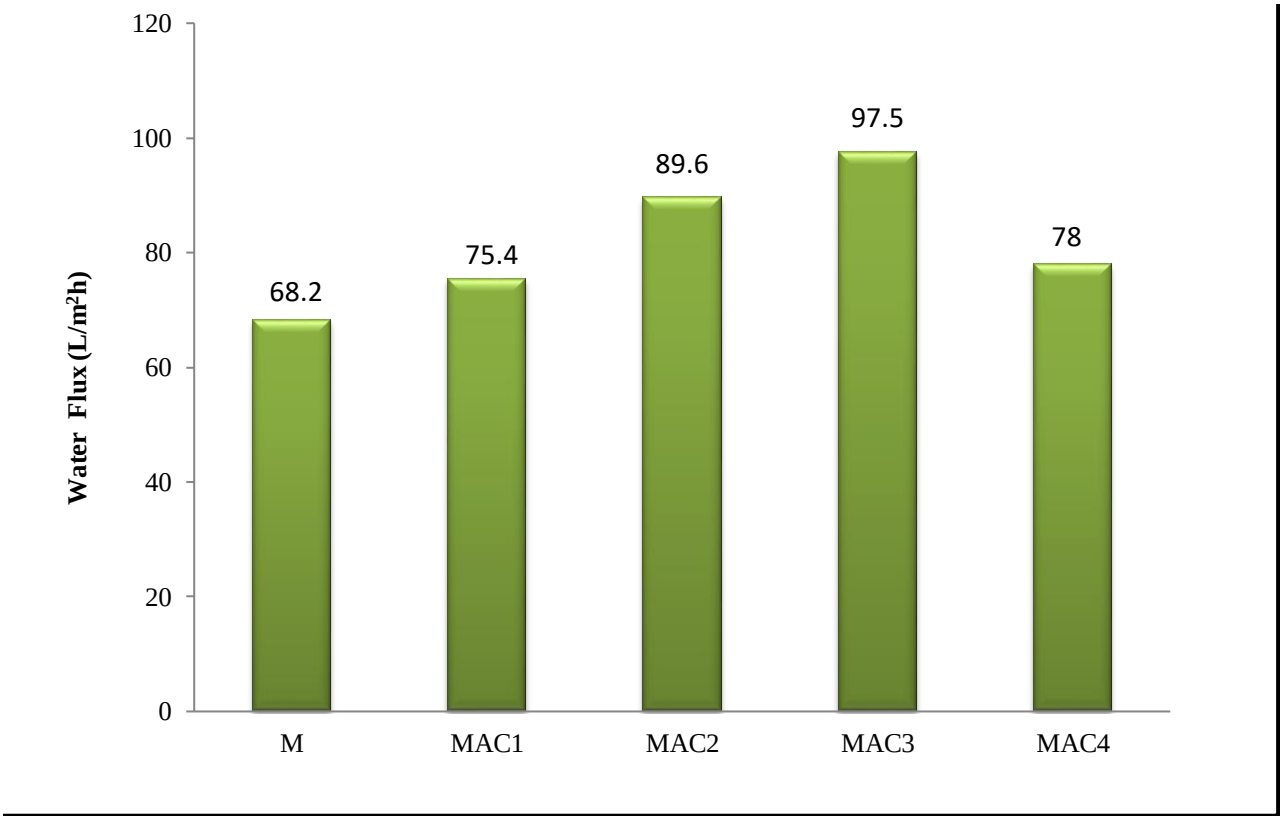

Figure 4.6 Water Fluxes of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

4.6 Salt Rejection:

The salt rejection performance of both Pristine and AC-filled MMNMs (Figure 4.6a, 4. 6b). In this study, monovalent (NaCl) and bivalent ($MgSO_4$) salts were used to evaluate the membranes' selectivity. The figures reveal that increasing the AC content up to 2.5 wt. % enhances the membranes' selectivity towards salts. However when the AC content is further increased from 2.5wt% to 5wt%, the selectivity for both salts decreases. The observed rejection behavior suggests that the synthesized Nanofiltration membranes are negatively charged, leading to stronger repulsion of divalent anions compared to monovalent anions. This trend aligns with the Donnean exclusion principle, which is widely recognized as the primary mechanism for salt rejection in NF membranes[112].

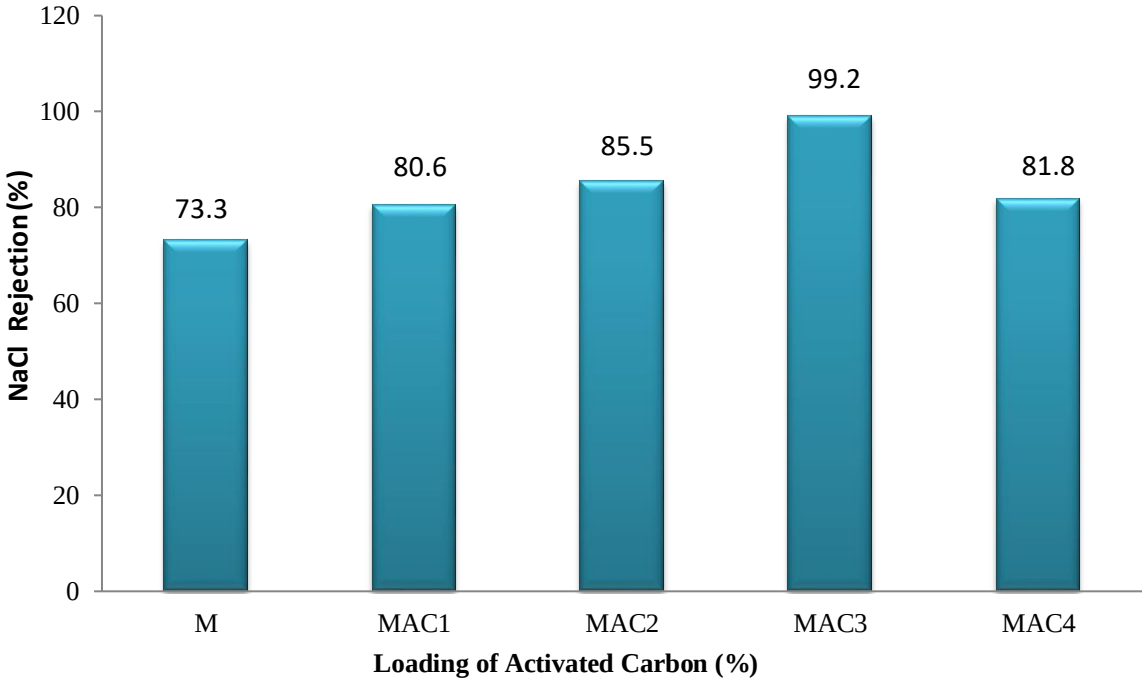

Figure 4.7 NaCl Rejections of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC),MAC3 (2.5%AC), MAC4 (5%AC).

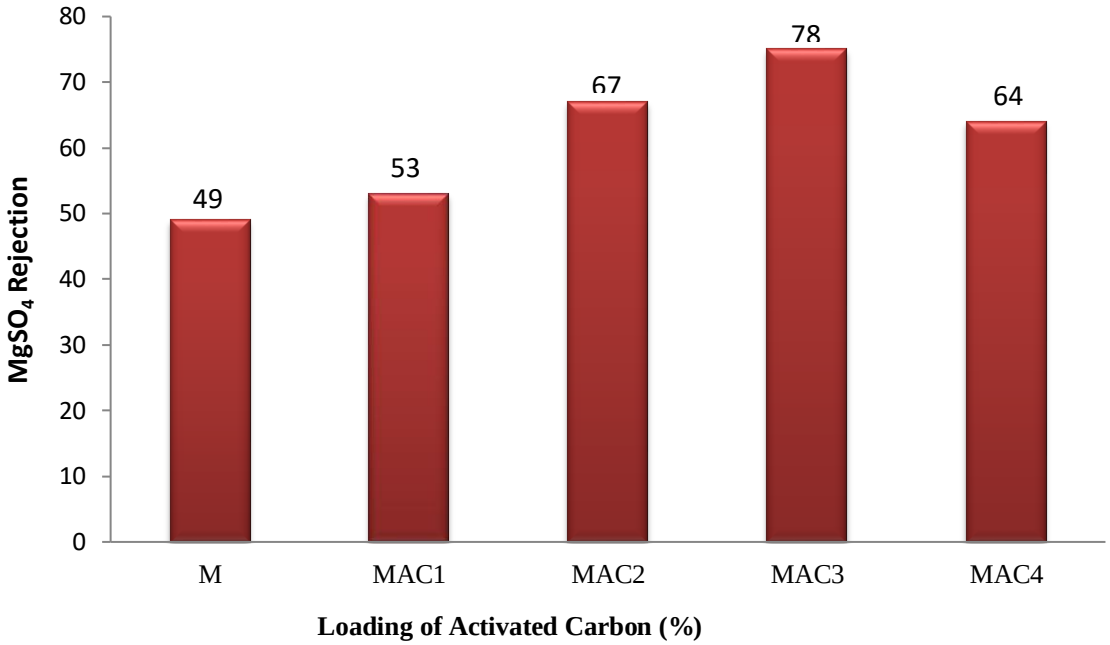

Figure 4.8 $MgSO_4$ Rejections of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC) .

