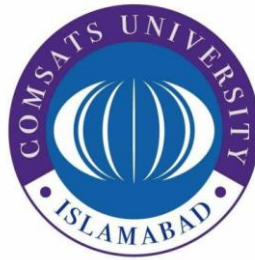# Fabrication of Thin Film Composite Forward Osmosis Membranes for Desalination

By

Haider Ali Shah

CIIT/FA20-RCH-001/LHR

MS thesis

In

Chemical Engineering

COMSATS University Islamabad, Lahore Campus

FALL 2022

COMSATS University Islamabad, Lahore Campus

Fabrication of Thin Film Composite Forward Osmosis Membranes for Desalination

A Thesis Presented to

COMSATS University Islamabad

In partial fulfillment

Of the requirement for the degree of

MS (Chemical Engineering)

By

Haider Ali Shah

CIIT/FA20-RCH-001/LHR

FALL 2022

Fabrication of Thin Film Composite Forward Osmosis Membranes for Desalination

A Post Graduate Thesis submitted to the name of Chemical Engineering department as partial fulfillment of the requirement for the award of Degree of M.S (Chemical Engineering)

Name	Registration number
Haider Ali Shah	CIIT/FA20-RCH-001/LHR

Supervisor

Dr. Muhammad Yasin

Associate Professor

Department of Chemical Engineering

COMSATS University Islamabad,

Lahore Campus

January 2023

Co-supervisor

Dr. Asim Laeeq Khan

Associate Professor

Department of Chemical Engineering

COMSATS University Islamabad,

Lahore Campus

January 2023

Final Approval

This thesis entitled

Fabrication of Thin Film Composite Forward Osmosis Membranes for Desalination

By

Haider Ali Shah

CIIT/FA20-RCH-001/LHR

Has been approved

For the COMSATS University Islamabad, Lahore Campus Pakistan

External Examiner: _____

Dr. Abdul-Sattar Nizami

Sustainable Development Study Centre, Government College University, Lahore.

Research Supervisor: _____

Dr. Muhammad Yasin

Department of Chemical Engineering, CUI, Lahore Campus

HoD: _____

Dr. Asim Laeeq Khan

Department of Chemical Engineering, CUI, Lahore Campus

Declaration

I <u>Haider Ali Shah</u> having registration number <u>CIIT/FA20-RCH-001/LHR</u> hereby declare that I have done the work conferred in this thesis, during the regular period of study. I also declare that I have not taken any material from any source except mentioned to wherever due that amount of plagiarism is within satisfactory range. If a violation of HEC rules on research has happened in this thesis, I shall be responsible to punishable action under the plagiarism rules of the HEC.

Date: --------------

Haider Ali Shah

CIIT/FA20-RCH-001/LHR

Certificate

It is certified that <u>Haider Ali Shah</u> having registration number <u>CIIT/FA20-RCH-001/LHR</u> has done all the work attached to this thesis under my supervision at the Department of Chemical Engineering COMSATS University Islamabad, Lahore Campus and work fulfills the requirement for award of MS degree.

Date: ----------------

Dr. Muhammad Yasin
Supervisor

Dr. Asim Laeeq Khan
Head of Department
Department of Chemical Engineering

DEDICATION

To all who have participated and supported throughout the completion of
my thesis including my supervisors Dr. Muhammad Yasin and Dr. Asim
Laeeq Khan, my friends and
Especially
To my parents, for their utmost passion, concern & support; to my sisters,
brother and nephews till
the end.

ACKNOWLEDGEMENT

Table of Content

List of Figures

List of Abbreviations

TFA   Tri-flouro acetic acid

DCM   Di-choloro methane

PEG   Poly-ethylene Glycol

FTIR   Fourier transform infrared spectroscopy

NMP   N-Methyl-2-pyrrolidone

MOF   metal organic framework

TMC   Tri-mesoyl chloride

MPD   m-phenylene diamine

TFC   thin film composite

List of Tables

Abstract

Fabrication of Thin Film Composite Forward Osmosis Membranes for Desalination

Forward osmosis is a greener desalination process as compared to reverse osmosis, which is the most dominant desalination technology in the world. The most dominant membrane morphology used in forward osmosis is thin film composite (TFC) membranes. TFC membranes consist of a selective polyamide top layer and a support layer in the ultrafiltration range. The supports are composed of commercial polymers such as polysulfone (PSf), polyether sulfone (PES), polyimides (PI), polyamides (PA), and polyacrylonitrile (PAN). These commercial polymers are derived from fossil fuels. This research work aimed to replace the commercial polymers with recycled PET (polyethylene terephthalate), which is a sustainable alternative to commercial polymers and can be used to fabricate TFC membranes in a more sustainable way. The effects of varying evaporation time, reaction time and additives on the performance of TFC membranes were studied. The fabricated TFC membranes showed good performance during a forward osmosis process to desalinate water. They had a comparable selectivity to conventional TFC membranes made with polyether sulfone (PES) support. For 1 M NaCl draw solution, they exhibited a water flux of 10.6 LMH and a reverse salt flux of 4.2 gMH with a selectivity of 0.4 g/L. The performance of TFC membranes synthesized during the study needs further study to assess their performance during long term operation.

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

In recent years, due to an increase in population as well as an increase in economic development, the demand for freshwater has been growing rapidly. Although 70% of the Earth's surface consists of water, most of it is seawater. Only 3% of the water in the world is freshwater, and even most of that is in the form of glaciers, so freshwater is a precious resource [1]. Logically, desalination will be an attractive option to meet freshwater needs. Countries in desert climates as well as those that have limited water resources, focus on desalination and wastewater reuse to meet their needs [2, 3]. Currently, some countries depend on desalination to meet their freshwater requirements, especially Middle Eastern countries like Saudi Arabia, Kuwait, and the U.A.E. [4]. Other than these countries, the United States is also a large user of desalinated water. Actually, it is among the largest users among industrialized countries. It has desalination facilities mostly in California and Florida [5]. National water requirements met by desalination in different countries is presented in Figure 1.1 [6].
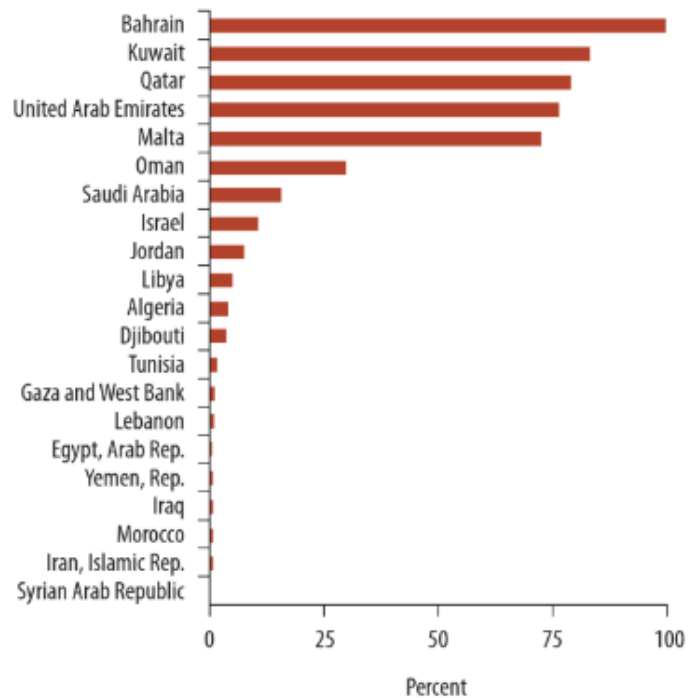
Figure 1.1: Share of National Water Demand Met by Desalination, 2010

Application of membranes for desalination involves synthesis of membranes in the nanofiltration range by interfacial polymerization (IP). However, the conventional

2

supports, i.e., polysulfone, poly acrylonitrile and poly ether sulfone, used in the IP are not environmentally friendly. Thus, there is a strong need to replace these supports with the greener ones to achieve the concept of sustainability in membrane fabrication. In addition, the replacement of expensive polymers with the cheaper alternatives will help to reduce the overall cost of the membranes. This MS thesis is aimed at developing a green synthesis method for TFC membranes using recycled polyethylene terephthalate (PET) as a polymeric material to substitute the harmful conventional supports. Membranes thus fabricated will be used to achieve high water permeability while maintaining high solute rejection at low pressure.

TFC FO could be one of the suitable potential options to achieve high water permeability as well as salt rejection during desalination. However, the high cost of the polymers used for membranes support and the fact that they are products of environmentally unfriendly fossil fuel industry, make them costly and unsafe for humans and the environment. Thus, replacing the current polymeric materials with waste recycled materials such as PET bottles would be a great contribution towards green membrane synthesis with waste recycled materials.

1.2 Waste Plastic and its Reuse

Nowadays plastics are widely used and have become a big part of modern life, because of attributes like production cost is small, ability to be molded into different shapes, and other unique properties [7]. The applications of plastics includes packaging, electronics, construction, etc. [8]. Plastics have low biodegradability which leads to a plastic waste crisis, hence they need to be recycled and reused [9]. The production of plastics was reported to be around 359 metric tons in 2018, and it is predicted that it will only triple in the next 30 years [10]. PET (polyethylene terephthalate), because of its properties like: excellent durability, it is transparent, and has good resistance to gases, is a popular polymeric material used for food and beverage products packaging. These days it has become convenient to use single-use PET bottles for packaging beverages like mineral water, soft drinks, juices, etc. Consequently, now there are millions PET bottles that need to be disposed of every day, and since these bottles are non-biodegradable, this leads to environmental pollution [11]. It is estimated that 18% of the world's plastic production

3

consists of PET [12]. Only a small amount of the waste PET bottles are recycled, which means that the PET bottles need to be used in more different ways and not just thrown away, which causes pollution on the Earth [13]. It is estimated millions of bottles are thrown in the trash daily and it is projected to double over the many coming years and many of these bottles are made from PET [14]. It is clear that there is a need to reduce the pollution caused by these plastic bottles by reusing and recycling them.

Currently the used PET bottles that are recycled are used for the production of new bottles through various recycling processes. These waste PET bottles are already used to produce different lower value items such as plastic furniture, more bottles, carpets, etc. There is a need for processes that use waste PET bottles to produce high-value products like for example, membranes for waste water treatment or membranes for treatment of sea water and brackish water. If these waste plastic bottles can be used to make nanofiltration membranes capable of good salt rejection, this will solve two great issues, one is the recycling of waste PET bottles as well as provide freshwater form sea water or brackish water by different membrane processes. Figure 1.2 shows an example of the plastic waste pollution worldwide [15].

Figure 1.2: Beach in Lebanon littered with plastic waste, 2019

1.3 Desalination

Desalination is the technological process that provides freshwater using saltwater or brackish water as feed. Usually, seawater is the feed that is purified by the process [16].

4

All over the world, desalination is used to provide fresh water. There are several desalination technologies. They can be classified on the basis of their working principles:

- Evaporation and Condensation
- Filtration
- Crystallization

Another way to classify these technologies is based on which type of energy they use either thermal or electrical. The thermal technologies are multi-effect distillation (MED), multi-stage flash distillation (MSF), thermal vapor compression (TVC), solar chimney (SC), humidification dehumidification (HDH), membrane distillation (MD), solar still distillation (SSD). While the electrical technologies are mechanical vapor compression (MVC), reverse osmosis (RO), forward osmosis (FO), nanofiltration (NF), electrodialysis (ED), capacitive deionization (CDI), hydration (HY), secondary refrigerant freezing (SRF), ion-exchange resin (IXR). The desalination technologies are shown in Figure 1.3.
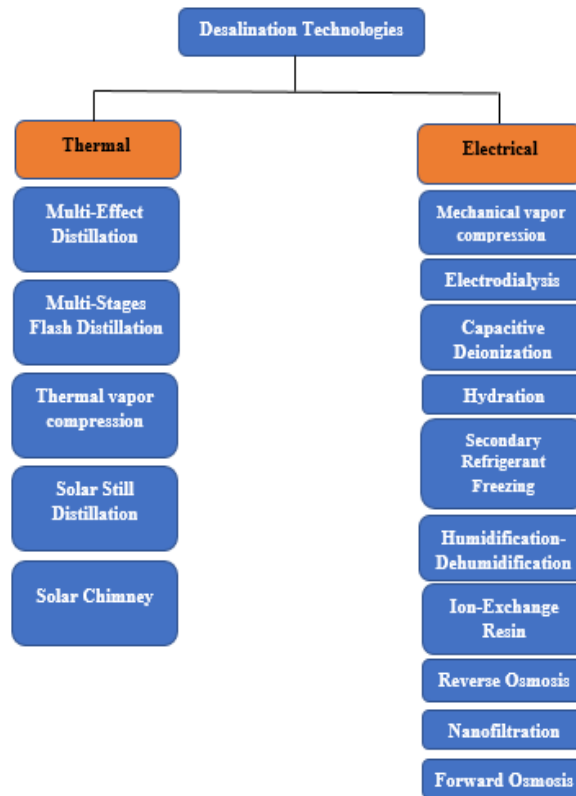
Figure 1.3: Desalination technologies based on the energy type used

1.3.1 Multi-Effect Distillation (MED)

The multiple effect distillation, MED, plant consists of the following equipments: a boiler for supplying the steam, condensers, evaporators in series called as effects, recovery heat exchangers. The pressure inside each evaporator, now called as effects, is reduced using dedicated vacuum systems. Only in the first effect is heat provided from the boiler to boil the feedwater. The tubes are sprayed by the feedwater for fast heat transfer. The vapors formed in the first effect are transferred to the next effect. The internal pressure of the consecutive effects becomes lower when compared to the preceding effect so this results in the boiling points of the constituents of every evaporator to be lowered. Using the previously mentioned evaporators, the seawater feed will be boiled multiple times without any additional heat while condensing the vapors from the previous chamber. This process allows the production of more and more vapors at lower pressure. Finally, the vapors from the effects are entered into a condenser (in which the cold stream is the feed water) and condensed to provide freshwater [4, 16]. A simple schematic diagram of a MED plant is presented in Figure 1.4.
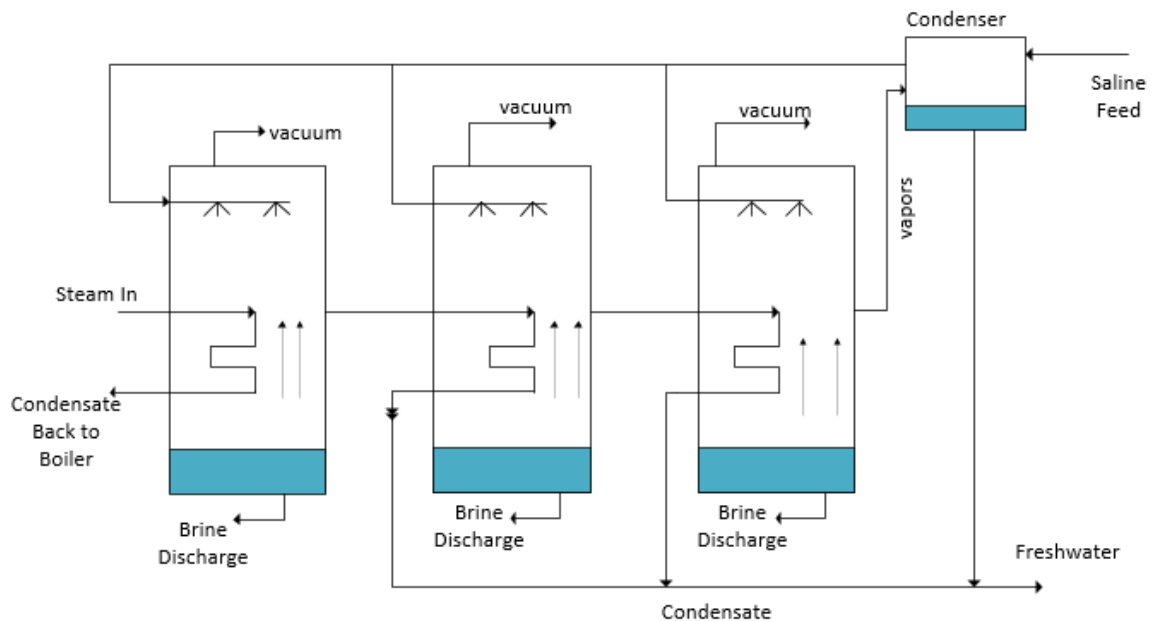
Figure 1.4: Schematic of a Multiple Effects Distillation plant