4.7 Porosity and Mean Pore Radius:

The porosity and mean pore radius of the membranes were determined using Equation (1) and (2). The changes in porosity and mean pore radius with varying activated carbon concentrations for different membranes (Figure 4.7 and 4. 8). In conclusion, the addition of filler has led to an increase in both the porosity and the average pore radius of the membranes, which in turn enhances the pure water flux compared to the unmodified membrane. As documented in the literature, activated carbon has also been utilized as an orogen due to its porous structure, which enhances the porosity of modified Nanofiltration membranes[113]. The porosity and mean pore radius decrease when the concentration of activated carbon exceeds 5wt %. This could be due to the increased viscosity of the polymer solution, which results in slower phase inversion and the formation of fewer pores and smaller pore sizes [114]. In other words, the reduction in porosity and average pore radius can be attributed to the agglomeration of activated carbon within the polymer matrix, which leads to pore blockages and consequently decreases both porosity and mean pore radius [115]. As the loading of activated carbon increases, the pore size distribution of the MMMs tends to broaden. This is primarily due to the introduction of AC particles, which can create additional voids in the membrane structure. At lower loadings(0.5wt%) the distribution may remain relatively narrow, but as loading increases, from 0.5-2.5wt%) the presence of larger AC aggregates can lead to a wider range of pore sizes. Within this range, the membranes exhibit enhanced permeability while maintaining a desirable pore size distribution for effective separation processes. Beyond this optimal loading, the pore structure may become less uniform, leading to a decrease in performance due to excessive agglomeration of AC particles. Research indicates that an optimal range of AC loading exists, typically between 0.5-2.5 wt%.This indicating that the choice of AC can also significantly influence the overall membrane performance.

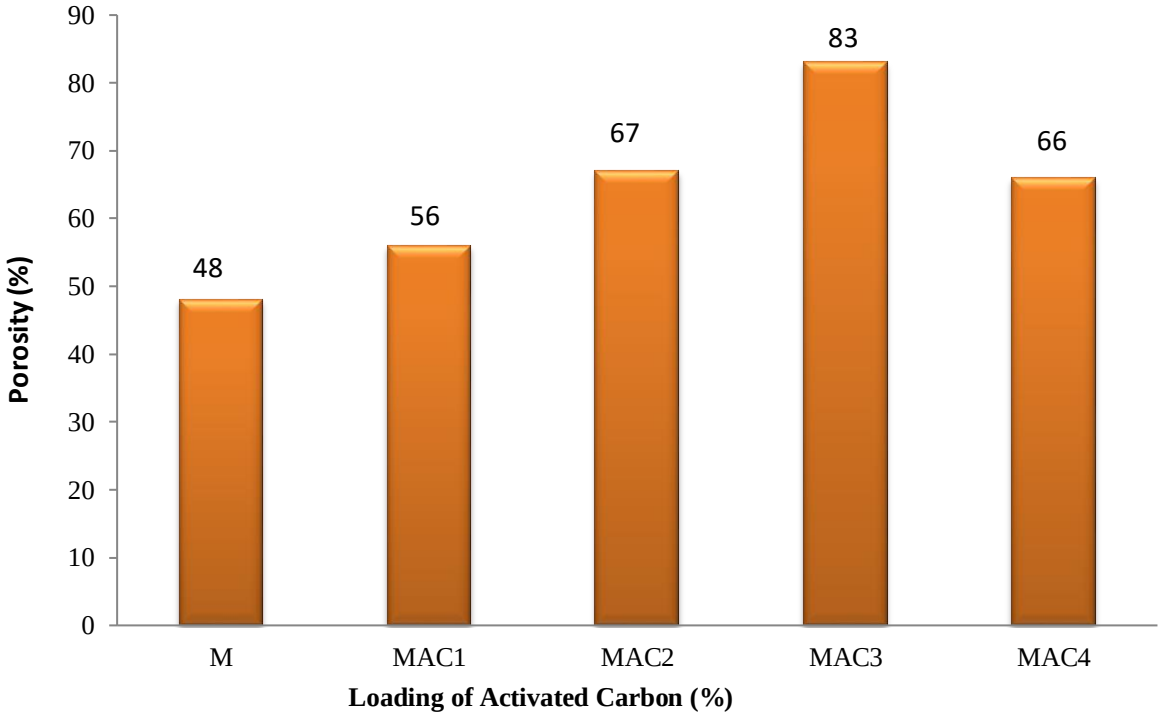

Figure 4.9 Porosity Analysis of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

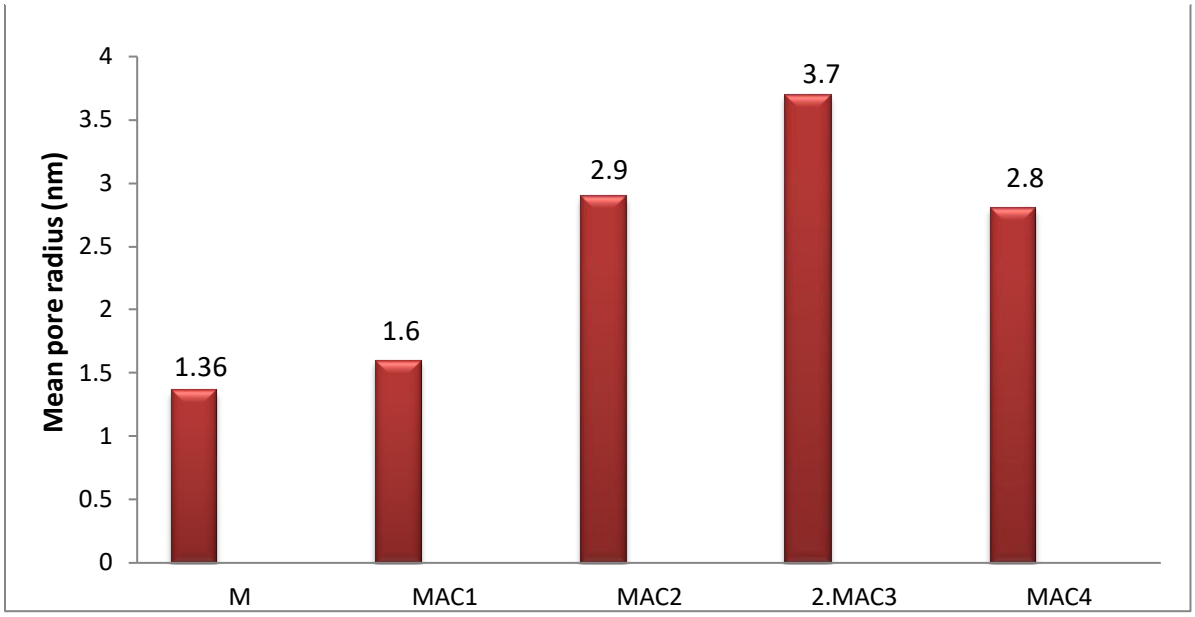

Figure 4.10 Mean Pore Radius of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC, MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

4.8 Water Uptake Analysis:

At room temperature, the water uptake of the membranes was analyzed. The fully dried membrane samples were first weighed, then immersed in distilled water, and weighed again after 24 hours. The water filtration performance of a composite membrane is directly influenced by its water uptake capacity. It was observed that as the concentration of activated carbon (AC) particles increased up to 2.5 wt%, water uptake also increased; however, beyond this concentration, the water uptake began to decrease as the AC content continued to rise. The water uptake values for membranes with neat to 5 wt% AC (Figure 4.8). Initially, water uptake increased with the rise in AC content, and then declined to approximately the same level as the pristine membrane. This initial increase is strongly associated with the membrane's hydrophilicity. The higher water uptake at increased AC concentrations can be attributed to strong interactions between the pore former, the polymer matrix, and the AC filler, which likely restrict polymer chain mobility and reduce the free volume within the polymer matrix. Additionally, the water absorption of the composite membrane increases with a temperature rise [116]. A membrane with 2.5 wt% AC loading exhibited the highest water uptake capacity at 75.66%. However, further increasing the AC concentration to 5wt% may lead to a

decrease in water uptake capacity. This reduction is likely due to the agglomeration of AC nanoparticles at higher concentrations, which significantly diminishes the effective hydrophilicity of the AC particles[117, 118].