1.3.2 Multi-Stages Flash Distillation (MSF)

An MSF process is similar to the MED process that it also requires initial heat supply from

steam from a boiler and that the pressure is reduced for vapor production. Two plant sections are:

- Brine heating section, where feedwater is heated by an external supply
- Heat recovery section, where heat is recovered to preheat the feedwater

The saline feedwater is used to cool the condenser and as the raw feed to produce freshwater. The feedwater temperature is progressively increased while flowing inside the heat exchanger pipes of the flash stages. Initially steam from a boiler or some other source such as a power plant is used to preheat feed seawater. The saline feedwater is then introduced into the first flash chamber. The vapors produced are then condensed inside the heat exchanger pipes inside of the chamber where the cold stream is feed seawater. This condensate which is freshwater is collected. Inside these chambers the heated seawater is also sent to other flashing chambers which have their pressures being decreased using either steam ejectors or by vacuum pumps. The pressure drop causes the brine to boil rapidly producing a flashing effect [4, 16, 17]. The schematic of the workings of MSF plant is shown in Figure 1.5 [17].
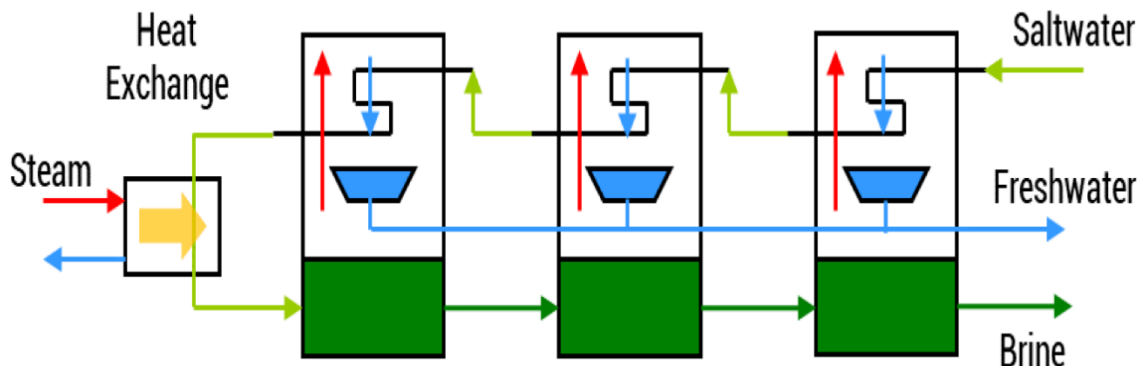
Figure 1.5: Schematic of a Multiple Stages Flash Distillation plant

1.3.3 Different Vapor Compressions

There is a desalination technology known as vapor compression desalination, which is based on liquid–vapor phase transition. There are two types:

- Mechanical vapor compression (MVC)
- Thermal vapor compression (TVC)

In mechanical vapor compression (MVC), initially the feedwater is preheated by a recovery heat exchanger and then it is sprayed onto heat exchange pipes inside of a chamber to produce vapors, which are then compressed using mechanical compressor so their temperature and pressure, and compressed vapors are entered into the main heat exchanger, where they are condensed by transferring heat to the feedwater. The brine is collected at the bottom of the chamber and is recirculated. The outflow of the main heat exchanger is further condensed by the recovery heat exchanger and freshwater is obtained [16, 17]. A simple schematic diagram of a MVC plant is depicted in Figure 1.6.
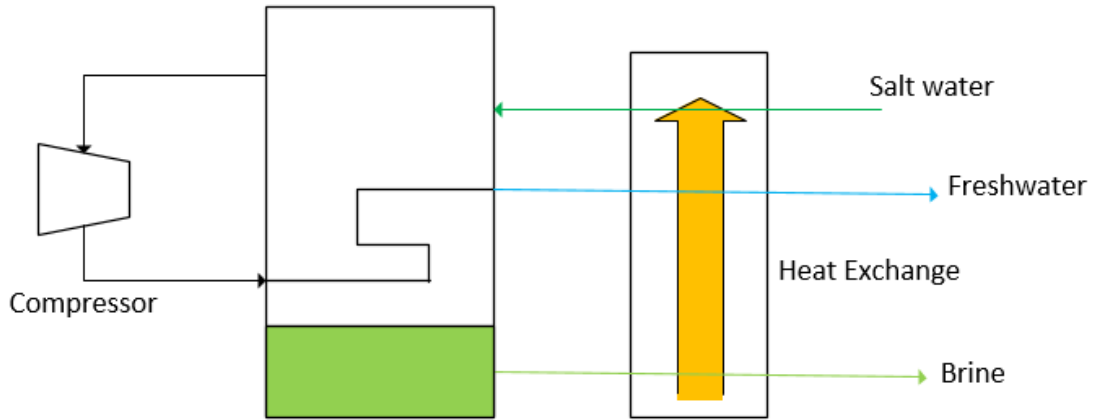
Figure 1.6: Schematic of a MVC plant

Thermal Vapor Compression (TVC) works on the basis of a similar approach. The only difference between TVC and MVC is that in TVC a steam powered compressor is used for increasing the pressure of the vapor. The high temperature steam for operating the compressor is obtained from a boiler or recycled steam from a turbine. Other than the compressor used instead of a mechanical compressor, otherwise the procedure is the same [16, 17]. The schematic of a simple TVC plant is presented in Figure 1.7.

1.3.4 Use of Solar Stills (SSD) and Solar Chimneys (SC) for Distillation

An SSD uses a black tank full of saline water covered with inclined glass. Solar radiation evaporates the water and then it condenses on the glass surface. The condensate is then collected. This only has small scale application [16]. Figure 1.8 shows the schematic of a simple solar still. A solar chimney plant (SC) is made up of many smaller stills where

freshwater is collected into. The chimney is a large plastic sheet fashioned into a specific shape [18]. Figure 1.9 shows the schematic of a basic solar chimney.
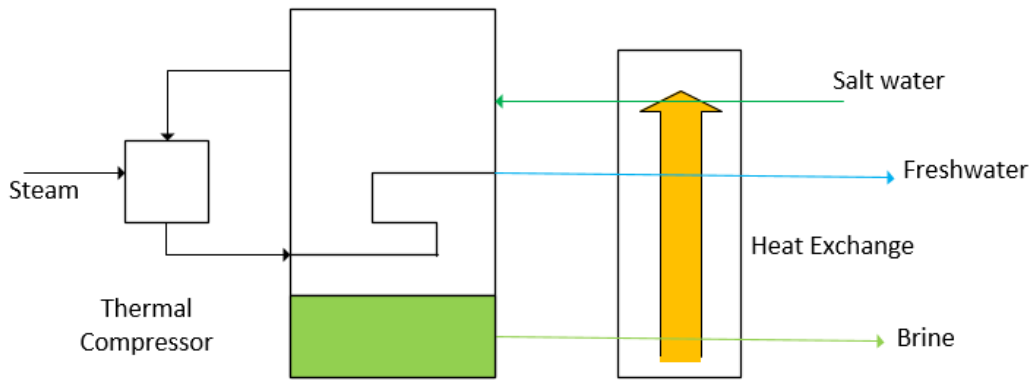
Figure 1.8: Schematic of a Thermal vapor compression (TVC) unit
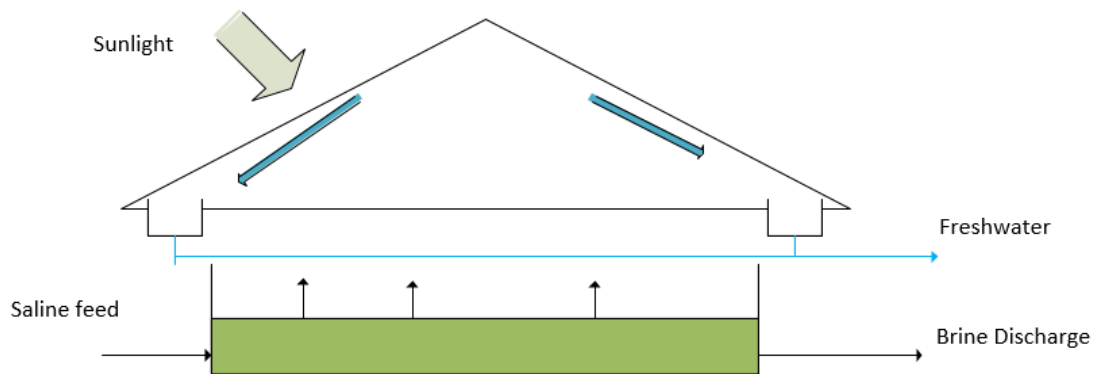
Figure 1.7: Solar Still

1.3.5 Desalination by Electro-dialysis

This electrochemical desalination technique. The technique is composed of the electrical field between two electrodes to attract the ions and a semipermeable membrane is installed between the electrodes to stop the motion of either cations or anions depending on the membrane [16]. Figure 1.10 depicts the basic schematic of electrodialysis process.

1.3.6 Desalination by Capacitive Deionization

In capacitive de-ionization desalination (CDI), there are two electrodes, one positively charged and one negatively charged, and the ions are attracted towards their respective charge and then trapped in micropores in the electrodes. The electrodes need to be regenerated which limits the efficiency of this process [16]. Figure 1.11 demonstrates the

working principle.
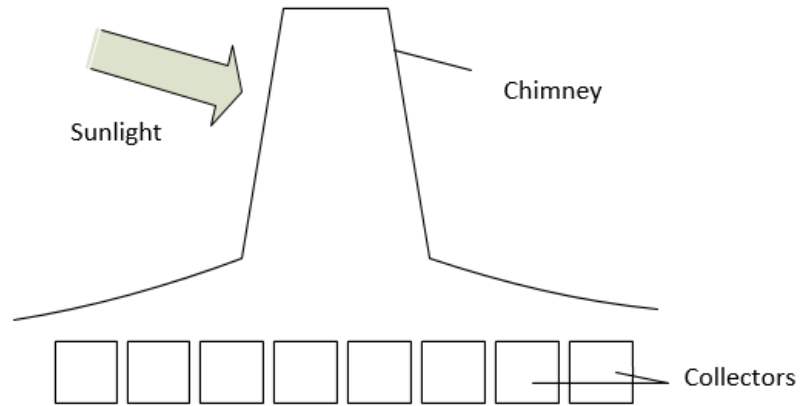
Figure 1.9: Solar Chimney desalination
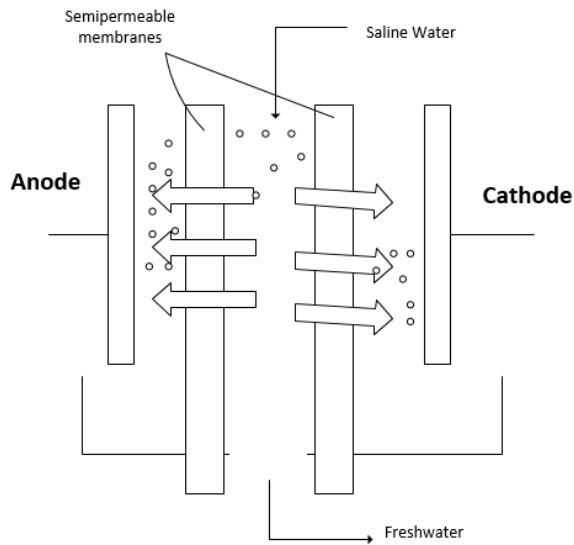
Figure 1.10: Schematic of an Electrodialysis desalination unit
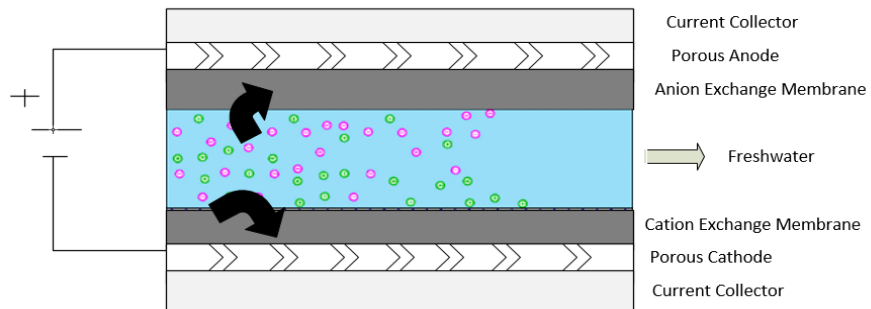
Figure 1.11: Schematic of an Electrodialysis desalination unit

1.3.7 Hydration (HY)

In hydration (HY) desalination, gas hydrates are formed, which consist of a host molecule (water) and a guest molecule (gas), and are crystalline solids [19, 20]. It can be seen that 1 m^3 of hydrates dissociates to give 164 m^3 of gas and 0.8 m^3 of water [21]. In this process seawater is refrigerated and mixed with propane and CO_2 and then crystallized to form hydrates. The hydrates are decomposed to form freshwater and gas, which is then recycled [21]. Figure 1.12 shows a basic schematic of hydration desalination [22].
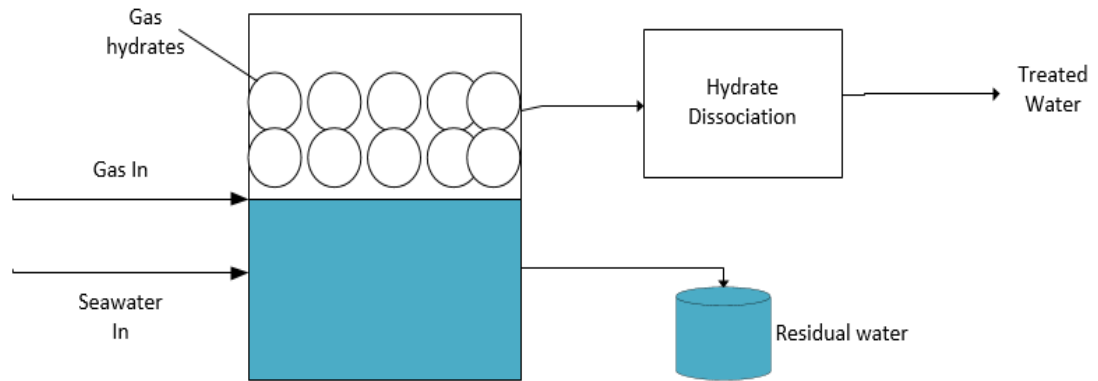
Figure 1.12: Schematic of a Hydration desalination unit

1.3.8 Desalination by Secondary Refrigerant Freezing

The desalination technique that utilizes solid-liquid phase transition of seawater is known as desalination by SRF, secondary refrigerant freezing [23]. The process involves the refrigerant freezing the sea water. The heat is transferred from one chamber to the other to melt the frozen saline water. Saline water refrigerated and frozen and then melted to produce freshwater. The main problem in this process is cleaning the ice [18]. Figure 1.13 shows a schematic of SRF desalination [24].

1.3.9 Humidification–Dehumidification (HDH)

HDH consists of a humidifier and a dehumidifier. Inside the humidification chamber, the sea water is nebulized to promote evaporation. The vapors that are produced then move to the dehumidification chamber. In this process a refrigerant refrigerates the saline water and then the cold sea water induces condensation of the air humidity in the dehumidification chamber and freshwater is obtained [25]. Figure 1.14 shows a basic schematic of HDH [26].

11
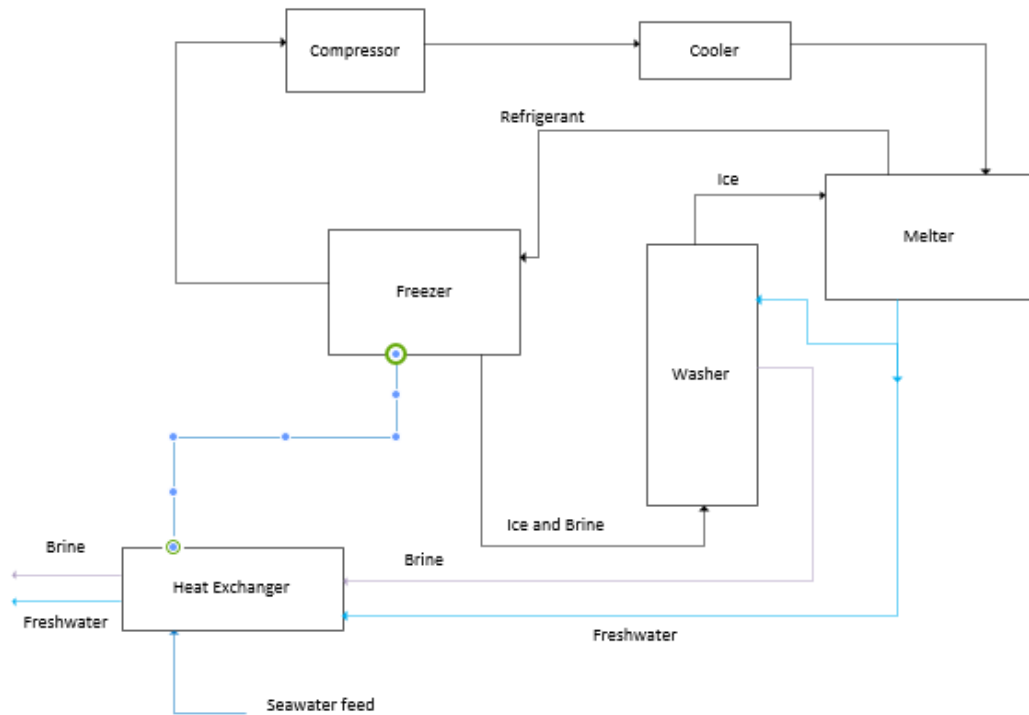
Figure 1.13: Schematic of Secondary Refrigerant Freezing desalination unit
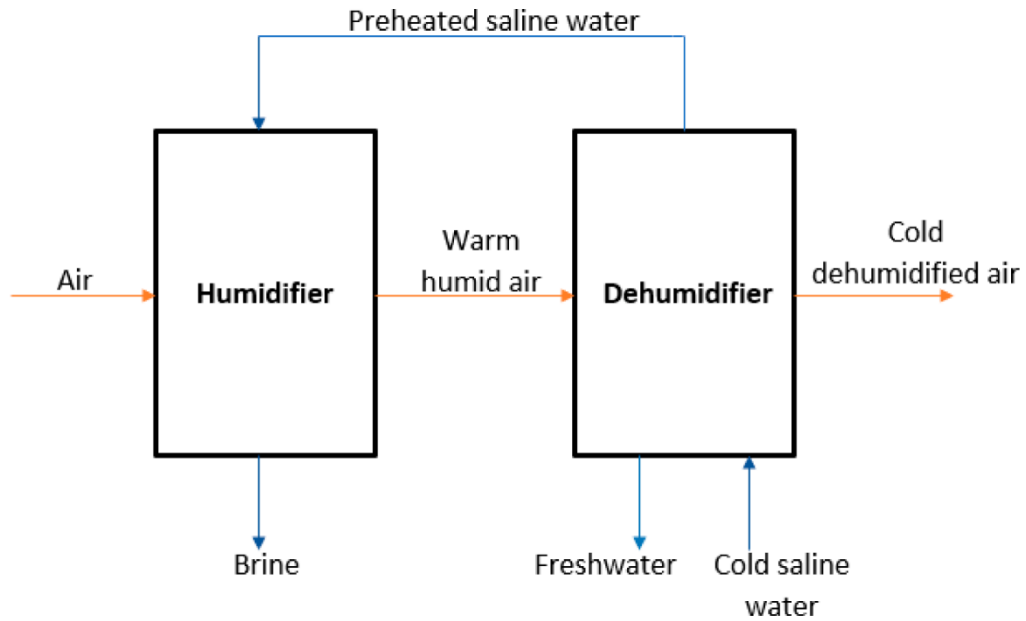
Figure 1.14: Schematic of HDH unit

1.3.10 Desalination by Ion Exchange

In desalination by ion exchange, saline water passes though acidic or basic resins, adsorption occurs and the ions are captured to give freshwater. To completely remove all ions an amphoteric resin is used which consists of a mix of acidic and basic [16, 24].

Figure 1.15 represents a schematic of this process.
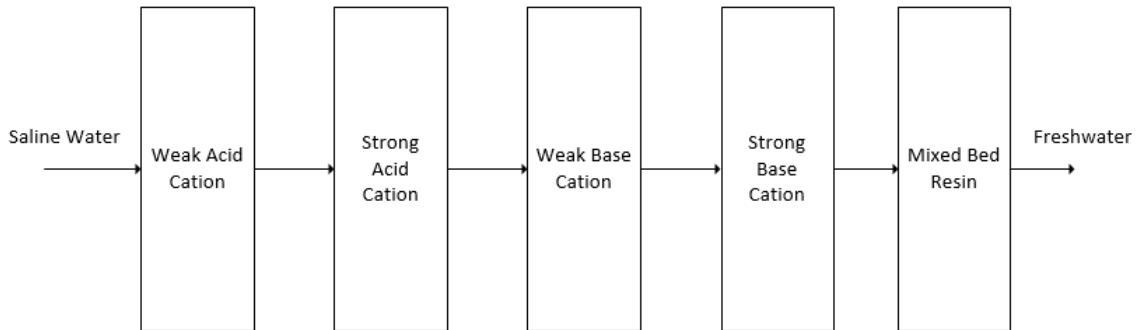
Figure 1.15: Schematic of an Ion-Exchange Resin desalination unit

1.3.11 Membrane Distillation (MD)

MD utilizes hydrophobic membranes since water vapors are able to pass while salts are rejected [27]. A major disadvantage is the heat energy used in the phase change and incomplete latent heat recovery in the MD process [28]. MD consumes less heat than MSF and MED, and operates at lower pressure than other membranes-based technologies such as RO. The drawbacks of MD are fouling and wetting which are mitigated by pretreatments [29], by surface modification [30], by increasing turbulence [31], and periodical cleanings [32-34]. Figure 1.16 shows the different configurations of MD [35].

In DCMD, the two solutions are directly in contact with the membrane. The vapors produced on the surface of the hot solution cross through the membrane into cold solution due to the pressure difference [16]. In AGMD, there is an air gap in between the membrane and the cold solution. The vapors cross from the hot solution into the cold solution then the vapors are stopped by a buffer layer of air which aids the vapors in not losing excess heat and reduces heat loss in hot solution at expense of lower mass flow rate [16]. In SGMD, there is a sweeping gas that flows between the layers of the cold side and the membrane. This process works similarly to AGMD. Only difference is that sweeping gas increases the mass flow rate of the vapors while increasing the thermal efficiency [16]. In the VMD configuration, there is vacuum in between the layers of membrane and the cold side which greatly increases the configuration, there is vacuum in between the layers of membrane and the cold side which greatly increases the thermal efficiency [16].

13
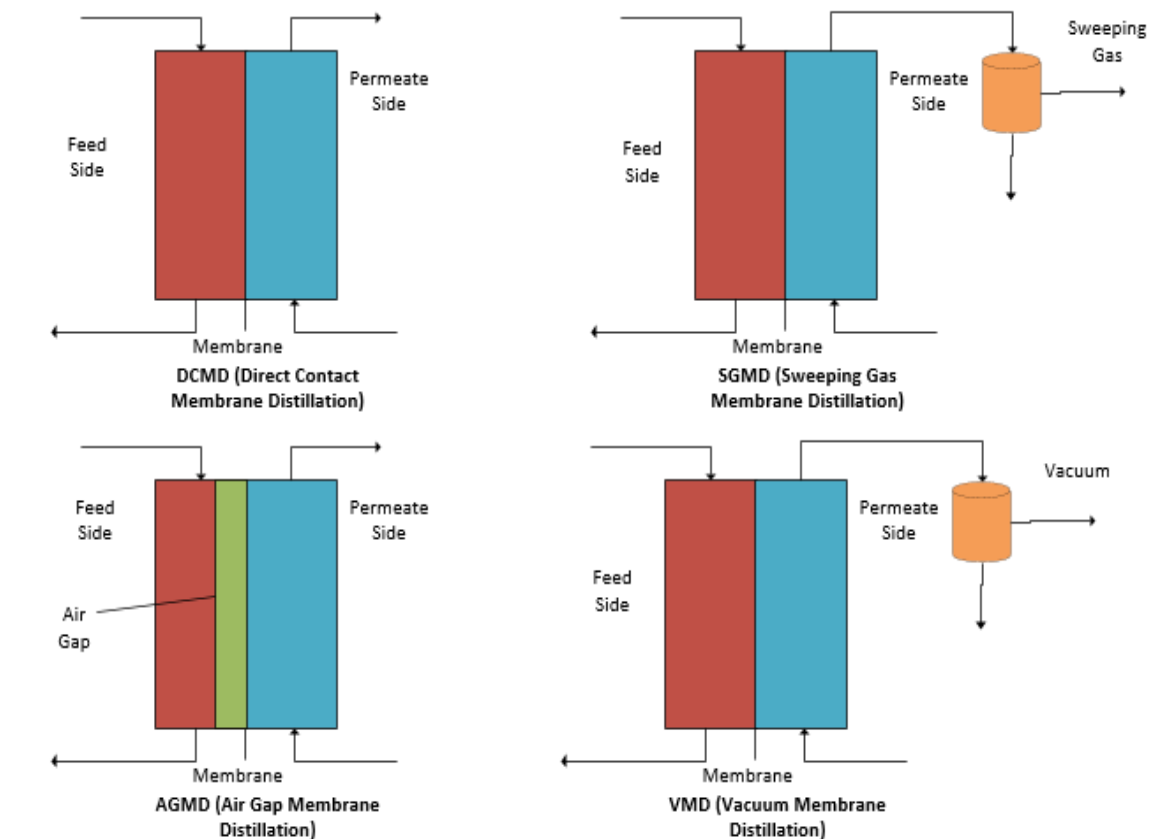
Figure 1.16: Different configurations of a Membrane Distillation (MD) unit

1.3.12 Reverse Osmosis (RO)

RO is a pressure driven membrane process. During the RO process, pressure is applied to overcome the osmotic pressure so that the water flows against the gradient across the membrane leaving a greater concentration of salt on one side [4]. The permeate obtained is freshwater while the retentate (brine) is discarded. Figure 1.17 shows the basic schematic of RO.

1.3.13 Nanofiltration (NF)

Among the pressure driven membrane processes, nanofiltration removes all contaminants including multivalent ions such as Ca^{2+}, Mg^{2+}, etc. as well as organic material and produces soft water. It is called nanofiltration because the pore size of the membranes ranges from 1 to 10 nm, which is a smaller pore size than other water treatment membranes. Only the pore sizes of reverse osmosis membranes are smaller [16, 24]. Figure 1.18 shows the basic schematic of nanofiltration.

14
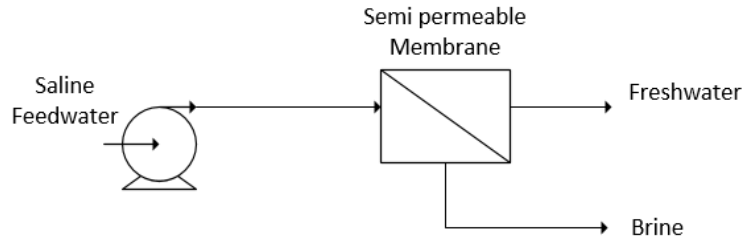
Figure 1.17: Basic Reverse Osmosis desalination unit
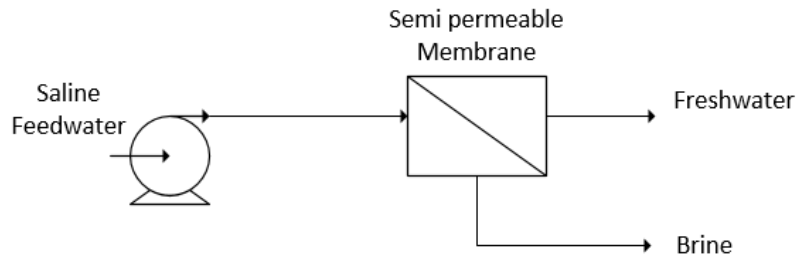
Figure 1.18: Schematic diagram of a nanofiltration unit

1.3.14 Forward Osmosis (FO)

Forward osmosis (FO) is a membrane-based separation technique that uses the osmotic pressure difference as a driving force. During the process the lower osmotic pressure side, called the feed solution (FS), is concentrated, and the higher osmotic pressure side, called the draw solution (DS), is continuously diluted by water. In contrast to RO, no additional pressure is required [36]. The main membrane morphology used in FO is the TFC membrane. The major drawback of FO is internal concentration polarization (ICP). The fouling of the pores of the support by salt particles due to the reverse salt flux leads to ICP. ICP is basically when the inside of the membrane active layer becomes diluted and the diffusion gradient decreases which leads to decrease in mass transfer and FO performance [37]. Figure 1.19 shows the basic schematic of forward osmosis [36].