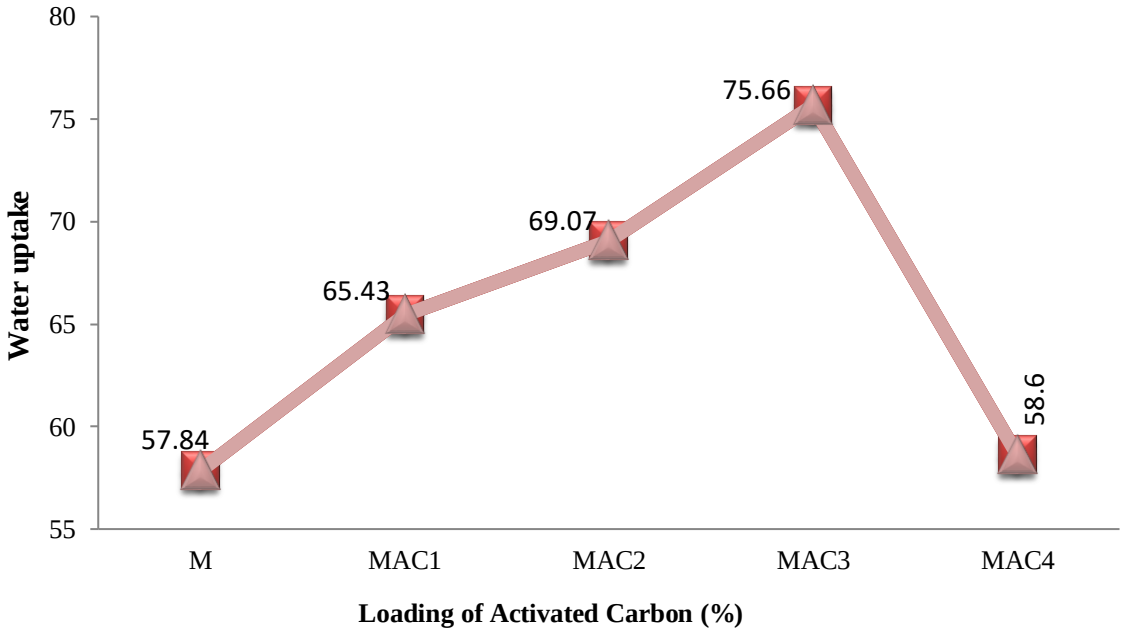

Figure 4.11 Water Uptake Analysis of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

4.9 Fouling Test:

Cake layer formation and concentration polarization are two of the most significant challenges encountered in membrane separation processes. These phenomena directly impact the membrane surface, leading to a decline in membrane performance by obstructing the pores. Consequently, this not only reduces the efficiency of the membrane but also shortens its operational lifespan[119]. The antifouling properties of AC-filled MMNMs were examined in this study using a 1000 ppm BSA protein solution. Since BSA molecules are larger than the membrane pores, they were unable to penetrate and instead caused biofouling on the membrane surface. The antifouling efficiency of the neat CA/PAN membranes and the AC-filled MMNMs was assessed by measuring the water flux recovery ratio (FRR) after exposure to the BSA solution. (Figure 4.9b) presents these

findings. The FRR of the neat CA/PAN membrane was 65.3%, whereas the FRR of the 2.5 wit% AC-filled membrane was 91.4%, demonstrating that the AC-filled CA/PAN membranes significantly outperformed the unmodified CA/PAN membranes in antifouling performance. It is widely recognized that a higher FRR and a lower total fouling ratio (Rt) are indicative of superior antifouling properties[120]. The total fouling ratio (Rt) of the neat membrane was 75%, while that of the 2.5 wet% AC-filled membrane was 60%, indicating that the unmodified membrane had inferior antifouling properties. Moreover, the irreversible fouling ratio (Rir) of the membranes decreased significantly from 56% for the neat membrane to 15% for the 2.5 wet% AC-filled membranes. These results indicate that the AC-filled MMNMs with 2.5 wet% AC loading exhibit excellent antifouling capabilities.

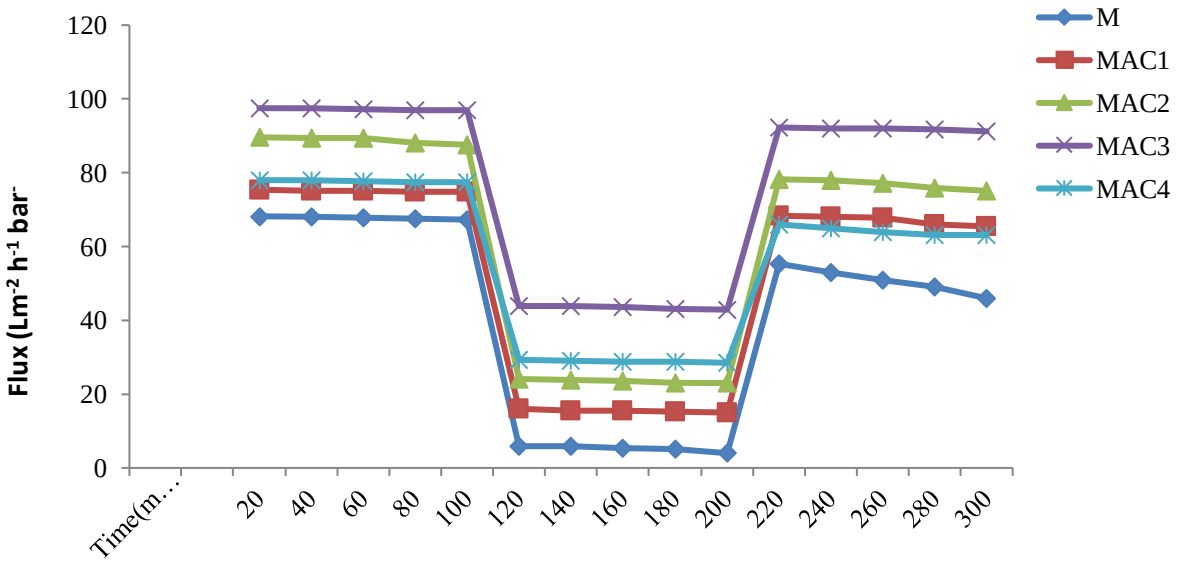

Figure 4.12 Flux for Fouling analysis of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

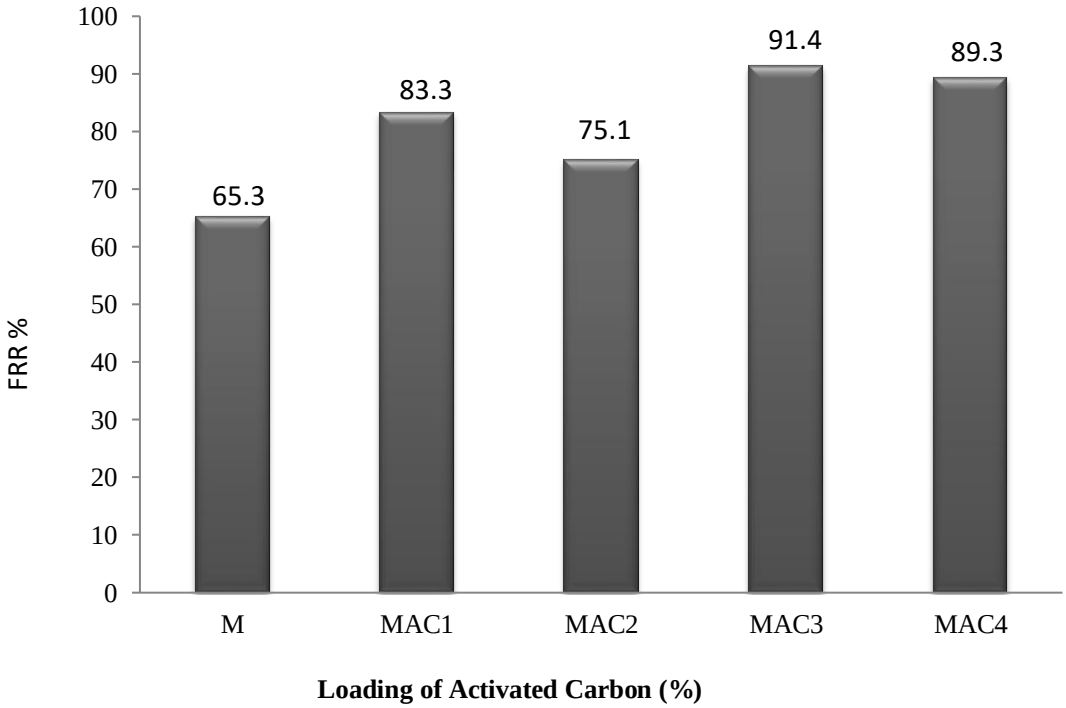

Figure 4.13 Flux Recovery Ratios of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