1.4 Comparison of Technologies

The most dominant desalination technology used worldwide is RO. The installed global capacity for various technologies is as follows: 68.7% RO ,17.6% MSF, 6.9% MED 3.4% NF, 2.4% ED, and 1% others out of a total 95.37×10^6 m³/day [38]. Figure 1.20 shows the energy consumption of different technologies [39].
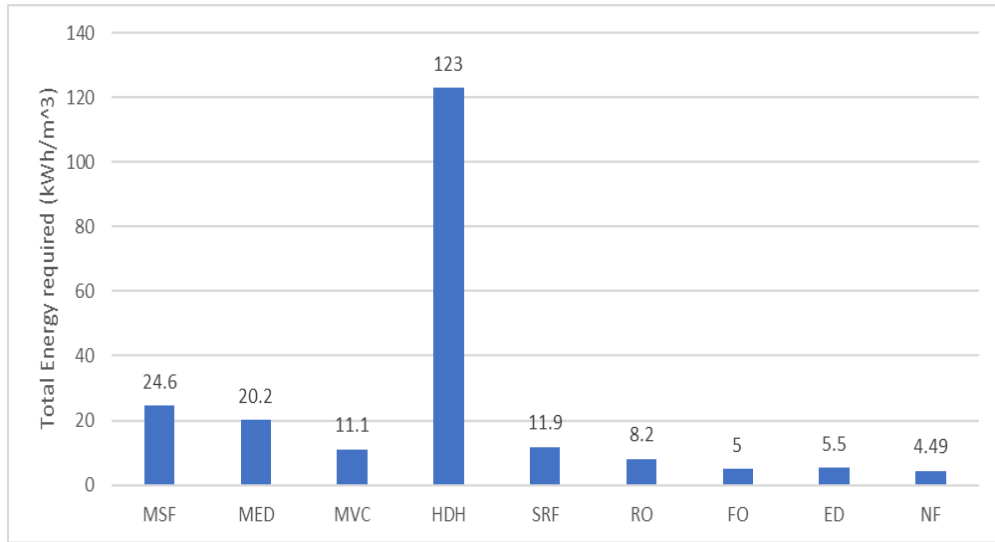
Figure 1.19: Energy Required for Different Technologies
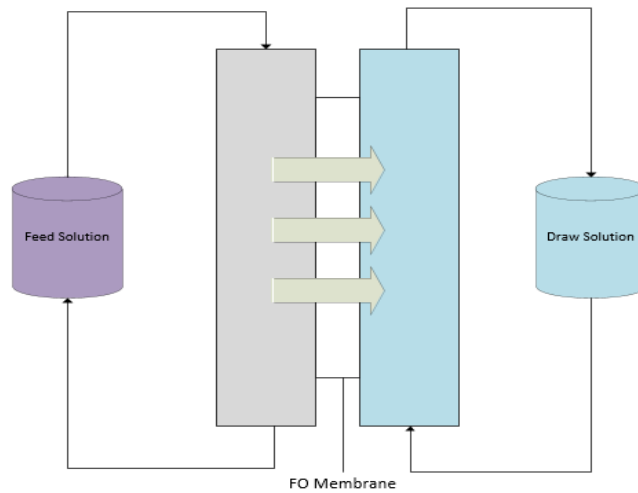
Figure 1.20: Working of a basic forward osmosis desalination unit

Figure 1.20 clearly shows that forward osmosis (FO) consumes less energy than the dominant commercial technologies. Furthermore, pressure-driven membrane technologies all face the same drawbacks, i.e., membrane fouling, pretreatments and high energy requirement. FO is an osmotic pressure-driven membrane process that has the potential to mitigate these drawbacks.FO has been gaining interest mainly due to its low fouling tendency and lower energy consumption [40, 41]. FO is widely used in desalination and waste water treatment because of its lower energy demand [42]. Different desalination technologies are compared in Table 1.1 [16].

16

Table 1.1: Comparison of Desalination Technologies

Technique	Advantage	Disadvantage
Multiple effects distillation	- Requirement of energy is relatively low	- Scaling on the pipes
MSF	- Maintenance is easier than MED with high quality product and higher capacity	- High investment with greater energy demand - Needs to be stopped for maintenance and has corrosion problem
MVC	- High quality product and requires less energy	- Low production capacity
RO	- Low capital investment and only uses electricity - Modular design and can be coupled	- Lower water quality - Fouling and high cost of membranes
NF	- Less energy needed	- Produces soft water (a diluted saline solution)
FO	- Lower energy demand	- Fouling and internal concentration polarization
ED	- High quality product with energy requirement is proportional to feed	- Bacteria are not removed - Brackish feed only

CDI	-	Greater efficiency than ED	-	Brackish feed only
HY	-	Could be more efficient than other technologies in the future	-	High costs
SRF	-	Has energy efficiency potential	-	Uses large amount of electricity - Not easily operatable
Membrane Distillation	-	Operation with no pressure requirement	-	Needs pretreatments - Fouling
IXR	-	Only need to pump water	-	Brackish feed only
SSD	-	Runs off sunlight and inexpensive	-	Small scale
SC	-	Runs off sunlight	-	Small scale
HDH	-	Low temperature requirement	-	Needs optimization

1.5 Thin Film Composite Membranes

The dominant morphology used in nanofiltration (NF) and reverse osmosis (RO) processes is thin film composite membrane. TFC membranes are primarily composite membranes made up of a polymeric support layer (usually made of polysulfone (PSf), polyether sulfone (PES) or polyacrylonitrile (PAN)) followed by a selective ultrathin top layer. The support layer is in the ultrafiltration range and phase inversion process makes it. The polyamide top layer is deposited during IP, interfacial polymerization [43]. Figure 1.21 depicts the structure of TFC [43].

1.6 Interfacial Polymerization

A polymerization reaction that occurs between two very reactive monomers at the interface of two immiscible solvents after which a very thin layer is deposited upon the porous support. Typically the support layer is immersed in an aqueous solution containing an amine monomer and is then contacted with an immiscible organic (typically hexane) acyl chloride solution [43]. Figure 1.22 shows a typical IP reaction [44].
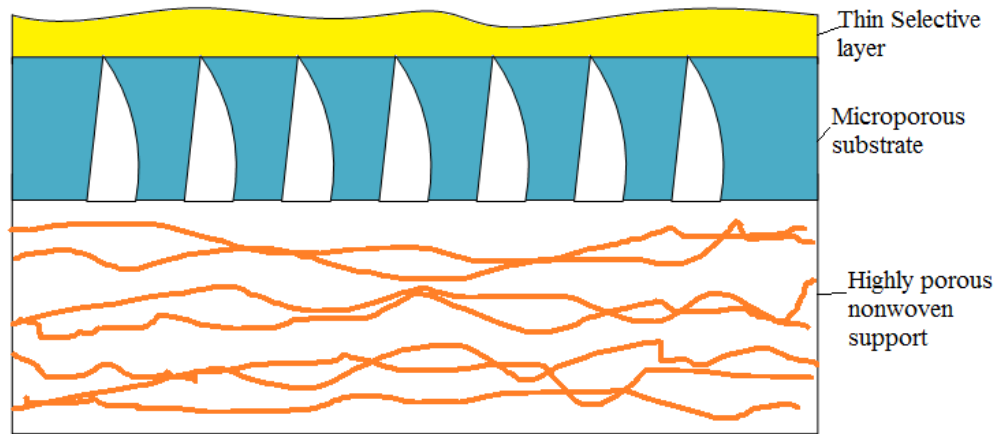
Figure 1.21: Structure of a thin film composite (TFC) membrane
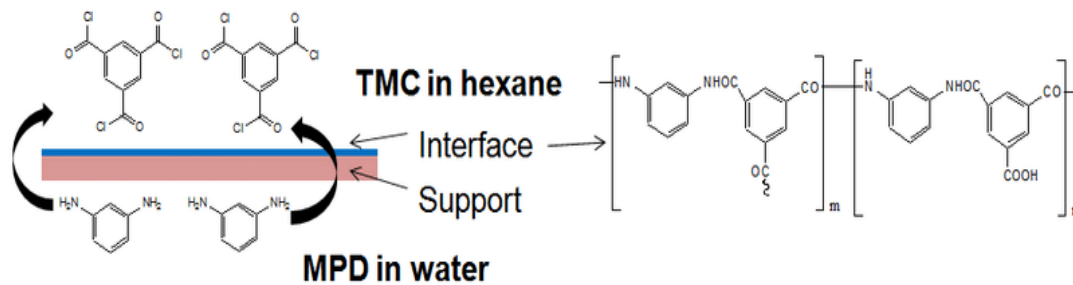
Figure 1.22: Typical Interfacial Polymerization Reaction

1.7 Phase Inversion

Phase inversion by immersion precipitation is widely used for the preparation of microfiltration (MF) and ultrafiltration (UF) membranes. The process involves the transformation of polymer solution into a solid porous sheet by immersion in nonsolvent. During immersion the pores are formed by the demixing of solvents. During the solidification phase the demixing leads to pores forming in the polymer matrix [45]. There are multiple factors affecting phase inversion.

1.7.1 Polymer Solution Concentration

The polymer solution concentration determines the amount of polymer present at the interface and consequently higher weight fraction of polymer will lead to lower porosity and higher membrane thickness [45].

1.7.2 System of the Solvent Combination

Nonsolvent miscibility in the solvent is important during the demixing stage. The polymer must be completely miscible in the solvent and must not be miscible in the nonsolvent. The solvent and nonsolvent must also be miscible with each other. The degree of miscibility will determine the rate of demixing which will affect amount of porosity obtained [45].

1.7.3 Evaporation Time

When using a volatile solvent or cosolvent, the amount evaporation time after casting solution is casted onto a sheet of metal or glass determines the amount of polymer present at the interface during the immersion step. This will affect the thickness of membrane and the porosity [45].

1.7.4 Composition of Polymer Solution

The solvent used in the polymer solution must be able to completely dissolve the polymer and also have affinity towards the nonsolvent in the coagulation bath. Additive s may also be added to the solution such as nonsolvent or pore forming agent. This will affect whether the demixing will be delayed or instantaneous, which affect the degree of porosity [45].

1.7.5 Composition of Coagulation Bath

The composition and the temperature of the coagulation bath is very important. The choice of the solvent, addition of another solvent to the coagulation bath and the temperature of the bath will affect the rate of demixing and ultimately the porosity of the membrane [45].

1.8 PET as Support

Pulido et al. (2019) fabricated ultrafiltration membranes from recycled PET using phase inversion technique. Commercial water bottles were used as the source of PET. TFA was used as solvent. The polymer concentration in the casting solution was varied to optimize the membrane characteristics. PEG use as an additive was investigated. PEG acted as a pore forming additive. The membranes produced were ultrafiltration membranes with a MWCO of 40,000 g mol^{-1} and able to withstand temperatures up to 100 °C. However, these membranes are limited to ultrafiltration application [46]. Park et al. (2019) fabricated sustainable green TFC membranes using supports made from recycled polymer waste (PET) and conducted interfacial polymerization using plant-based monomers and green

solvents. The selective layer was ultrathin (30 nm). It had acetone permeance of 13.7 LMBH with a 90% of styrene dimer (235 Da) rejection. The long-term stability was checked in six different solvents for one week. However, this membrane has very poor monovalent and divalent salt rejection and pure water permeance was not checked [47]. Kusumocahyo et al. (2021) fabricated ultrafiltration membranes from PET from waste plastic bottles. PEG 400 as the additive was used as an additive. Increasing the PEG 400 concentration resulted in a membrane with smaller pore size that was more hydrophilic and more porous. The casting solution was made by dissolving PET in phenol and heating to 100 °C. The coagulation bath contained 1:12 water-ethanol solution as non-solvent. The best performing membrane had 94% bovine serum albumin (BSA) rejection. These membranes are limited to ultrafiltration application and their fabrication requires heat, additives and special conditions [48]. Lu et al. (2021) fabricated eco-friendly ultrafiltration membranes using polysulfone (PSf) with green solvent mixture of gamma-valerolactone and PolarClean and recycled PET as an additive. The fabricated membranes with evaporation time of 30 seconds outperformed conventional polysulfone membranes by having 3.5% higher permeance (23 LMBH) and 53.2% higher BSA, bovine serum albumin, rejection of 85%. By increase the evaporation time after casting to 1 minute decreased the permeance by 32.4% and led to only a negligible solute rejection increase. Using zero seconds waiting time after casting caused 235% permeance increase. These membranes also only have ultrafiltration application and the use of PET as an additive had a negligible role in the membrane performance [49]. Rajesh et al. (2014) fabricated ultrafiltration membranes using recycled PET and polyvinyl pyrrolidone (PVP) and m-cresol is used as the solvent. They were fabricated using phase inversion method. PEG was used as additive and the effect was investigated. Increasing PEG concentration increased the pure water permeance. These membranes are limited to ultrafiltration application and have low permeances compared to other membranes. The use of recycled PET does yield membranes suitable for water separation processes [50].

1.9 Performance Comparison of Forward Osmosis Membranes

The performances of different novel forward osmosis membranes were compared in the table below.

Table 1.2: Comparison of performances of different membranes

Type of membrane	Filler	Water Flux (J_w) (L/m^{2}h, LMH)	Reverse Salt Flux (J_s) (g/m^{2}h, gMH)	Js/Jw (g/L)	FS (feed solution)	DS (draw solution)	Year	Reference
PSf/PA thin-film nanocomposite (TFN) membranes	0.1 wt% UiO-66 MOF	20.7	4.3	0.21	DI (deionized water)	1 M NaCl	2017	[51]
PSf/PA thin-film nanocomposite (TFN) membranes	6.5 wt% UiO-66 MOF	24.5	4.4	0.18	DI	1 M NaCl	2017	[52]
TFC formed using glass nanofiber support layer and bovine serum albumin (BSA)-embedded PA active layer	BSA, bovine serum albumin, loading at 0.2 wt%	54	5	0.09	DI	2 M NaCl	2018	[53]

PSf/PA thin-film nanocomposite (TFN) membranes	0.05 wt% ZIF-8@PDA	20.8	5.2	0.25	DI	1 M MgCl$_2$	2019	[54]
PSf/PA TFC membranes	Polydopamine over graphene oxide interlayer, 0.5 g/L GO	24.296	3.818	0.157	DI	1 M NaCl	2019	[55]
PES/PA thin-film nanocomposite (TFN) membranes	0.1 wt% UiO-66-(F)$_4$	38.7	11.6	0.3	DI	1 M NaCl	2019	[56]
PES/PA thin-film nanocomposite (TFN) membrane	250 ppm graphene quantum dots (GQDs) @ UiO-66-NH$_2$	59.3	19.1	0.32	DI	1 M NaCl	2020	[57]

Membrane	Nanomaterial				Feed	Salt	Year	Ref
PSf/PA thin-film nanocomposite (TFN) membranes	0.5 wt.% titania nanotubes and magnetite oxide hybrid nanoparticles (TNT–Fe_3O_4)	2.54, 2.82	0.15, 0.19	0.06, 0.07	10 mg/L Pb^{2+}, 10 mg/L Cd^{2+}	1 M NaCl	2020	[58]
PAN/PA thin-film nanocomposite (TFN) membranes	0.04 wt% Sulfonated graphene oxide (SGO) @ UiO-66	14.77	2.95	0.2	DI	1 M NaCl	2020	[59]
PES/PA thin-film nanocomposite (TFN) membranes	0.0005 wt% Size-controlled graphene oxide (SGO) nanosheets	39	6.24	0.16	DI	1 M NaCl	2020	[60]
PAN/PA thin-film nanocomposite (TFN) membranes	0.01 wt% PDA/MOF-801	16.5	3.3	0.2	DI	1 M NaCl	2020	[61]

PES/PA thin-film nanocomposite (TFN) membranes	0.1 wt% PVA/PDA @ZIF-8	14.2	6.1	0.43	DI	1 M MgCl$_2$	2021	[62]
PES/PA thin-film nanocomposite (TFN) membranes	0.5 wt% Charcoal-based carbon nanomaterial (charcoal-CNM	12.08	2.97	0.24	DI	1 M NaCl	2021	[63]