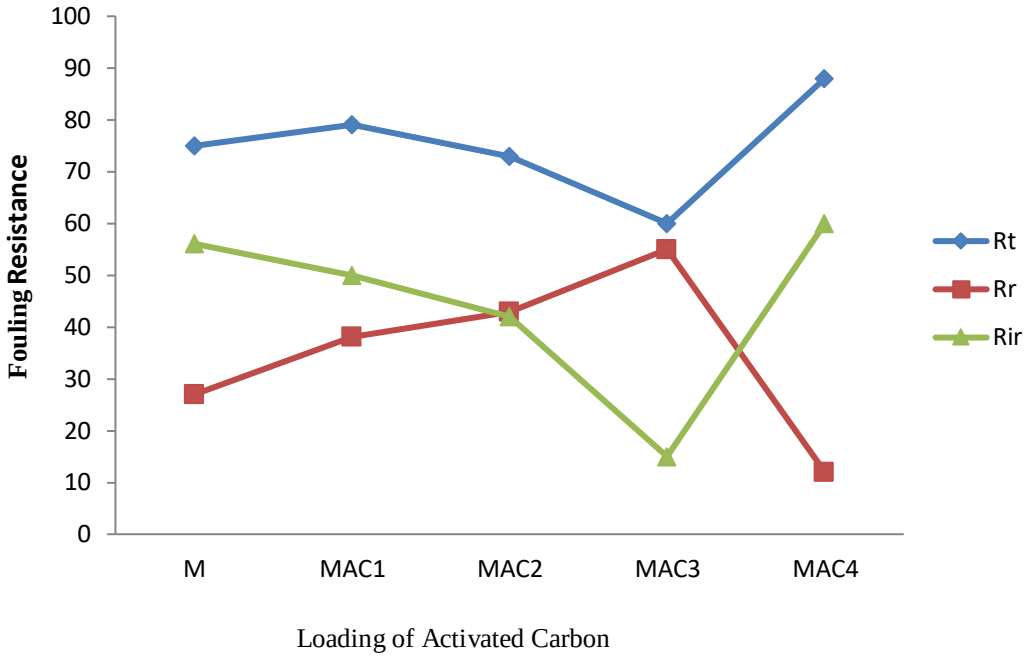

Figure 4.14 Fouling Resistance of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

4.10 Dye Rejection:

Three different dyes—methylene blue, Congo red, and rose Bengal—were selected, each with distinct molecular weights of 373, 696, and 1017 g/mol, respectively, to assess the separation performance of nanofiltration (NF) membranes. This study aimed to explore the effectiveness of pristine membranes and activated carbon (AC)-filled mixed matrix nanocomposite membranes (MMNMs) in treating textile dye wastewater. Methylene blue carries a positive charge, while both Congo red and rose Bengal are negatively charged. The dye permeation flux and rejection rates for the NF membranes tested (Figure 4.10 a,b,c). All modified NF membranes exhibited an overall increase in flux and higher retention compared to the unmodified (neat) NF membranes. At a concentration of 2.5 wet%, the rejection rates for methylene blue, Congo red, and rose Bengal were 94%, 96%, and 99.8%, respectively, with corresponding permeate fluxes of 87%, 68%, and 59%. The graphs indicate that the dye with the lowest molecular weight exhibited the highest flux but the lowest rejection among all the dyes tested. Conversely, the dye with the highest molecular weight showed the lowest flux and the highest rejection. As the AC loading increased from 0.5 to 2.5 wet%, a decrease in rejection was observed. The enhanced dye rejection with increasing molecular weight could be attributed to the larger size of the dye molecules relative to the pores of the cellulose acetate (CA)-based membranes resulting in the dye retention by the membranes. This effect can be attributed to the interaction between the dye molecules and the well-dispersed AC particles[121]. The lower rejection of the positively charged methylene blue (MB) is likely due to its smaller molecular size (373 g/mol), which diminishes the size exclusion effect.

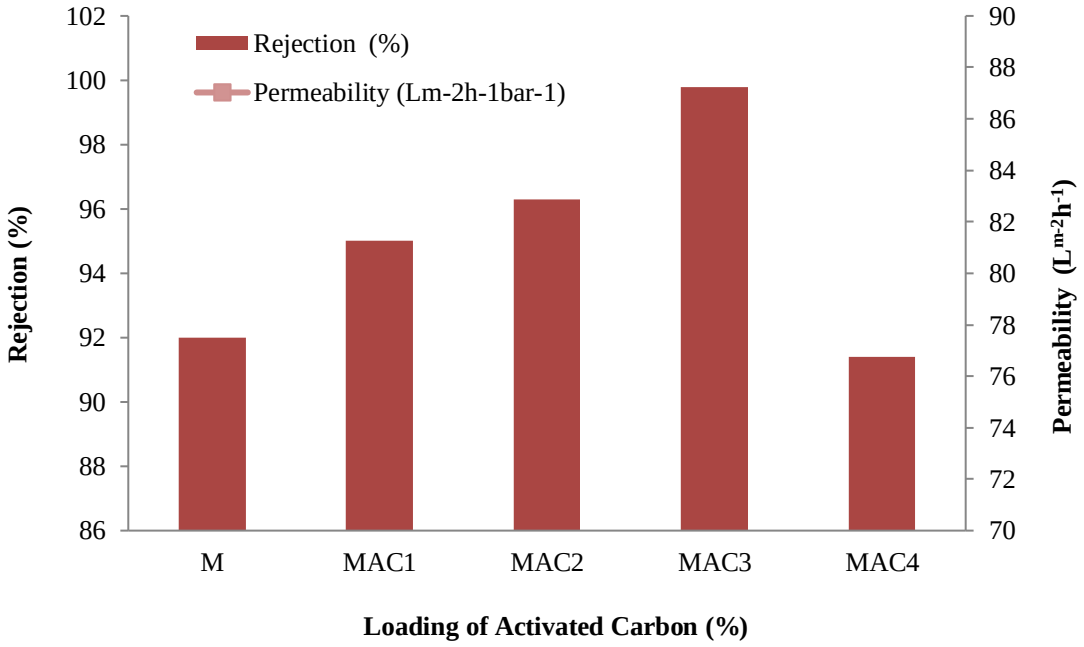

Figure 4.15 Methylena Blue Dye Rejection of CA/PAN Mixed Matrix Membranes M 90%AC), MAC1 (1%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

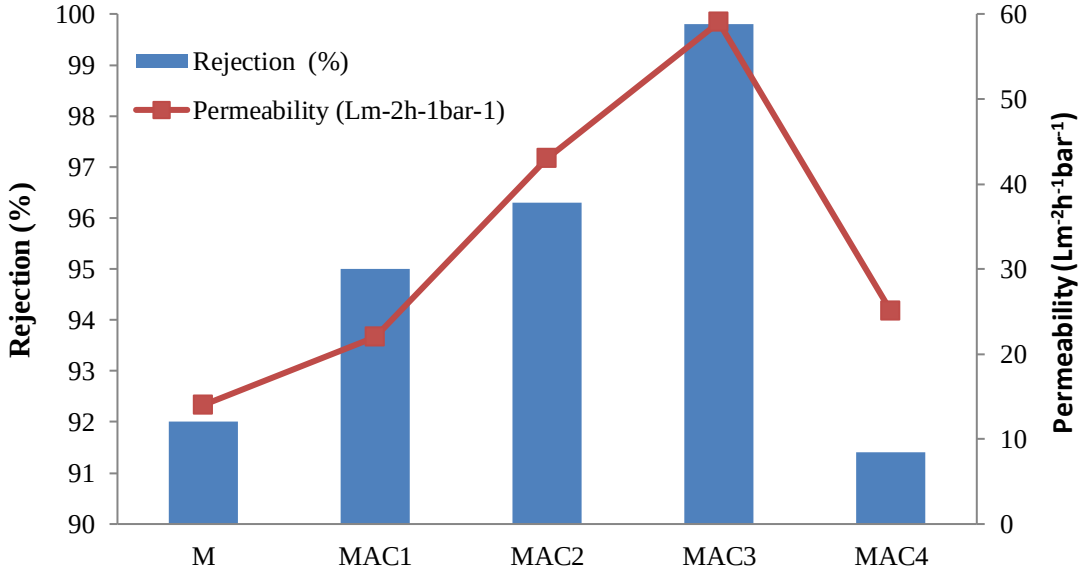

Figure 4.16 Congo red Dye Rejection of CA/PAN Mixed Matrix Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC) .