Ma et al. (2017) incorporated UiO-66 nanoparticles into the active layer of TFC to fabricate TFN membrane which resulted in a 52% increase in water permeability over pristine TFC membrane while maintaining salt rejection levels at ~95% [51]. Then later Ma et al. (2017) incorporated UiO-66 nanoparticles into active layer as well as support to investigate ICP mitigation. They found that 50% increased water flux over the pristine membrane and observed no significant degradation of water permeability is observed over 72-h operation [52]. Zhao et al. (2018) prepared a TFC with support membranes made from glass fibers and employed the strategy of increasing the hydrophilicity of the top layer by using BSA as an additive in the interfacial polymerization. The prepared membranes fulfilled the application of forward osmosis and rejection of heavy metals was also tested [53]. Qiu et al. (2019) used polydopamine (PDA) to modulate ZIF-8 nanoparticle to increase the compatibility of the MOF with the membrane. Compared with pristine TFC membrane, the membrane exhibited a increase of the water flux (80%) without losing of selectivity (ratio of J_s/J_w) [54]. Hyeon-gyu et al. (2019) made a TFC with PDA and graphene oxide (GO) interlayer on a PSf support. This interlayer improved the membrane's hydrophilicity and the water flux improved 56% [55]. Bagherzadeh et al. (2019) synthesized UiO-66-(F)$_4$ and incorporated it into active layer. Due to hydrophilic property and owning specific pore size, the utilized MOF improved the water permeability by 85% while maintaining selectivity [56]. Bagherzadeh et al. (2020) modified UiO-66-NH$_2$ MOFs to increase their hydrophilicity by using graphene quantum dots, GQD. Incorporating the modulated MOFs in the top layer of TFC improved permeability by 102% as well as the selectivity by 150% [57]. Soo et al. (2020) synthesized (TNT–Fe$_3$O$_4$) nanoparticles and made TFN with them. This increased the hydrophilicity of the TFN. The incorporation of nanoparticles did not impact the selectivity but increased the flux by 100% [58]. He et al. (2020) developed a sulfonated graphene oxide modulated MOF to make a TFN for forward osmosis application. Compared to unmodified TFC and the TFN made with UiO-66 MOF, the pure water flux of SGO@UiO-66 TFN was increased by 41% and 8% and the reverse salt flux was reduced by 49% and 51% [59]. Lim et al. (2020) incorporated size-controlled graphene oxide (SGO) into the top layer of TFN. The membranes had increased resistance to fouling and when compared to TFN with bulk GO, results showed flux increased by 30% with same selectivity [60]. Miaolu et al. (2020) made a PDA modulated MOF-801 to

make a TFN and the results showed that the 30% increased flux while the selectivity increased by 56% as well as 94% heavy metal rejection [61]. Fu et al. (2021) added polyvinyl alcohol/polydopamine coated ZIF-8 into active layer of TFN membrane. This increased the resistance to fouling and the flux increased by 100% with same selectivity and showed great antifouling property as well as a permeation recovery ability of greater than 95% [62]. Hadadpour et al. (2021) added charcoal-based nanomaterial (CNM) to the support layer and prepared a TFC. The TFC had reduced ICP (internal concentration polarization) and the flux increased by 300% and the selectivity increased by 82% [63]. The above-mentioned membranes face the same challenge of achieving high water permeability and salt rejection along with controlling internal concentration polarization (ICP). All of them either used nanomaterials or an interlayer to increase the membranes' hydrophilicity, water flux and selectivities as well as modifying the support layer to mitigate internal concentration polarization (ICP) and increase hydrophilicity. However, these membranes were fabricated using environmentally harmful commercial polymeric supports, such polysulfone, poly acrylonitrile and poly ether sulfone. There needs to be focus on making the process of fabricating TFC more sustainable and cost effective. This can be achieved by using recycled polyethylene terephthalate (PET) as a polymeric material to substitute the harmful conventional supports. Membranes thus fabricated will be used to achieve high water permeability while maintaining high solute rejection at low pressure while reducing overall cost of the membranes.

1.10 Problem Statement

TFC FO could be one of the suitable potential options to achieve high water permeability as well as salt rejection during desalination. However, the high cost of the polymers used for membranes support and the use of toxic solvents during IP make them costly and unsafe for humans and the environment. Thus, replacing the current polymeric materials with waste recycled materials such as PET bottles and conventional solvents with green solvents such as deep eutectic solvents would be a great contribution towards green membrane synthesis with waste recycled materials and environmentally friendly solvents.

1.11 Research Objectives

This MS thesis is aimed at developing a green synthesis method for TFC membranes using

recycled polyethylene terephthalate (PET) for desalination using the green process of forward osmosis and performance of these membranes will be competitive with membranes prepared through conventional means. The objectives of this study are to:

- Fabricate high performance thin-film composite forward osmosis membranes for desalination using a more sustainable method.
- Fabricate the support layer using waste polymer from recycled PET bottles.
- Physiochemical characterization and performance assessment of the fabricated membranes.

CHAPTER 2

FABRICATION OF THIN FILM COMPOSITE MEMBRANES FOR DESALINATION USING FORWARD OSMOSIS

2.1 Introduction

Nowadays plastics are widely used and have become a big part of modern life, because of attributes like production cost is small, ability to be molded into different shapes, and other unique properties [7]. The production of plastics was reported to be around 359 metric tons in 2018, and it is predicted that it will only triple in the next 30 years [10]. It is estimated that 18% of the world's plastic production consists of PET [12]. Only a small amount of the waste PET bottles are recycled, which means that the PET bottles need to used in more different ways and not just thrown away, which causes pollution on the Earth [13]. It is estimated millions of bottles are thrown in the trash daily and it is projected to double over the many coming years and many of these bottles are made from PET [14]. It is clear that there is a need to reduce the pollution caused by these plastic bottles by reusing and recycling them.

Currently the used PET bottles that are recycled are used for the production of new bottles through various recycling processes. These waste PET bottles are already used to produce different lower value items such as plastic furniture, more bottles, carpets, etc. There is a need for processes that use waste PET bottles to produce high-value products like for example, membranes for waste water treatment or membranes for treatment of sea water and brackish water. If these waste plastic bottles can be used to make nanofiltration membranes capable of good salt rejection, this will solve two great issues, one is the recycling of waste PET bottles as well as provide freshwater form sea water or brackish water by different membrane processes.

Application of membranes for desalination involves synthesis of membranes in the nanofiltration range by interfacial polymerization (IP). However, the conventional supports, i.e., polysulfone, poly acrylonitrile and poly ether sulfone, used in the IP are not environmentally friendly. Thus, there is a strong need to replace these supports with the greener ones to achieve the concept of sustainability in membrane fabrication. In addition, the replacement of expensive polymers with the cheaper alternatives will help to reduce the overall cost of the membranes. This MS thesis is aimed at developing a green synthesis method for TFC membranes using recycled polyethylene terephthalate (PET) as a polymeric material to substitute the harmful conventional supports. Membranes thus

fabricated will be used to achieve high water permeability while maintaining high solute rejection at low pressure.

TFC FO could be one of the suitable potential options to achieve high water permeability as well as salt rejection during desalination. However, the high cost of the polymers used for membranes support and the fact that they are products of environmentally unfriendly fossil fuel industry, make them costly and unsafe for humans and the environment. Thus, replacing the current polymeric materials with waste recycled materials such as PET bottles would be a great contribution towards green membrane synthesis with waste recycled materials.

2.2 Materials and Methods

2.2.1 Chemicals

All chemicals and solvents for the procedure were analytical grade. Tri-mesoyl chloride (TMC) from Shanghai Greenearth Chemicals (China). Sodium chloride, Ethanol, and Acetone were bought from Sigma Aldrich (Germany). Other solvents such as Di-chloromethane (DCM), Trifluoroacetic acid (TFA) and NMP were provided by DaeJung Chemicals & Metals (South Korea). Sodium carbonate were purchased from Penta Chemicals (Czech Republic). Piprazine was provided by Oakwood chemicals. Polypropylene non-woven supports provided Freudenberg Filtration Technologies (Germany).

2.3 Extraction of PET

The method for PET extraction was adopted from Pulido et al. (2019), with little changes. The PET was extracted from unpigmented transparent waste plastic bottles. The waste plastic bottles were first washed with dish soap and then washed with acetone. Then the bottles were cut into smaller pieces and then followed by air drying. The pieces were then dissolved in a 1:2 solution of in TFA (trifluoroacetic acid) and DCM (dichloromethane) to make 20 wt% PET solution. 32 g of PET were dissolved in a mixture of 30 mL of trifluoroacetic acid (TFA) and 60 mL of dichloromethane (DCM). The solution was stirred for 24 hours using a magnetic stirrer. The PET was then precipitated in ethanol and then dried at 70°C for 24 hours. The pure PET obtained was like white fibers and was further

used for membrane fabrication [46]. Figure 2.1 gives a visual representation of the process.

Figure 2.1: Extraction of PET

2.4 Fabrication of Support

The extracted PET was then dissolved in TFA to make a 16 wt% solution, followed by 24 hours of stirring using magnetic stirrer. The ideal concentration of 16% was determined from a previous study. The extracted PET fibers and the washed and air-dried PET pieces were used interchangeably, since from a previous study, it was found that this does not affect the membrane performance [46]. The supports were fabricated by phase inversion.

A non-woven polypropylene support was taped onto a glass plate. The polypropylene supports were soaked in NMP and the excess NMP was removed from the surface using paper towels. The polymer solution was cast onto the support using Elcometer 4340 automatic film applicator device. After casting, evaporation time of 0 seconds was given, then immersed in a water bath for 15 minutes. The prepared membrane was rinsed with water and then stored in DI water for further use. Figure 2.2 shows the support preparation process and figure 2.3 shows the prepared membrane.
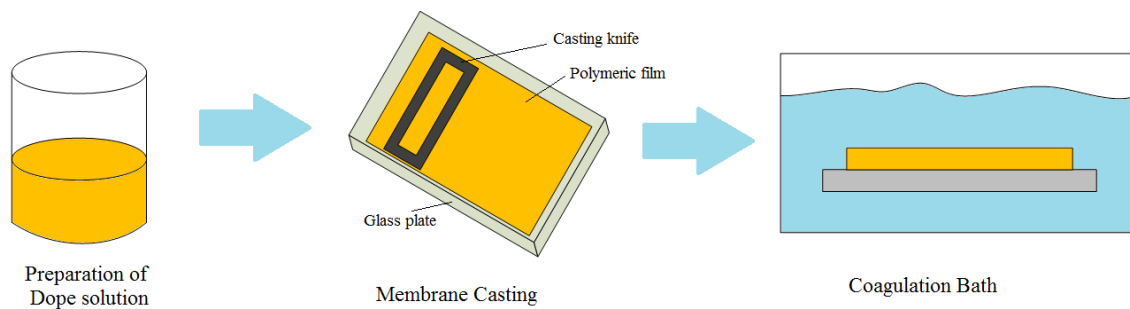
Figure 2.2: Fabrication of Membranes by Phase Inversion Method

Figure 2.3: Synthesized PET Membrane

2.5 Fabrication of Thin film Composite Membrane

The PET supports were taped onto the interfacial polymerization membrane module and the soaked in 2% (w/v) aqueous piperazine solution for 10 minutes followed by air drying for 5 min. Excess amine solution was dabbed off using foam. They were then contacted with 0.1% (w/v) TMC solution in hexane for 2 minutes followed by air drying for 5 minutes and then were cured at 80°C for 5 minutes to obtain thin film composite (TFC) membrane. The prepared membrane was rinsed with water and then stored in DI water for further use [64]. Figure 2.4 shows the TFC preparation process and figure 2.5 shows the prepared membrane.


| Soaked with Piperazine | Contacted with TMC | Cured at 80°C | Fabricated TFC |
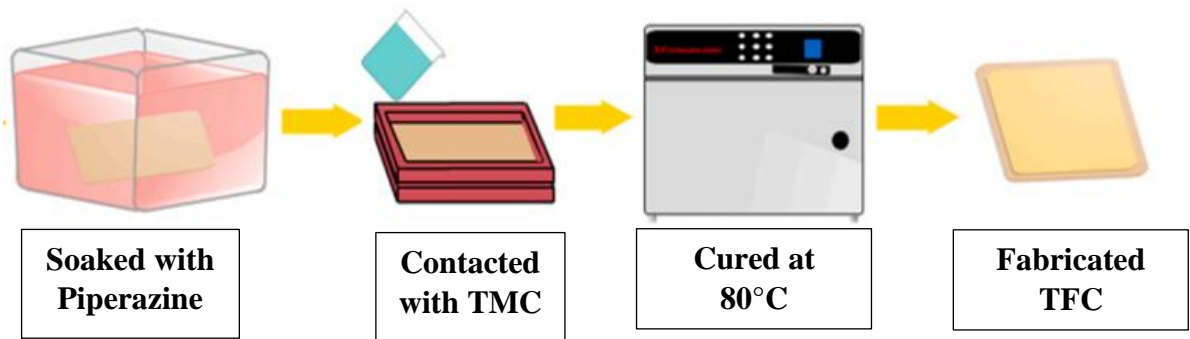
Figure 2.4: Preparation of TFC

Figure 2.5: Fabricated TFC

2.5 Characterization techniques

2.5.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy, FTIR, is the technique for determining the functional groups of a sample. Fourier transform infrared spectroscopy (FTIR) shows the absorption of the infrared spectrum of the sample. Due to the bending and stretching of different functional groups different wavelengths are absorbed. Thus, corresponding functional groups are identified by comparing the absorbance. Thermo-Nicolet 6700 P FTIR Spectrometer (USA) was used to obtain results for the PET sample.