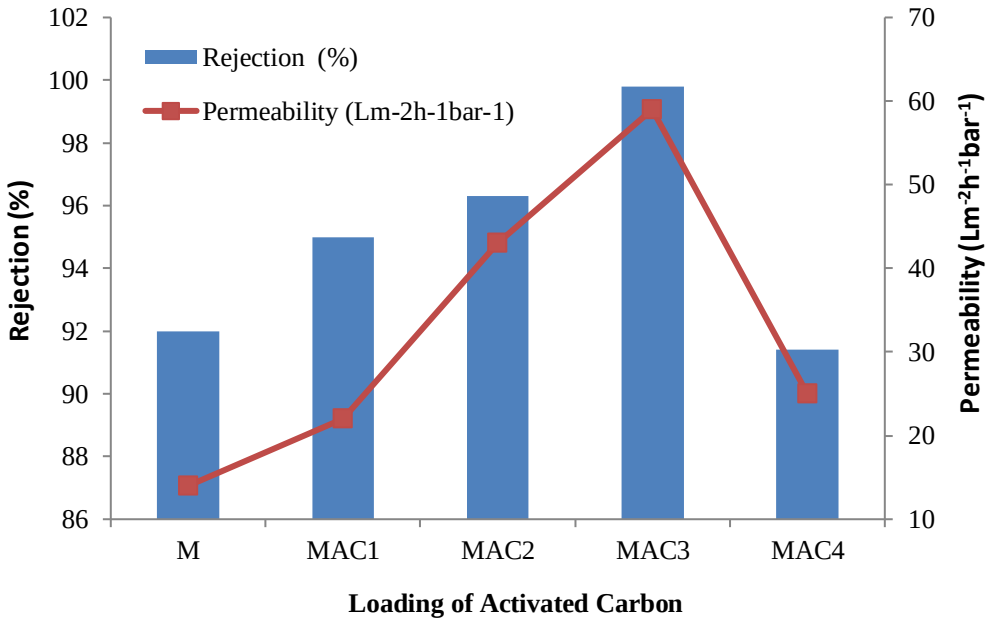

Figure 4.17 Rose Bengal Dye Rejections of CA/PAN Mixed Matrix Nanocomposite Membranes M (0%AC), MAC1 (0.5%AC), MAC2 (1%AC), MAC3 (2.5%AC), MAC4 (5%AC).

CHAPTER 5

DISCUSSION

Water scarcity is one of the most pressing global challenges, and desalination has emerged as a critical solution to provide fresh water from seawater or brackish water. Traditional desalination methods, such as MED, and VCD while effective, have limitations including high energy consumption, fouling, and environmental concerns. In this context, Date seed activated carbon (DSAC) crosslinked with Vinyle triethoxysilane (VTES), combined with cellulose acetate (CA), polyacrylonitrile (PAN), and PVP, offers a cost-effective, sustainable, and high-performance solution for desalination of water.Compared to other bioadsorbent and nanocomposite membranes, DSAC-based membranes excel in terms of desalination efficiency, fouling resistance, scalability, and environmental impact. While membranes based on materials like GO, CNT, and zeolites may offer higher water flux or selectivity, DSAC-based membranes provide a more balanced solution that is both commercially viable and environmentally sustainable, making them a strong candidate for desalination of water.

Bioadsorbent - based mixed matrix nanocomposite membranes (MMNMs) represent a promising alternative for enhancing desalination performance. This discussion will delve into the potential of these membranes, focusing on their materials, mechanisms, challenges, and future prospects.

Bio-adsorbent-based MMNMs can improve desalination performance by enhancing water permeability, salt rejection, and resistance to fouling. The incorporation of bio-adsorbent such as activated carbon into a polymeric matrix provides enhanced adsorption capacity due to the presence of functional groups like hydroxyl, amine, and carboxyl groups, which can effectively capture salts and other impurities. These membranes demonstrate several key scientific outcomes that enhance the efficiency and sustainability of water desalination processes.

One of the major outcomes of using DSAC crosslinked with VTES in a polymeric matrix of CA and PAN is the significant increase in water permeability:

PVP’s role as a pore former improves the membrane’s pore structure, facilitating higher water flux by creating a controlled pore size distribution. This allows water to pass more

easily while rejecting larger ions. CA's moderate hydrophilicity and PAN's robustness ensure efficient water transport through the membrane, while maintaining the structural integrity under high-pressure desalination conditions. DSAC's high surface area and microporosity, enhanced by VTES crosslinking, create additional channels for water transport, leading to higher water flux compared to conventional membranes. A notable improvement in water permeability (flux) compared to traditional polymeric membranes due to the synergistic effects of bioadsorbent. The crosslinking of DSAC with VTES introduces amine functional groups that enhance the membrane's ion selectivity and salt rejection capacity. The vinyle groups from VTES enable electrostatic interactions between the membrane and ionic species, particularly targeting salts like NaCl. This improves the membrane's ability to selectively reject salt ions while allowing water molecules to pass. The activated carbon derived from date seeds provide significant adsorption sites for ions and other contaminants, improving the desalination process by removing both salts and organic pollutants. Enhanced salt rejection efficiency due to the ion-exchange capabilities of the functionalized DSAC, achieving competitive desalination performance compared to standard commercial membranes.

5.1 Superior Antifouling Properties:

Fouling is a common issue in desalination membranes, reducing operational efficiency over time. The combination of CA, PAN, and functionalized DSAC in these membranes results in superior antifouling characteristics

5.2 Hydrophilic Surface:

The natural hydrophilicity of CA, combined with the crosslinked DSAC, reduces the adsorption of hydrophobic foulants like organic compounds. The hydrophilic surface minimizes the tendency of contaminants to adhere to the membrane. DSAC's microporous structure, enhanced by VTES functionalization, helps trap foulants within its pores, reducing the formation of a fouling layer on the membrane surface. Moreover, the well-distributed pores structure from PVP limits pore blockage.

5.3 Energy Efficient and Low-Cost Desalination:

Energy consumption remains one of the most significant challenges in desalination technologies, particularly in reverse osmosis (RO) systems. Bio-adsorbent-based MMNMs offer a potential solution by enhancing water permeability, thereby lowering the required operating pressure and reducing energy consumption.

5.4 Other Bio-Adsorbents:

5.4.1 Chitosan

Chitosan derived from chitin (crustacean shells), chitosan is another popular bioadsorbent used in desalination. Chitosan has excellent heavy metal adsorption properties due to its amino groups but generally requires chemical modification to achieve high desalination efficiency. Chitosan has Biocompatibility and ability to be chemically functionalized. Chitosan has some disadvantages like relatively higher cost and processing complexity compared to DSAC. Chitosan membranes have demonstrated good salt rejection and contaminant removal capabilities, especially when modified with nanoparticles like TiO_2 or silver. However, water flux tends to be lower than DSAC-based membranes due to chitosan's dense structure.

5.4.2 Cellulose

Cellulose is derived from plant fibers and is widely used in bioadsorbent membranes. While it is renewable and biodegradable, cellulose has lower adsorption capacity compared to DSAC and often requires chemical modification to improve desalination performance. Cellulosa has some advantages like it is abundant and inexpensive.It has some disadvantages like Less efficient in salt rejection without chemical functionalization or blending with nanomaterials.

5.5 CHallenges in Bio-Adsorbent-Based Nanocomposite Membranes:

Despite the promise of these membranes, several challenges need to be addressed:

5.5.1 Uniform Dispersion of Nanomaterials:

Achieving a uniform distribution of nanomaterials and bioadsorbents in the polymer matrix is critical for consistent membrane performance. Agglomeration of nanomaterials can create defects that reduce selectivity and increase fouling.

5.5.2 Trade-Off between Permeability and Selectivity:

Increasing permeability often comes at the expense of selectivity. Finding the optimal

balance between these two properties is essential for efficient desalination.

5.5.3 Stability of Bioadsorbents:

Some bioadsorbents may degrade in harsh desalination environments, such as high salinity or pH extremes. Improving their stability through chemical modification is a critical research area.

5.5.4 Scaling and Commercialization:

Although lab-scale studies have shown significant promise, scaling up the production of bioadsorbent-based nanocomposite membranes for industrial desalination remains challenging, particularly regarding cost and reproducibility.

5.6 Future Perspective:

Research in bioadsorbent-based nanocomposite membranes is still in its early stages, but the potential applications are vast. Future developments are likely to focus on:

5.6.1 Functionalization and Surface Modification:

Research on surface modification techniques to introduce functional groups or nanomaterials that enhance adsorption, ion selectivity, and anti-fouling properties will be critical to advancing bio-adsorbent MMNMs.

5.6.2 Hybrid Systems:

Investigating the potential of hybrid desalination systems that combine bio-adsorbent membranes with other desalination processes (e.g., forward osmosis or capacitive deionization) could unlock new pathways for energy-efficient water treatment.

5.6.3 Biopolymer-Nanocomposite Integration:

The combination of biopolymers with emerging nanomaterials offers vast opportunities for creating advanced membranes with customized functionalities, such as enhanced mechanical properties, contaminant selectivity, and photocatalytic degradation.

Bio-adsorbent-based mixed matrix nanocomposite membranes offer a promising and sustainable solution for future desalination applications. Their potential to enhance desalination efficiency, reduce fouling, lower energy consumption, and minimize environmental impacts makes them a key technology in the global effort to address water scarcity. However, further research and development are needed to overcome challenges

related to scalability, long-term stability, and cost-effectiveness. As material science and nanotechnology continue to evolve, bio-adsorbent-based MMNMs are likely to play an increasingly significant role in sustainable water desalination, contributing to global water security.