2.6 Testing membrane performance

2.6.1 Dead-end Filtration

The membranes were tested using dead end filtration system (Sterlitech HP 2950, USA). The experimental setup is shown in figure 2.6.
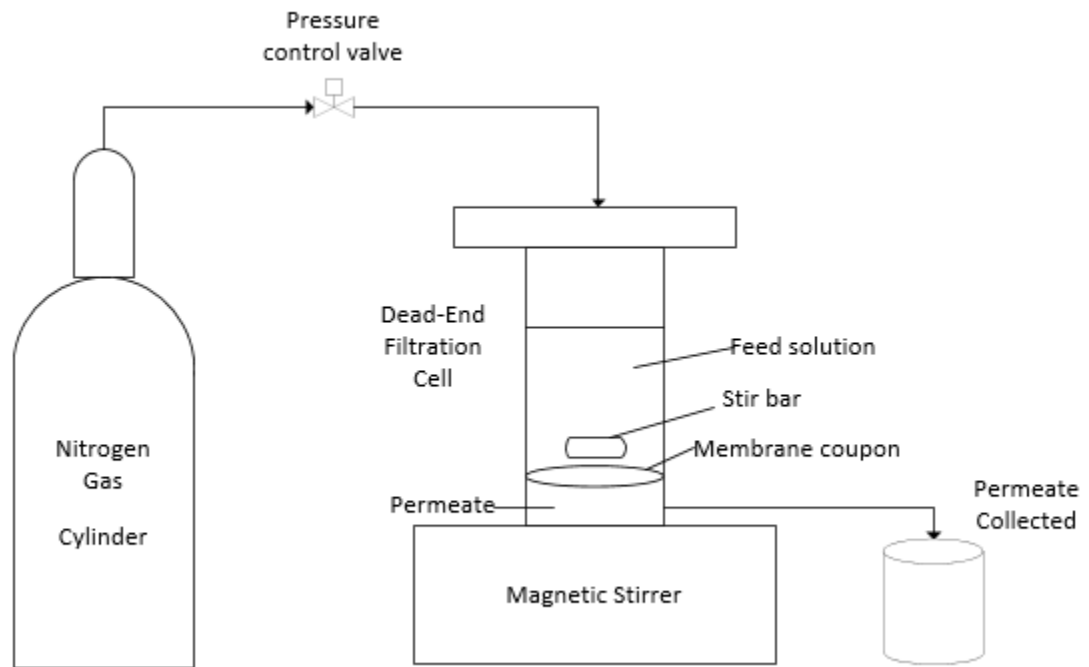
Figure 2.6: Dead-end Filtration Setup

A circular membrane coupon with, effective area of 0.008 m^2, was cut a placed at the bottom of the dead-end filtration cell and held in place using a porous disc. The cell was filled with about 250 ml of feed solution. Then pressure was applied using the nitrogen gas

cylinder and regulated using the control valve. The membranes were compacted for 10 minutes after which permeate was collected at regular intervals at constant pressure. The pure water permeances and salt rejections of various membranes were calculated using the formulas given below [65].

$$\mathbf{Permeance} = \frac{\mathbf{V}}{\mathbf{At\Delta P}}$$

Where,

V = permeate volume (L)

A = effective membrane area (m^2)

ΔP = applied pressure (bar)

t = time elapsed (hr)

$$\boldsymbol{Salt\ Rejection}(\%) = \frac{\boldsymbol{C_{feed}} - \boldsymbol{C_{Permeate}}}{\boldsymbol{C_{feed}}} \times \mathbf{100}$$

Where ,

C_{feed} = feed conductivity (µS/cm)

$C_{Permeate}$ = permeate conductivity (µS/cm)

2.6.2 Forward Osmosis Experimental Setup

The prepared membranes were investigated under two modes:

- Forward osmosis (FO) mode i.e., active layer towards feed solution
- Pressure retarded osmosis (PRO) mode i.e., active layer towards draw solution

Figure 2.7 shows a visual representation of these different orientations.
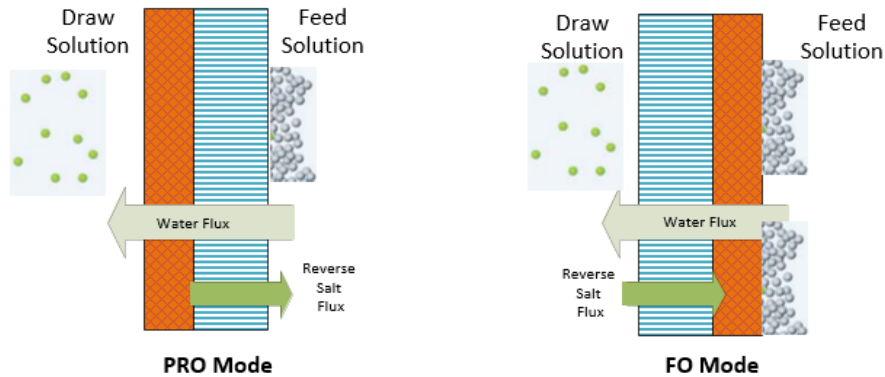
Figure 2.7: Forward Osmosis Operating Modes

36

Figure 2.8 below shows experimental setup used for conducting the experiments. The feed solution was DI water and draw solutions of different concentrations of NaCl solutions of 0.5, 1.0 and 2 M were used. All experiments were performed at 25 °C. The total experimentation time was 1.5 hours and the change in weight of the feed solution and the conductivity of the feed solution were measured at 30 minute intervals. The FO water flux Jw (LMH) and the solute reverse flux Js (gMH) were calculated using formulas given below [56].
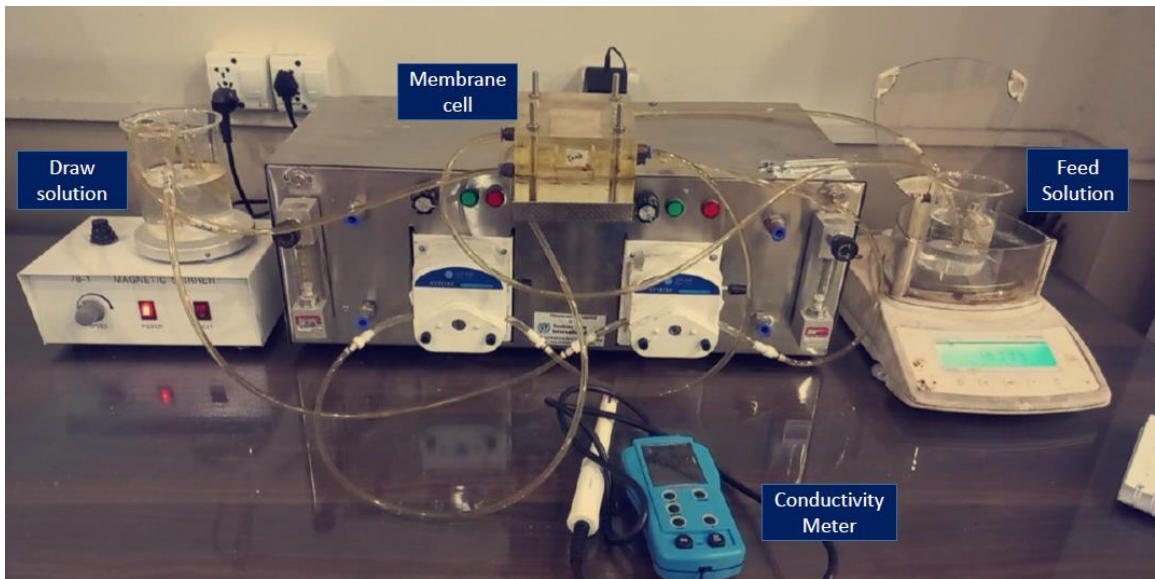
Figure 2.8: Forward Osmosis Setup

Water flux $(J_w) = \dfrac{\Delta V}{A_m \Delta t}$

Where,

ΔV= change in volume of feed solution (L)

A_m= effective membrane area (m^2)

Δt= time elapsed (hr)

Reverse Salt Flux $(J_s) = \dfrac{(C_{final} V_{final} - C_{initial} V_{initial})}{A_m \Delta t}$

Where,

C_{final} = final concentration of salt (g/L)

V_{final} = final feed solution volume (L)

$C_{initial}$ = initial concentration of salt (g/L)

$V_{initial}$ = initial feed solution volume (L)

A_m= effective area membrane (m^2)

Δt= time elapsed (hr)

The NaCl concentrations were obtained from conductivity-concentration calibration curve drawn by measuring conductivities at different NaCl concentrations. It is presented in Figure 2.9.
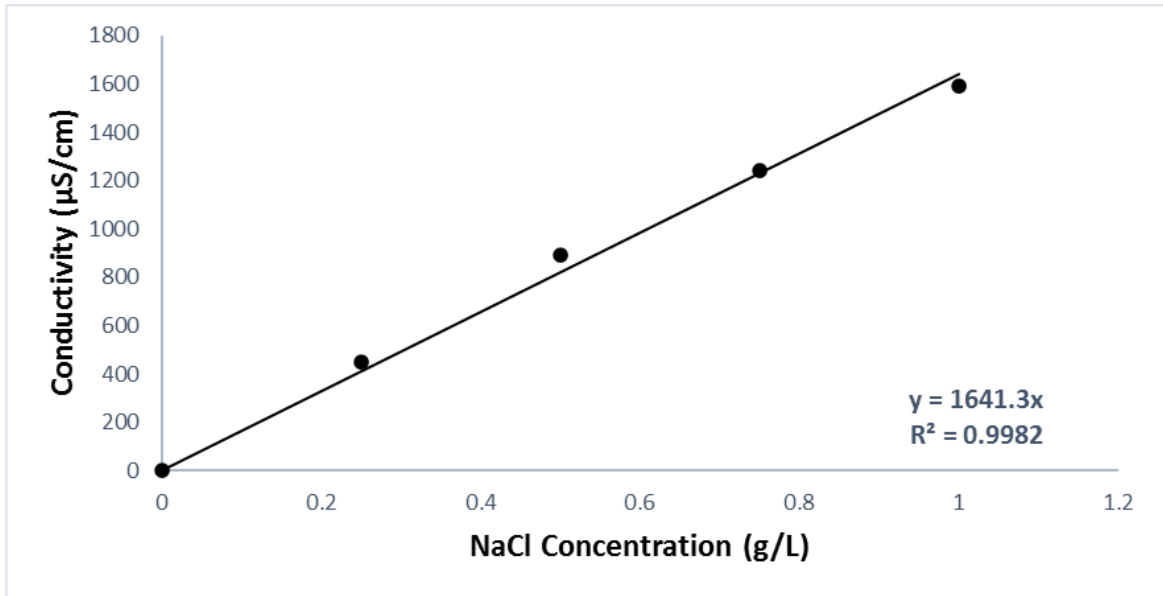
Figure 2.9: Conductivity-Concentration Calibration Curve

Selectivity $= J_s/J_w$

Where,

Js= reverse salt flux (gMH)

Jw= water flux (LMH)

2.5 Results & Discussions

2.5.1 Characterization of PET

The characteristic peaks of the ATR-FTIR spectra are at 2964, 1712, 1408, 1241, 1094, 1017, 871, and 722 cm^{-1}. The stretching of carbonyl of the ester group is shown by the peak at 1712 cm^{-1}. The peak at 2964 cm^{-1} is due to aliphatic CH stretching. The peak at 1408 cm^{-1} is due to the vibrations of the phenyl ring. The peak at 1241 cm^{-1} is due to the stretching

of CO bond from the ester group. The peak at 722 cm^{-1} is due to ethyl group stretching [46].
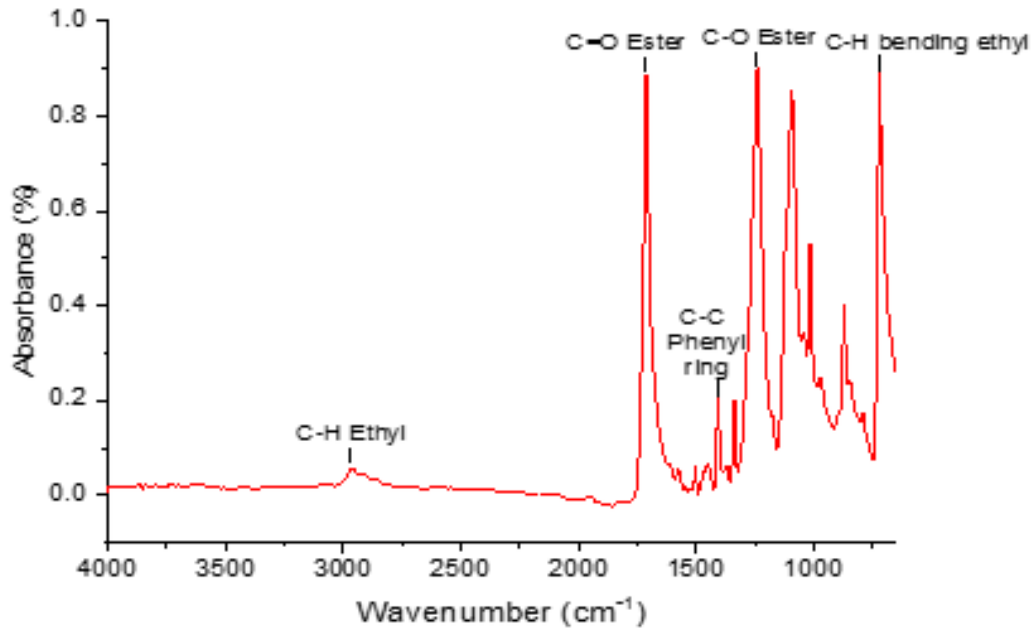
Figure 2.10: PET support FTIR spectrum

2.5.2 Optimization of PET support

The effect of casting speed on the PET support was studied. The casting solution consisted of 16 wt% PET with TFA as a solvent. TFA is a highly volatile solvent so the evaporation time after the membrane was casted played a big role in morphology of the final membrane formed. During phase inversion process, the evaporation time controls the membrane porosity, membrane thickness and its permeance [66]. More evaporation time resulted in the formation of denser membranes. For desalination, more porous support membrane are preferred. Faster casting speeds resulted in lower evaporation times and more porous membranes were formed. Three membranes, M1, M2 and M3 were prepared at 5, 6, 7 cm/sec casting speeds respectively. The results are shown in figure 2.11. The optimal support membrane was obtained at 7 cm/sec with a performance of 13 ± 2 LMBH.

2.5.3 Effect of Curing Temperature

In a TFC membrane, the polyamide top layer is responsible for majority of salt rejection. During the process of fabricating TFC, the polyamide top layer was cross-linked due to heat of the oven. A higher curing temperature would result in a higher degree of cross-

linking of the polyamide layer which would result in greater salt rejection [67]. The results of varying the curing temperature are shown in Figure 2.12. The optimal curing temperature of 80 °C was obtained with a permeance of 10.6 ± 0.4 LMBH and a NaCl rejection of 22 ± 2 %.
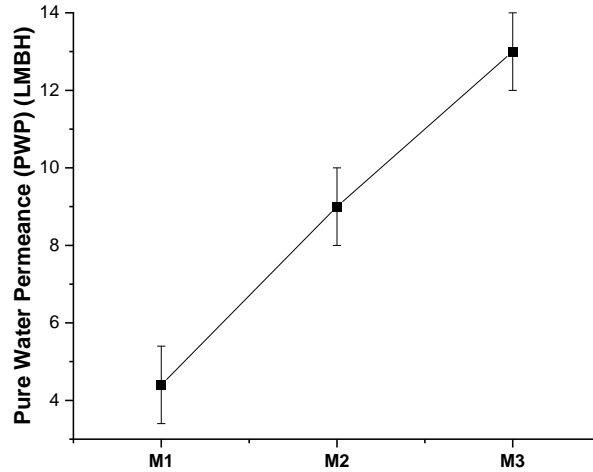
Figure 2.11: Effect of Casting Speed of Support Performance
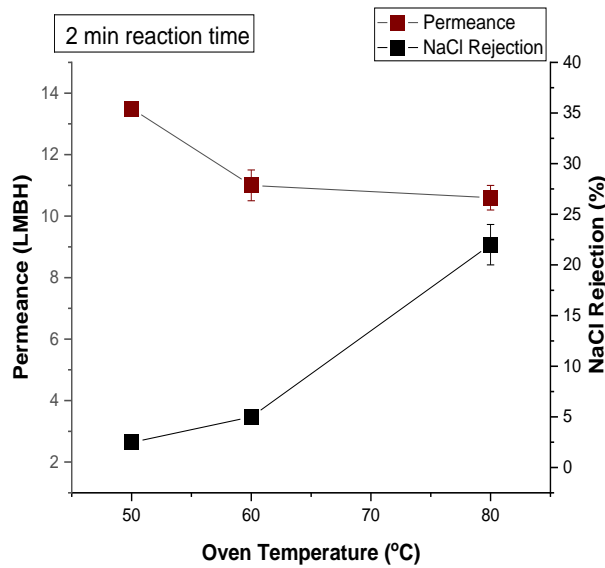
Figure 2.12: Effect of Curing Temperature on TFC Performance