CHAPTER 6

CONCLUSIONS

This study focused on assessing the performance of a new type of activated carbon as filler in mixed matrix nanocomposite membranes for water desalination. The start of the thesis provided an overview of the importance of freshwater, and the effect of industrialization on freshwater resources. Need of water desalination. The Impact of water shortage on the lives of people of Pakistan. Brief overview of desalination techniques used in Pakistan. Detail of the process of desalination. The use of activated carbon-based MMNMs and a comprehensive literature review of current desalination techniques were also discussed. The thesis also discussed the history of membrane technology, its use in water desalination, and recent advancements in the field. The literature review emphasized the core principles of MMNMs, particularly focusing on recent research involving bio-adsorbent-based MMNMs for water desalination.

After that the synthesis of a novel date seed AC and MMNM's with different loading of AC incorporated into a CA/PAN polymer matrix (0.5wt%, 1wt%, 2.5wt%, and 5wt %) discussed. The MMNMs were characterized, and their performance was evaluated in terms of pure water flux (PWF), salt and dye rejection, as well as antifouling properties, to determine the effect of activated carbon on the efficiency of the MMNMs. The findings showed enhanced water permeability, better contaminant rejection, antifouling capabilities, long-term stability, and the effect of solvents on the MMNMs. Among the different AC loadings, the MMNMs with 2.5 wt.% exhibited the best performance across all tests. The characterization of the MMNMs through techniques like FTIR and TGA confirmed the presence of functional groups and their thermal resistance. The bio-adsorbent-based MMNMs achieved a flux recovery ratio of 91.4%, indicating strong performance in membrane regeneration. The study also confirmed the good phase inversion compatibility of the polymer matrix and the activated carbon filters, as demonstrated by the long-term stability of the membranes.

The thesis work led to the following conclusions:

- Bio-adsorbent MMNMs outperformed pure CA/PAN membranes in terms of water desalination.

- Activated carbon showed potential for desalination of water given its substantial surface area and the existence of Carboxylic acid groups, which have a strong affinity for positively charged contaminants in seawater.
- Activated carbon demonstrated good compatibility with CA/PAN membranes, exhibiting exceptional mechanical, thermal, and long-term stability.
- The incorporation of activated carbon not only improved pure water permeability but also enhanced the rejection of various salts present in sea and brackish water as compared to neat CA/PAN membrane.
- The filler showed excellent compatibility with the polymer matrix, leading to the long-term stability of the MMNMs.

In conclusion, this study highlights the potential of bio-adsorbent-based mixed matrix Nano- composite membranes (MMNMs) for seawater and brackish water treatment, demonstrating their enhanced performance and promising capability for water desalination.

REFERENCES

1. Sweetman MJ, May S, Mebberson N, Pendleton P, Vasilev K, Plush SE, et al. Activated carbon, carbon nanotubes and graphene: materials and composites for advanced water purification. C. 2017;3(2):18.
2. Camargo JA, Alonso Á. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. Environment international. 2006;32(6):831-49.
3. Gleick PH. The World's Water: The Biennial Report on Freshwater Resources. Volume 8: Island press; 2014.
4. Shatat M, Riffat SB. Water desalination technologies utilizing conventional and renewable energy sources. International Journal of Low-Carbon Technologies. 2014;9(1):1-19.
5. Ghebremichael KA, Gunaratna K, Henriksson H, Brumer H, Dalhammar G. A simple purification and activity assay of the coagulant protein from Moringa oleifera seed. Water research. 2005;39(11):2338-44.
6. Yamamoto KR, Alberts BM, Benzinger R, Lawhorne L, Treiber G. Rapid bacteriophage sedimentation in the presence of polyethylene glycol and its application to large-scale virus purification. Virology. 1970;40(3):734-44.
7. Natarajan S, Bajaj HC, Tayade RJ. Recent advances based on the synergetic effect of adsorption for removal of dyes from waste water using photocatalytic process. Journal of Environmental Sciences. 2018;65:201-22.
8. Lalwani S. Pakistan in 2019: Navigating Major Power Relations amid Economic Crisis. Asian Survey. 2020;60(1):177-88.
9. Du Plessis A, du Plessis A. Current and future water scarcity and stress. Water as an inescapable risk: current global water availability, quality and risks with a specific focus on South Africa. 2019:13-25.
10. Ragheb M. Fresh Water Augmentation. Nuclear Power Engineering Cambridge. 2016.
11. Alvez A, Aitken D, Rivera D, Vergara M, McIntyre N, Concha F. At the crossroads: can desalination be a suitable public policy solution to address water scarcity in Chile's mining zones? Journal of Environmental Management. 2020;258:110039.
12. Liu Q, Li J, Zhou Z, Xie J, Lee JY. Hydrophilic mineral coating of membrane substrate for reducing internal concentration polarization (ICP) in forward osmosis. Scientific reports. 2016;6(1):1-10.
13. Ong RC, Chung T-S, de Wit JS, Helmer BJ. Novel cellulose ester substrates for high

performance flat-sheet thin-film composite (TFC) forward osmosis (FO) membranes. Journal of Membrane Science. 2015;473:63-71.

14. Zaib Q, Fath H. Application of carbon nano-materials in desalination processes. Desalination and Water Treatment. 2013;51(1-3):627-36.
15. Sedlak D. Water 4.0: The Past, Present, and Future of the World? s Most Vital Resource: Yale University Press; 2014.
16. Sanchez-Ruiz FJ. Reactive Distillation Modeling Using Artificial Neural Networks. Distillation Processes-From Solar and Membrane Distillation to Reactive Distillation Modelling, Simulation and Optimization: IntechOpen; 2022.
17. Islam M, Sultana A, Saadat A, Shammi M, Uddin M. Desalination technologies for developing countries: a review. Journal of Scientific Research. 2018;10(1):77-97.
18. Mohamed A-MO, Paleologos EK, Howari F. Pollution assessment for sustainable practices in applied sciences and engineering: Butterworth-Heinemann; 2020.
19. Löwenberg J, Baum JA, Zimmermann Y-S, Groot C, van den Broek W, Wintgens T. Comparison of pre-treatment technologies towards improving reverse osmosis desalination of cooling tower blow down. Desalination. 2015;357:140-9.
20. Shatat M, Worall M, Riffat S. Opportunities for solar water desalination worldwide. Sustainable cities and society. 2013;9:67-80.
21. Micale G, Rizzuti L, Cipollina A. Seawater desalination: conventional and renewable energy processes: Springer; 2009.
22. Al-Obaidi MA, Zubo RH, Rashid FL, Dakkama HJ, Abd-Alhameed R, Mujtaba IM. Evaluation of solar energy powered seawater desalination processes: a review. Energies. 2022;15(18):6562.
23. Qasim M, Darwish NA, Sarp S, Hilal N. Water desalination by forward (direct) osmosis phenomenon: A comprehensive review. Desalination. 2015;374:47-69.
24. Taleshi MSA, Azimzadeh HR, Ghaneian MT, Namayandeh SM. Performance evaluation of reverse osmosis systems for water treatment required of hemodialysis in Yazd educational hospitals, 2013. Journal of Research in Environmental Health. 2015;1(2):95-103.
25. Ghasemzadeh K, Aghaeinejad-Meybodi A, Basile A. Separation Theory of Silica Membranes. Current Trends and Future Developments on (Bio-) Membranes: Elsevier; 2017. p. 65-95.
26. Raman LP, Cheryna M, Rajagopalan N. Consider nanofiltration for membrane separations. Chemical Engineering Progress;(United States). 1994;90(3).

27. Porter MC. Handbook of industrial membrane technology. 1989.
28. Jyoti G, Keshav A, Anandkumar J. Review on pervaporation: theory, membrane performance, and application to intensification of esterification reaction. Journal of Engineering. 2015;2015(1):927068.
29. Achilli A, Cath TY, Childress AE. Selection of inorganic-based draw solutions for forward osmosis applications. Journal of membrane science. 2010;364(1-2):233-41.
30. McCutcheon JR, Elimelech M. Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. Journal of membrane science. 2006;284(1-2):237-47.
31. Nghiem LD, Schäfer AI, Elimelech M. Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms. Environmental science & technology. 2004;38(6):1888-96.
32. Alturki AA, McDonald JA, Khan SJ, Price WE, Nghiem LD, Elimelech M. Removal of trace organic contaminants by the forward osmosis process. Separation and Purification Technology. 2013;103:258-66.
33. Tian M, Wang Y-N, Wang R. Synthesis and characterization of novel high-performance thin film nanocomposite (TFN) FO membranes with nanofibrous substrate reinforced by functionalized carbon nanotubes. Desalination. 2015;370:79-86.
34. Garcia-Ivars J, Iborra-Clar M-I, Alcaina-Miranda M-I, Mendoza-Roca J-A, Pastor-Alcañiz L. Surface photomodification of flat-sheet PES membranes with improved antifouling properties by varying UV irradiation time and additive solution pH. Chemical Engineering Journal. 2016;283:231-42.
35. Lau W, Gray S, Matsuura T, Emadzadeh D, Chen JP, Ismail A. A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches. Water research. 2015;80:306-24.
36. Obaid M, Ghouri ZK, Fadali OA, Khalil KA, Almajid AA, Barakat NA. Amorphous SiO2 NP-incorporated poly (vinylidene fluoride) electrospun nanofiber membrane for high flux forward osmosis desalination. ACS applied materials & interfaces. 2016;8(7):4561-74.
37. Liu Z, Hu Y. Sustainable antibiofouling properties of thin film composite forward osmosis membrane with rechargeable silver nanoparticles loading. ACS applied materials & interfaces. 2016;8(33):21666-73.
38. Shen L, Xiong S, Wang Y. Graphene oxide incorporated thin-film composite membranes for forward osmosis applications. Chemical Engineering Science. 2016;143:194-205.