2.5.4 Effect of Reaction Time

During TFC membrane fabrication process, the reaction time plays a big role in the formation of the top layer. The polyamide top layer is responsible for majority of salt rejection during the filtration process. Therefore, greater reaction time would provide more

time for the monomers to interact with each other and lead to the formation of a more cross-linked top layer [67]. For desalination applications, greater salt rejection of the membrane would be a desirable trait. The results of varying the reaction times are shown in the Figure 2.13. From these results, an optimal reaction time of 4 minutes was obtained with a permeance of 2 ± 0.1 LMBH and a NaCl rejection of 33 ± 2 %.
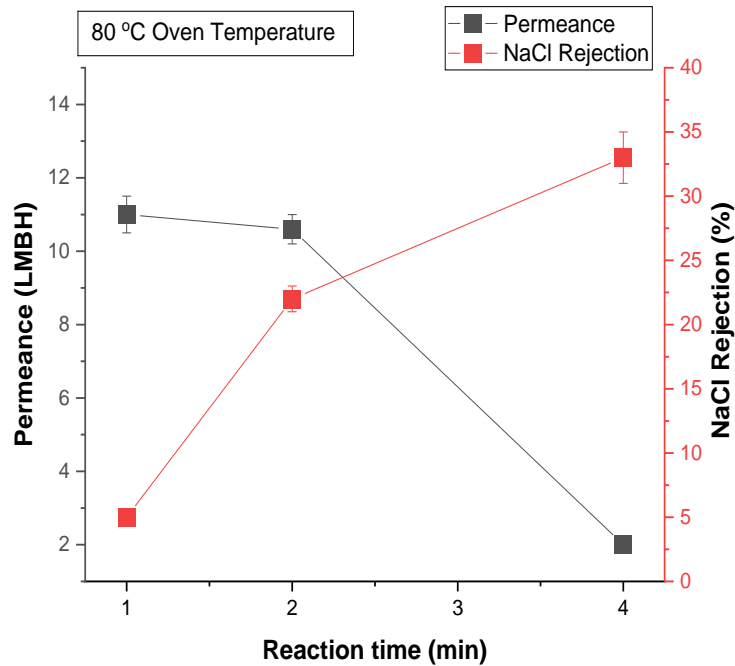
Figure 2.13: Effect of Reaction Time on TFC Performance

2.5.5 Effect of Additives

During TFC fabrication, additives can be added to the aqueous solution of amine monomer to enhance membrane performance. Some common additives are TEA (triethylamine) as an acylation catalyst and SDS (sodium dodecyl sulfate) as a surfactant. TEA captures the hydrogen chloride side product of condensation polymerization reaction between TMC and piperazine, while SDS facilitates transportation of piperazine monomers inside the support membrane pores. Addition of SDS or TEA alone does not significantly improve the membrane performance, however the combination of both TEA and SDS can improve the membrane performance [65]. In the case of TFC made with PET support the additives resulted in an increase in the permeance by 250% but greatly decreased the rejection by 68%. This can be explained by the increase in the rate of reaction due to TEA which resulted less cross-linking of the polyamide layer [68]. The results are shown in figure 2.14.

41
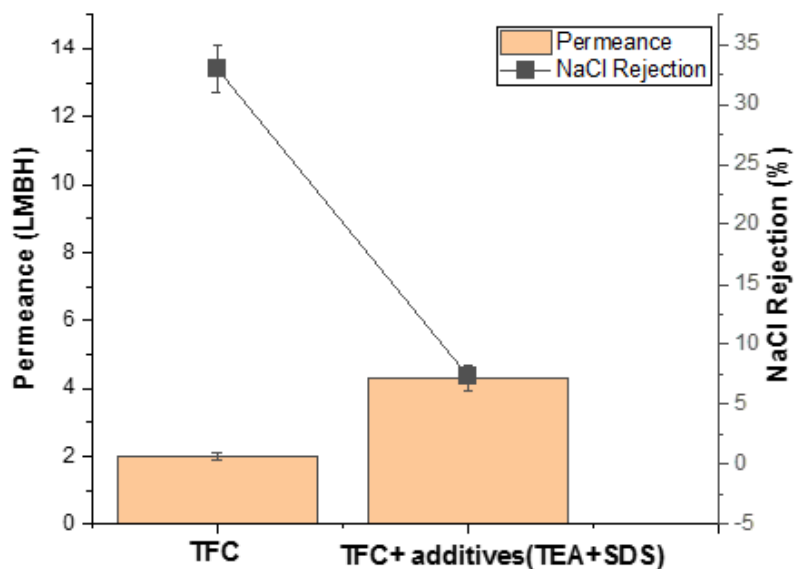
Figure 2.14 : Effect of Additives on TFC Performance

2.5.6 Forward Osmosis Results

The optimal membrane selected for forward osmosis operation had a permeance of 2 ± 0.1 LMBH and a NaCl rejection of 33 ± 2 % during dead-end filtration tests. The water fluxes and the reverse salt fluxes were obtained at different draw solution concentrations during forward osmosis testing. The higher NaCl concentrations in the draw solutions had higher osmotic pressures which led to greater water fluxes as well as greater reverse salt fluxes. Lower selectivity value indicates higher salt rejection in the membranes. The results obtained had similar selectivity to conventional TFC made with PES support [56]. The results of the testing conducted in forward osmosis orientation are shown in table 2.1 and figure 2.15.

Table 2.1: FO Orientation Results

Draw Solution Concentration	Water flux (LMH)	Reverse salt flux (gMH)	Selectivity (g/L)
0.5 M	4.8 ± 0.4	2.4 ± 0.7	0.49 ± 0.02
1 M	10.6 ± 0.5	4.2 ± 0.1	0.4 ± 0.01
2 M	13.8 ± 0.1	5.8 ± 0.4	0.42 ± 0.04
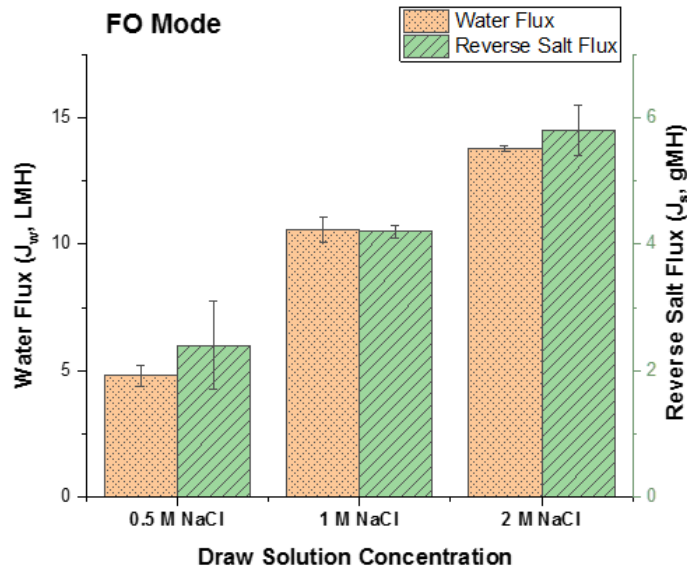
Figure 2.15: Forward Osmosis Results

The PRO mode results are shown in table 2.2 and figure 2.16. They showed a similar trend as compared to the FO results. Th e water fluxes and the reverse salt fluxes increased as the draw solution concentration increased. Increasing concentration of the draw solution led to an increase in osmotic pressure which resulted in higher water fluxes and reverse salt fluxes. When the results of operation in FO mode and PRO mode are compared, PRO mode showed greater water flux and reverse salt flux as well as a lower selectivity value at 0.5 M draw solution concentration. This was due to the lower tendency of internal concentration polarization (ICP) in PRO mode [36]. It was also noted that PRO mode had greater fouling tendency as compared to FO mode.

Table 2.2: PRO Orientation Results

Draw Solution Concentration	Water flux (LMH)	Reverse salt flux (gMH)	Selectivity (g/L)
0.5 M	12.8 ± 0.1	4.26 ± 0.01	0.33 ± 0.05
1 M	15.7 ± 0.3	6.7 ± 0.7	0.43 ± 0.05
2 M	20.6 ± 0.4	10.7 ± 0.6	0.52 ± 0.01
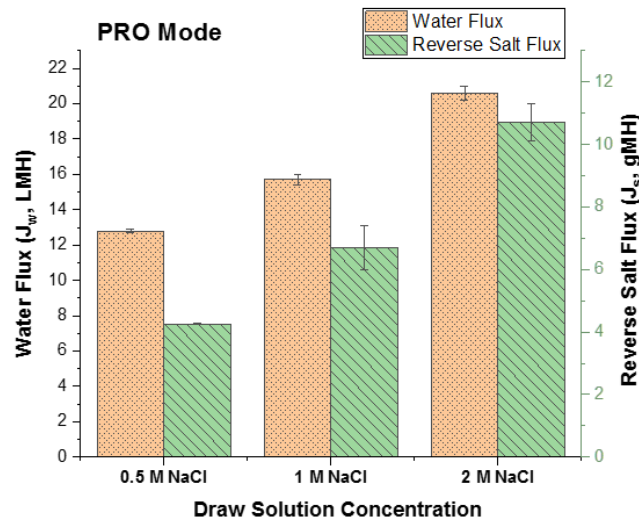
Figure 2.16: PRO Results

Figure 2.17 shows a comparison of the changing selectivities of both FO and PRO modes at different draw solution concentrations. PRO mode exhibited a lower selectivity value at 0.5 M draw solution concentration as compared to FO mode. The selectivities of both modes were more or the same at 1 M draw solution concentration. At 2 M draw solution concentration, PRO mode showed little higher selectivity value as compared to FO mode. Greater selectivity values indicate greater reverse salt flux for every liter of water that passes through the membrane [56].
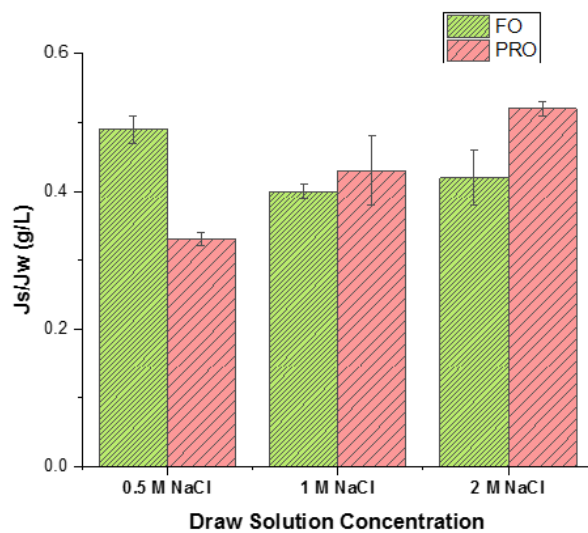
Figure 2.17: Selectivity of Membranes

44

CHAPTER 3

CONCLUSION AND FUTURE WORK

3.1 Conclusion

PET bottles were carefully selected and purified into pure PET fibers. The purified PET was used to successfully to fabricate supports for TFC membranes. The various parameters governing permeance and salt rejection of TFC were optimized. The effect of increasing the casting speed of support membranes from 5 cm/s to 7 cm/s resulted in a 190% increase in the pure water permeability. Increasing curing temperature during the TFC fabrication process to 80 $^{\circ}$C from 50 $^{\circ}$C increased the NaCl rejection from 2% to 22%. Furthermore, it was found that increasing the reaction time from 2 minutes to 4 minutes increased the NaCl rejection from 22% to 33% with a permeance of 2 $Lm^{-2}bar^{-1}h^{-1}$. The addition of TEA and SDS to the amine monomer solution worsened the membrane performance by decreasing the NaCl rejection by 68%. In this way an optimized TFC was obtained using optimal reaction time of 4 minutes and optimal curing temperature of 80 $^{\circ}$C. The FO performance of the optimized TFC was tested by using varying draw solution concentrations of 0.5 M, 1 M, and 2 M NaCl and using different operating modes.

The following results were obtained from this research work:

- TFC membranes were successfully fabricated using recycled waste PET supports
- The TFC membranes had FO performance of 10.6 LMH and a selectivity of 0.4 g/L for 1M NaCl draw solution concentration.
- The fabricated TFC had comparable selectivity in FO performance compared to conventional TFC membranes

In summation, this research showed the potential for transforming waste plastic bottles into viable forward osmosis membranes. The effects of different parameters were investigated in order to optimized the fabrication of membranes however the long-term performance of these membranes could not be tested.

3.2 Future Work

There is a great potential for further study such as employing a modulated interfacial polymerization approach to fabricating the TFC using different additives and solvents. Nanoparticles could also be incorporated into the TFC to make thin film nano-composite membranes. Nanoparticles could also be incorporated into the PET support to make mixed matrix membranes. Membrane fouling studies could be conducted. The rejections of other

salts, dyes and heavy metals could also be checked. The effect of adding hydrophilic additives, co-solvents and pore forming agents to the casting solution could be tested. Long term performance of membranes as well as long term stability in different solvents could be tested.

3.3 Research Limitations

The fabricated membranes had a hydrophobic nature owing to the fact that they were fabricated using inherently hydrophobic PET, so they are better suited to organic solvent nanofiltration rather than desalination application. The fabricated membranes also had greater fouling tendency than conventional TFC membranes, which could greatly limit their long term performance.

During the fabrication of PET supports, some amounts of material was wasted due to the presence of pin hole defects in the formed membranes. These pinholes were caused by entrapped air bubbles in the casting solution as well as the interaction between NMP and the casting solution. NMP, which was used to wet the polypropylene supports prior to casting, was not the ideal option and a better option could be investigated.

3.2 Practical Implications of Study

Recently, Pakistan has resolved to adopt the 17 sustainable development goals set forth in agenda 2030. Goal 12 of the agenda is to ensure sustainable consumption and production patterns. 4 out of the 11 targets of this goal are concerned with reducing waste and managing it in a sustainable way. Target 5 is concerned with reducing and recycling waste [69]. This study could help in the fulfillment of this goal.

Chapter 4

References

4.1 References

1. Yeit Haan, Teow, and Mohammad Abdul Wahab. "New Generation Nanomaterials for Water Desalination: A Review." *Desalination* 451 (2019): 2-17.

2. Marrium Almas, Dutt, Hanif Muhammad Asif, Nadeem Farwa, and Bhatti Haq Nawaz. "A Review of Advances in Engineered Composite Materials Popular for Wastewater Treatment." *Journal of Environmental Chemical Engineering* 8, no. 5 (2020): 104073.

3. Elimelech, Menachem, and William A. Phillip. "The Future of Seawater Desalination: Energy, Technology, and the Environment." 333, no. 6043 (2011): 712-17.

4. Akili, D. Khawaji, K. Kutubkhanah Ibrahim, and Wie Jong-Mihn. "Advances in Seawater Desalination Technologies." *Desalination* 221, no. 1 (2008): 47-69.

5. "What Is Desalination?", 2021, accessed July 27, 2022, 2022, https://www.fluencecorp.com/what-is-desalination/#:~:text=Nations%20that%20rely%20heavily%20on,mostly%20in%20California%20and%20Florida.

6. Negewo, B.D. *Renewable Energy Desalination: An Emerging Solution to Close the Water Gap in the Middle East and North Africa.* World Bank Publications, 2012.

7. Barnes, David KA, Francois Galgani, Richard C Thompson, and Morton %J Philosophical transactions of the royal society B: biological sciences Barlaz. "Accumulation and Fragmentation of Plastic Debris in Global Environments." 364, no. 1526 (2009): 1985-98.

8. Idumah, CI, M Zurina, J Ogbu, JU Ndem, and EC %J Composite Interfaces Igba. "A Review on Innovations in Polymeric Nanocomposite Packaging Materials and Electrical Sensors for Food and Agriculture." (2019).