39. Emadzadeh D, Lau W, Rahbari-Sisakht M, Ilbeygi H, Rana D, Matsuura T, et al. Synthesis, modification and optimization of titanate nanotubes-polyamide thin film nanocomposite (TFN) membrane for forward osmosis (FO) application. Chemical Engineering Journal. 2015;281:243-51.
40. Ulbricht M. Advanced functional polymer membranes. Polymer. 2006;47(7):2217-62.
41. Ghanim ASH, Alsalhy Q. Preparation and characterization of PLA polymeric membrane for pervaporation applications: University of Technology; 2012.
42. Mohshim DF, Mukhtar Hb, Man Z, Nasir R. Latest development on membrane fabrication for natural gas purification: a review. Journal of Engineering. 2013;2013(1):101746.
43. Kayvani Fard A, McKay G, Buekenhoudt A, Al Sulaiti H, Motmans F, Khraisheh M, et al. Inorganic membranes: Preparation and application for water treatment and desalination. Materials. 2018;11(1):74.
44. Xu Z, Liao J, Tang H, Efome JE, Li N. Preparation and antifouling property improvement of Tröger's base polymer ultrafiltration membrane. Journal of Membrane Science. 2018;561:59-68.
45. Zargar M, Jin B, Dai S. Development and application of reverse osmosis for separation. Membrane Processing for Dairy Ingredient Separation. 2015:139-75.
46. Shafiq M, Yasin T, Saeed S. Synthesis and characterization of linear low-density polyethylene/sepiolite nanocomposites. Journal of applied polymer science. 2012;123(3):1718-23.
47. Padaki M, Murali RS, Abdullah MS, Misdan N, Moslehyani A, Kassim M, et al. Membrane technology enhancement in oil–water separation. A review. Desalination. 2015;357:197-207.
48. Liu J, Wang L, Tang J, Ma J. Photocatalytic degradation of commercially sourced naphthenic acids by TiO2-graphene composite nanomaterial. Chemosphere. 2016;149:328-35.
49. Hegab HM, Zou L. Graphene oxide-assisted membranes: fabrication and potential applications in desalination and water purification. Journal of Membrane Science. 2015;484:95-106.
50. Nunes SP, Peinemann K-V. Membrane technology: in the chemical industry: John Wiley & Sons; 2006.
51. Ismail AF, David L. A review on the latest development of carbon membranes for gas separation. Journal of membrane science. 2001;193(1):1-18.

52. Dong G, Li H, Chen V. Challenges and opportunities for mixed-matrix membranes for gas separation. Journal of Materials Chemistry A. 2013;1(15):4610-30.
53. Batool M, Shafeeq A, Haider B, Ahmad NM. TiO2 nanoparticle filler-based mixed-matrix PES/CA nanofiltration membranes for enhanced desalination. Membranes. 2021;11(6):433.
54. Esfahani MR, Aktij SA, Dabaghian Z, Firouzjaei MD, Rahimpour A, Eke J, et al. Nanocomposite membranes for water separation and purification: Fabrication, modification, and applications. Separation and Purification Technology. 2019;213:465-99.
55. Baker RW. Membrane technology and applications: John Wiley & Sons; 2023.
56. Baker RW. Membrane technology. Encyclopedia of polymer science and technology. 2002;3.
57. Gupta P, Lapalikar V, Kundu R, Balasubramanian K. Recent advances in membrane based waste water treatment technology: a review. Energy and Environment Focus. 2016;5(4):241-67.
58. Ganesh B, Isloor AM, Ismail AF. Enhanced hydrophilicity and salt rejection study of graphene oxide-polysulfone mixed matrix membrane. Desalination. 2013;313:199-207.
59. Zhang Q, Wang H, Fan X, Lv F, Chen S, Quan X. Fabrication of TiO2 nanofiber membranes by a simple dip-coating technique for water treatment. Surface and Coatings Technology. 2016;298:45-52.
60. Augello C, Liu H. Surface modification of magnesium by functional polymer coatings for neural applications. Surface Modification of Magnesium and Its Alloys for Biomedical Applications: Elsevier; 2015. p. 335-53.
61. Li G, Kujawski W, Válek R, Koter S. A review-The development of hollow fibre membranes for gas separation processes. International Journal of Greenhouse Gas Control. 2021;104:103195.
62. Jacobs P, Flanigen EM, Jansen J, van Bekkum H. Introduction to zeolite science and practice: Elsevier; 2001.
63. Fathizadeh M, Aroujalian A, Raisi A. Effect of added NaX nano-zeolite into polyamide as a top thin layer of membrane on water flux and salt rejection in a reverse osmosis process. Journal of membrane science. 2011;375(1-2):88-95.
64. Tang D, Yuan R, Chai Y. Magnetic control of an electrochemical microfluidic device with an arrayed immunosensor for simultaneous multiple immunoassays. Clinical Chemistry. 2007;53(7):1323-9.

65. Huang H, Qu X, Ji X, Gao X, Zhang L, Chen H, et al. Acid and multivalent ion resistance of thin film nanocomposite RO membranes loaded with silicalite-1 nanozeolites. Journal of Materials Chemistry A. 2013;1(37):11343-9.
66. Wu H, Tang B, Wu P. Optimizing polyamide thin film composite membrane covalently bonded with modified mesoporous silica nanoparticles. Journal of membrane science. 2013;428:341-8.
67. Bao M, Zhu G, Wang L, Wang M, Gao C. Preparation of monodispersed spherical mesoporous nanosilica–polyamide thin film composite reverse osmosis membranes via interfacial polymerization. Desalination. 2013;309:261-6.
68. Mills A, Le Hunte S. An overview of semiconductor photocatalysis. Journal of photochemistry and photobiology A: Chemistry. 1997;108(1):1-35.
69. Rajaeian B, Rahimpour A, Tade MO, Liu S. Fabrication and characterization of polyamide thin film nanocomposite (TFN) nanofiltration membrane impregnated with TiO2 nanoparticles. Desalination. 2013;313:176-88.
70. Akhavan O, Ghaderi E. Self-accumulated Ag nanoparticles on mesoporous TiO2 thin film with high bactericidal activities. Surface and Coatings Technology. 2010;204(21-22):3676-83.
71. Lee HS, Im SJ, Kim JH, Kim HJ, Kim JP, Min BR. Polyamide thin-film nanofiltration membranes containing TiO2 nanoparticles. Desalination. 2008;219(1-3):48-56.
72. Kim SH, Kwak S-Y, Sohn B-H, Park TH. Design of TiO2 nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem. Journal of Membrane Science. 2003;211(1):157-65.
73. Soroko I, Livingston A. Impact of TiO2 nanoparticles on morphology and performance of crosslinked polyimide organic solvent nanofiltration (OSN) membranes. Journal of Membrane Science. 2009;343(1-2):189-98.
74. Corry B. Designing carbon nanotube membranes for efficient water desalination. The Journal of Physical Chemistry B. 2008;112(5):1427-34.
75. Li H, Eddaoudi M, O'Keeffe M, Yaghi OM. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. nature. 1999;402(6759):276-9.
76. Rosi NL, Eckert J, Eddaoudi M, Vodak DT, Kim J, O'Keeffe M, et al. Hydrogen storage in microporous metal-organic frameworks. Science. 2003;300(5622):1127-9.
77. Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, O'Keeffe M, et al. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. Science. 2002;295(5554):469-72.

78. Férey G. Hybrid porous solids: past, present, future. Chemical Society Reviews. 2008;37(1):191-214.
79. Rowsell JL, Yaghi OM. Metal–organic frameworks: a new class of porous materials. Microporous and mesoporous materials. 2004;73(1-2):3-14.
80. Li W, Zhang Y, Li Q, Zhang G. Metal− organic framework composite membranes: Synthesis and separation applications. Chemical Engineering Science. 2015;135:232-57.
81. Sorribas S, Gorgojo P, Téllez C, Coronas J, Livingston AG. High flux thin film nanocomposite membranes based on metal–organic frameworks for organic solvent nanofiltration. Journal of the American Chemical Society. 2013;135(40):15201-8.
82. Banat F, Al-Asheh S, Al-Makhadmeh L. Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. Process Biochemistry. 2003;39(2):193-202.
83. Abuelnoor N, AlHajaj A, Khaleel M, Vega LF, Abu Zahra M, editors. Single step synthesis and characterization of activated carbon from date seeds for CO2 capture. Proceedings of the 15th Greenhouse Gas Control Technologies Conference; 2021.
84. Mahdi Z, El Hanandeh A, Yu QJ. Preparation, characterization and application of surface modified biochar from date seed for improved lead, copper, and nickel removal from aqueous solutions. Journal of Environmental Chemical Engineering. 2019;7(5):103379.
85. Alsulaili AD, Refaie AA, Garcia HA. Adsorption capacity of activated carbon derived from date seeds: Characterization, optimization, kinetic and equilibrium studies. Chemosphere. 2023;313:137554.
86. Ogungbenro AE, Quang DV, Al-Ali KA, Vega LF, Abu-Zahra MR. Synthesis and characterization of activated carbon from biomass date seeds for carbon dioxide adsorption. Journal of Environmental Chemical Engineering. 2020;8(5):104257.
87. Alazmi A, Nicolae SA, Modugno P, Hasanov BE, Titirici MM, Costa PM. Activated carbon from palm date seeds for CO2 capture. International journal of environmental research and public health. 2021;18(22):12142.
88. Reddy K, Al Shoaibi A, Srinivasakannan C. Preparation of porous carbon from date palm seeds and process optimization. International journal of environmental science and technology. 2015;12:959-66.
89. Mohammadnezhad F, Feyzi M, Zinadini S. A novel Ce-MOF/PES mixed matrix membrane; synthesis, characterization and antifouling evaluation. Journal of industrial and engineering chemistry. 2019;71:99-111.
90. Sali S, Mackey HR, Abdala AA. Effect of graphene oxide synthesis method on properties

and performance of polysulfone-graphene oxide mixed matrix membranes. Nanomaterials. 2019;9(5):769.

91. Shaari NZK, Abd Rahman N, Sulaiman NA, Tajuddin RM, editors. Thin film composite membranes: Mechanical and antifouling properties. MATEC Web of Conferences; 2017: EDP Sciences.
92. Zinadini S, Zinatizadeh AA, Rahimi M, Vatanpour V, Zangeneh H. Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates. Journal of Membrane Science. 2014;453:292-301.
93. Rahimi M, Zinadini S, Zinatizadeh AA, Vatanpour V, Rajabi L, Rahimi Z. Hydrophilic goethite nanoparticle as a novel antifouling agent in fabrication of nanocomposite polyethersulfone membrane. Journal of Applied Polymer Science. 2016;133(26).
94. Al-Shaeli M, Smith SJ, Jiang S, Wang H, Zhang K, Ladewig BP. Long-term stable metal organic framework (MOF) based mixed matrix membranes for ultrafiltration. Journal of Membrane Science. 2021;635:119339.
95. Kamari S, Shahbazi A. Biocompatible Fe3O4@ SiO2-NH2 nanocomposite as a green nanofiller embedded in PES–nanofiltration membrane matrix for salts, heavy metal ion and dye removal: Long–term operation and reusability tests. Chemosphere. 2020;243:125282.
96. Duong PH, Kuehl VA, Mastorovich B, Hoberg JO, Parkinson BA, Li-Oakey KD. Carboxyl-functionalized covalent organic framework as a two-dimensional nanofiller for mixed-matrix ultrafiltration membranes. Journal of membrane science. 2019;574:338-48.
97. Jamil TS, Mansor ES, Abdallah H, Shaban AM, Souaya ER. Novel anti fouling mixed matrix CeO2/Ce7O12 nanofiltration membranes for heavy metal uptake. Journal of Environmental Chemical Engineering. 2018;6(2):3273-82.
98. Perkins W. Fourier transform-infrared spectroscopy: part 1. Instrumentation J. 1986.
99. Silva GA. Introduction to nanotechnology and its applications to medicine. Surgical neurology. 2004;61(3):216-20.
100. Inkson BJ. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for materials characterization. Materials characterization using nondestructive evaluation (NDE) methods: Elsevier; 2016. p. 17-43.
101. Siddique H, Rundquist E, Bhole Y, Peeva L, Livingston A. Mixed matrix membranes for organic solvent nanofiltration. Journal of Membrane Science. 2014;452:354-66.
102. Vinodhini PA, Sangeetha K, Thandapani G, Sudha P, Jayachandran V, Sukumaran A. FTIR, XRD and DSC studies of nanochitosan, cellulose acetate and polyethylene glycol

blend ultrafiltration membranes. International journal of biological macromolecules. 2017;104:1721-9.

103. Ladewig B, Al-Shaeli MNZ. Fundamentals of membrane bioreactors. Springer Transactions in Civil and Environmental Engineering. 2363: Springer; 2017. p. 150.

104. Jun Y, Zarrin H, Fowler M, Chen Z. Functionalized titania nanotube composite membranes for high temperature proton exchange membrane fuel cells. international journal of hydrogen energy. 2011;36(10):6073-81.

105. Terrazas-Bandala LP, Gonzalez-Sanchez G, Garcia-Valls R, Gumi T, Beurroies I, Denoyel R, et al. Influence of humidity, temperature, and the addition of activated carbon on the preparation of cellulose acetate membranes and their ability to remove arsenic from water. Journal of Applied Polymer Science. 2014;131(8).

106. Eigler S, Grimm S, Hirsch A. Investigation of the thermal stability of the carbon framework of graphene oxide. Chemistry–A European Journal. 2014;20(4):984-9.

107. Pourjafar S, Rahimpour A, Jahanshahi M. Synthesis and characterization of PVA/PES thin film composite nanofiltration membrane modified with TiO2 nanoparticles for better performance and surface properties. Journal of Industrial and Engineering Chemistry. 2012;18(4):1398-405.

108. Ya KZ, Kumazawa K, Kawamura G, Muto H, Matsuda A. Cell performance enhancement with titania-doped polybenzimidazole based composite membrane in intermediate temperature fuel cell under anhydrous condition. Journal of the Ceramic Society of Japan. 2018;126(10):789-93.

109. Wu G, Gan S, Cui L, Xu Y. Preparation and characterization of PES/TiO2 composite membranes. Applied Surface Science. 2008;254(21):7080-6.

110. Hosseini S, Amini S, Khodabakhshi A, Bagheripour E, Van der Bruggen B. Activated carbon nanoparticles entrapped mixed matrix polyethersulfone based nanofiltration membrane for sulfate and copper removal from water. Journal of the Taiwan Institute of Chemical Engineers. 2018;82:169-78.

111. Abdel-Karim A, Leaper S, Alberto M, Vijayaraghavan A, Fan X, Holmes SM, et al. High flux and fouling resistant flat sheet polyethersulfone membranes incorporated with graphene oxide for ultrafiltration applications. Chemical Engineering Journal. 2018;334:789-99.

112. Teixeira MR, Rosa MJ, Nyström M. The role of membrane charge on nanofiltration performance. Journal of Membrane Science. 2005;265(1-2):160-6.

113. Vilakati GD, Wong MC, Hoek EM, Mamba BB. Relating thin film composite membrane

performance to support membrane morphology fabricated using lignin additive. Journal of Membrane Science. 2014;469:216-24.

114. Vatanpour V, Paziresh S. A melamine-based covalent organic framework nanomaterial as a nanofiller in polyethersulfone mixed matrix membranes to improve separation and antifouling performance. Journal of Applied Polymer Science. 2022;139(1):51428.

115. Wei L, Agarwal UP, Matuana L, Sabo RC, Stark NM. Performance of high lignin content cellulose nanocrystals in poly (lactic acid). Polymer. 2018;135:305-13.

116. Rusli UN, Alias NH, Shahruddin MZ, Othman NH, editors. Photocatalytic degradation of oil using polyvinylidene fluoride/titanium dioxide composite membrane for oily wastewater treatment. MATEC Web of Conferences; 2016: EDP Sciences.

117. Vatanpour V, Madaeni SS, Moradian R, Zinadini S, Astinchap B. Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO2 coated multiwalled carbon nanotubes. Separation and purification technology. 2012;90:69-82.

118. Vatanpour V, Madaeni SS, Moradian R, Zinadini S, Astinchap B. Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite. Journal of membrane science. 2011;375(1-2):284-94.

119. Koo CH, Mohammad AW, Talib MZM. Review of the effect of selected physicochemical factors on membrane fouling propensity based on fouling indices. Desalination. 2012;287:167-77.

120. Zhang J, Xu Z, Mai W, Min C, Zhou B, Shan M, et al. Improved hydrophilicity, permeability, antifouling and mechanical performance of PVDF composite ultrafiltration membranes tailored by oxidized low-dimensional carbon nanomaterials. Journal of Materials Chemistry A. 2013;1(9):3101-11.

121. Khosravi MJ, Hosseini SM, Vatanpour V. Performance improvement of PES membrane decorated by Mil-125 (Ti)/chitosan nanocomposite for removal of organic pollutants and heavy metal. Chemosphere. 2022;290:133335.