9. Li, Gaolin, Zhenhua Jiang, Weilin Wang, Zengyong Chu, Ye Zhang, and Chunhua %J Nanomaterials Wang. "Electrospun Pan/Mapbi3 Composite Fibers for Flexible and Broadband Photodetectors." 9, no. 1 (2019): 50.

10. Tournier, V, CM Topham, A Gilles, B David, C Folgoas, E Moya-Leclair, E Kamionka, *et al.* "An Engineered Pet Depolymerase to Break Down and Recycle Plastic Bottles." 580, no. 7802 (2020): 216-19.

11. Samuel, P. Kusumocahyo, K. Ambani Syarifa, Kusumadewi Sylvia, Sutanto Hery, I. Widiputri Diah, and S. Kartawiria Irvan. "Utilization of Used Polyethylene Terephthalate (Pet) Bottles for the Development of Ultrafiltration Membrane." *Journal of Environmental Chemical Engineering* 8, no. 6 (2020): 104381.

12. Leng, Zhen, Rabindra Kumar Padhan, and Anand Sreeram. "Production of a Sustainable Paving Material through Chemical Recycling of Waste Pet into Crumb Rubber Modified Asphalt." *Journal of cleaner production* 180 (2018): 682-88.

13. Chinchillas-Chinchillas, Manuel J, Alberto Gaxiola, Clemente G Alvarado-Beltrán, Víctor M Orozco-Carmona, Manuel J Pellegrini-Cervantes, Margarita Rodríguez-Rodríguez, and Andrés %J Journal of Cleaner Production Castro-Beltrán. "A New Application of Recycled-Pet/Pan Composite Nanofibers to Cement–Based Materials." 252 (2020): 119827.

14. Magnier, Lise, Ruth Mugge, and Jan %J Journal of cleaner production Schoormans. "Turning Ocean Garbage into Products–Consumers' Evaluations of Products Made of Recycled Ocean Plastic." 215 (2019): 84-98.

15. "Breaking the Plastic Wave: Top Findings for Preventing Plastic Pollution." 2020, accessed November 10, 2022, 2022, https://www.pewtrusts.org/en/research-and-analysis/articles/2020/07/23/breaking-the-plastic-wave-top-findings.

16. Curto, Domenico, Vincenzo Franzitta, and Andrea Guercio. "A Review of the Water Desalination Technologies." *Applied Sciences* 11, no. 2 (2021): 670.

17. Castro, Michael, Myron Alcanzare, Eugene Esparcia, and Joey Ocon. "A Comparative Techno-Economic Analysis of Different Desalination Technologies in Off-Grid Islands." 13, no. 9 (2020): 2261.

18. Sharon, H., and K. S. Reddy. "A Review of Solar Energy Driven Desalination Technologies." *Renewable and Sustainable Energy Reviews* 41 (2015): 1080-118.

19. Truong-Lam, Hai S., Suhkmann Kim, Seong Deok Seo, Changsu Jeon, and Ju Dong Lee. "Water Purifying by Gas Hydrate: Potential Applications to Desalination and Wastewater Treatments." *Chemical Engineering Transactions* 78 (2020): 67-72.

20. Qiunan, Lv, Li Xiaosen, and Li Gang. "Seawater Desalination by Hydrate Formation and Pellet Production Process." *Energy Procedia* 158 (2019): 5144-48.

21. Sangwai, Jitendra S, Rachit S Patel, Prathyusha Mekala, Deepjyoti Mech, and Marc Busch. "Desalination of Seawater Using Gas Hydrate Technology-Current Status and Future Direction." *Proceedings of Hydro International* (2013): 4-6.

22. Nallakukkala, Sirisha, Adeel ur Rehman, Dzulkarnain B. Zaini, and Bhajan Lal. "Gas Hydrate-Based Heavy Metal Ion Removal from Industrial Wastewater: A Review." 14, no. 7 (2022): 1171.

23. Wensheng, Lin, Huang Meibin, and Gu Anzhong. "A Seawater Freeze Desalination Prototype System Utilizing Lng Cold Energy." *International Journal of Hydrogen Energy* 42, no. 29 (2017): 18691-98.

24. Ullah, Ihsan, and Mohammad G. Rasul. "Recent Developments in Solar Thermal Desalination Technologies: A Review." 12, no. 1 (2019): 119.

25. Dahiru, Lawal, Antar Mohammed, Khalifa Atia, Zubair Syed, and Al-Sulaiman Fahad. "Humidification-Dehumidification Desalination System Operated by a Heat Pump." *Energy Conversion and Management* 161 (2018): 128-40.

26. Khraisheh, Majeda, Mehreen Inamdar, Fares AlMomani, and Samer Adham. "Humidification&Ndash;Dehumidification (Hdh) Desalination and Other Volume Reduction Techniques for Produced Water Treatment." 14, no. 1 (2022): 60.

27. Kujawa, Joanna, Sophie Cerneaux, Wojciech Kujawski, and Katarzyna Knozowska. "Hydrophobic Ceramic Membranes for Water Desalination." *Applied Sciences* 7, no. 4 (2017): 402.

28. Nick Guan Pin, Chew, Zhao Shanshan, and Wang Rong. "Recent Advances in Membrane Development for Treating Surfactant- and Oil-Containing Feed Streams Via Membrane Distillation." *Advances in Colloid and Interface Science* 273 (2019): 102022.

29. Hyeongrak, Cho, Choi Yongjun, and Lee Sangho. "Effect of Pretreatment and Operating Conditions on the Performance of Membrane Distillation for the Treatment of Shale Gas Wastewater." *Desalination* 437 (2018): 195-209.

30. Nick Guan Pin, Chew, Zhao Shanshan, Malde Chandresh, and Wang Rong. "Polyvinylidene Fluoride Membrane Modification Via Oxidant-Induced Dopamine Polymerization for Sustainable Direct-Contact Membrane Distillation." *Journal of Membrane Science* 563 (2018): 31-42.

31. Guizi, Chen, Yang Xing, Wang Rong, and G. Fane Anthony. "Performance Enhancement and Scaling Control with Gas Bubbling in Direct Contact Membrane Distillation." *Desalination* 308 (2013): 47-55.

32. Laqbaqbi, Mourad, Julio Antonio Sanmartino, Mohamed Khayet, Carmen García-Payo, and Mehdi Chaouch. "Fouling in Membrane Distillation, Osmotic Distillation and Osmotic Membrane Distillation." *Applied Sciences* 7, no. 4 (2017): 334.

33. Yuelian, Peng, Ge Ju, Li Zhehao, and Wang Shaobin. "Effects of Anti-Scaling and Cleaning Chemicals on Membrane Scale in Direct Contact Membrane Distillation Process for Ro Brine Concentrate." *Separation and Purification Technology* 154 (2015): 22-26.

34. Elena, Guillen-Burrieza, Ruiz-Aguirre Alba, Zaragoza Guillermo, and A. Arafat Hassan. "Membrane Fouling and Cleaning in Long Term Plant-Scale Membrane Distillation Operations." *Journal of Membrane Science* 468 (2014): 360-72.

35. Yan, Zhongsen, Yuling Jiang, Lingshan Liu, Zhongsheng Li, Xiaolei Chen, Mingqian Xia, Gongduan Fan, and An Ding. "Membrane Distillation for Wastewater Treatment: A Mini Review." 13, no. 24 (2021): 3480.

36. Obotey Ezugbe, Elorm, and Sudesh %J Membranes Rathilal. "Membrane Technologies in Wastewater Treatment: A Review." 10, no. 5 (2020): 89.

37. Mccutcheon, Jeffrey R., and Menachem Elimelech. "Modeling Water Flux in Forward Osmosis: Implications for Improved Membrane Design." 53, no. 7 (2007): 1736-44.

38. Edward, Jones, Qadir Manzoor, T. H. Michelle, Smakhtin Vladimir, and Kang Seong-mu. "The State of Desalination and Brine Production: A Global Outlook." *Science of The Total Environment* 657 (2019): 1343-56.

39. Youssef, P. G., R. K. Al- Dadah, and S. M. Mahmoud. "Comparative Analysis of Desalination Technologies." *Energy Procedia* 61 (2014): 2604-07.

40. Masafumi, Shibuya, Park Myoung Jun, Lim Sungil, Phuntsho Sherub, Matsuyama Hideto, and Shon Ho Kyong. "Novel Ca/Pvdf Nanofiber Supports Strategically Designed Via Coaxial Electrospinning for High Performance Thin-Film Composite Forward Osmosis Membranes for Desalination." *Desalination* 445 (2018): 63-74.

41. Wei Lun, Ang, Abdul, Johnson Daniel, and Hilal Nidal. "Forward Osmosis Research Trends in Desalination and Wastewater Treatment: A Review of Research Trends over the Past Decade." *Journal of Water Process Engineering* 31 (2019): 100886.

42. Zirehpour, Alireza, Ahmad Rahimpour, Saeed Khoshhal, Mostafa Dadashi Firouzjaei, and Ali Asghar Ghoreyshi. "The Impact of Mof Feasibility to Improve the Desalination Performance and Antifouling Properties of Fo Membranes." *RSC advances* 6, no. 74 (2016): 70174-85.

43. Seah, Mei Qun, Woei Jye Lau, Pei Sean Goh, Hui-Hsin Tseng, Roswanira Abdul Wahab, and Ahmad Fauzi Ismail. "Progress of Interfacial Polymerization Techniques for Polyamide Thin Film (Nano)Composite Membrane Fabrication: A Comprehensive Review." 12, no. 12 (2020): 2817.

44. Gabriel, Febrianto, Karisma Doni, and Mangindaan Dave. "Polyetherimide Nanofiltration Membranes Modified by Interfacial Polymerization for Treatment of Textile Dyes Wastewater." *IOP Conference Series: Materials Science and Engineering* 622, no. 1 (2019): 012019. https://doi.org/10.1088/1757-899X/622/1/012019.

45. Hołda, Agnieszka K., and Ivo F.J. Vankelecom. "Understanding and Guiding the Phase Inversion Process for Synthesis of Solvent Resistant Nanofiltration Membranes." 132, no. 27 (2015).

46. Pulido, Bruno A., Ola S. Habboub, Sandra L. Aristizabal, Gyorgy Szekely, and Suzana P. Nunes. "Recycled Poly(Ethylene Terephthalate) for High Temperature Solvent Resistant Membranes." *ACS Applied Polymer Materials* 1, no. 9 (2019/09/13 2019): 2379-87.

47. Park, Sang-Hee, Abdulaziz Alammar, Zsolt Fulop, Bruno A. Pulido, Suzana P. Nunes, and Gyorgy Szekely. "Hydrophobic Thin Film Composite Nanofiltration Membranes Derived Solely from Sustainable Sources." *Green Chemistry* 23, no. 3 (2021): 1175-84. https://doi.org/10.1039/D0GC03226C.

48. Kusumocahyo, Samuel P., Syarifa K. Ambani, and Shelly Marceline. "Improved Permeate Flux and Rejection of Ultrafiltration Membranes Prepared from

Polyethylene Terephthalate (Pet) Bottle Waste." *Sustainable Environment Research* 31, no. 1 (2021/05/04 2021): 19.

49. Lu, David, Parto Babaniamansour, Alex Williams, Kassandra Opfar, Parker Nurick, and Isabel C. Escobar. "Fabrication and Evaporation Time Investigation of Water Treatment Membranes Using Green Solvents and Recycled Polyethylene Terephthalate." 139, no. 35 (2022): e52823.

50. Rajesh, Smitha, and Z. V. P. Murthy. "Ultrafiltration Membranes from Waste Polyethylene Terephthalate and Additives: Synthesis and Characterization." *Química Nova* 37 (2014).

51. Ma, Dangchen, Shing Bo Peh, Gang Han, and Shing Bor Chen. "Thin-Film Nanocomposite (Tfn) Membranes Incorporated with Super-Hydrophilic Metal–Organic Framework (Mof) Uio-66: Toward Enhancement of Water Flux and Salt Rejection." *ACS Applied Materials \& Interfaces* 9, no. 8 (2017): 7523-34.

52. Ma, Dangchen, Gang Han, Shing Bo Peh, and Shing Bor Chen. "Water-Stable Metal–Organic Framework Uio-66 for Performance Enhancement of Forward Osmosis Membranes." *Industrial \& Engineering Chemistry Research* 56, no. 44 (2017): 12773-82.

53. Xinzhen, Zhao, and Liu Changkun. "Efficient Removal of Heavy Metal Ions Based on the Optimized Dissolution-Diffusion-Flow Forward Osmosis Process." *Chemical Engineering Journal* 334 (2018): 1128-34.

54. Ming, Qiu, and He Chunju. "Efficient Removal of Heavy Metal Ions by Forward Osmosis Membrane with a Polydopamine Modified Zeolitic Imidazolate Framework Incorporated Selective Layer." *Journal of Hazardous Materials* 367 (2019): 339-47.

55. Hyeon-gyu, Choi, Shah Aatif Ali, Nam Seung-Eun, Park You-In, and Park Hosik. "Thin-Film Composite Membranes Comprising Ultrathin Hydrophilic Polydopamine Interlayer with Graphene Oxide for Forward Osmosis." *Desalination* 449 (2019): 41-49.

56. Bagherzadeh, Mojtaba, Arshad Bayrami, and Mojtaba Amini. "Thin-Film Nanocomposite Forward Osmosis Membranes Modified with Zr-Based Metal–

Organic Framework to Improve Desalination Performance." 34, no. 2 (2020): e5339.

57. Mojtaba, Bagherzadeh, Bayrami Arshad, and Amini Mojtaba. "Enhancing Forward Osmosis (Fo) Performance of Polyethersulfone/Polyamide (Pes/Pa) Thin-Film Composite Membrane Via the Incorporation of Gqds@Uio-66-Nh2 Particles." *Journal of Water Process Engineering* 33 (2020): 101107.

58. Kar Weng, Soo, Wong Kar Chun, Goh Pei Sean, Ismail Ahmad Fauzi, and Othman Norasikin. "Efficient Heavy Metal Removal by Thin Film Nanocomposite Forward Osmosis Membrane Modified with Geometrically Different Bimetallic Oxide." *Journal of Water Process Engineering* 38 (2020): 101591.

59. He, Miaolu, Lei Wang, Zhe Zhang, Yan Zhang, Jiani Zhu, Xudong Wang, Yongtao Lv, and Rui Miao. "Stable Forward Osmosis Nanocomposite Membrane Doped with Sulfonated Graphene Oxide@Metal–Organic Frameworks for Heavy Metal Removal." *ACS Applied Materials \& Interfaces* 12, no. 51 (2020): 57102-16.

60. Sungil, Lim, Park Kwang Hyun, Tran Van Huy, Akther Nawshad, Phuntsho Sherub, Choi Joon Young, and Shon Ho Kyong. "Size-Controlled Graphene Oxide for Highly Permeable and Fouling-Resistant Outer-Selective Hollow Fiber Thin-Film Composite Membranes for Forward Osmosis." *Journal of Membrane Science* 609 (2020): 118171.

61. Miaolu, He, Wang Lei, Lv Yongtao, Wang Xudong, Zhu Jiani, Zhang Yan, and Liu Tingting. "Novel Polydopamine/Metal Organic Framework Thin Film Nanocomposite Forward Osmosis Membrane for Salt Rejection and Heavy Metal Removal." *Chemical Engineering Journal* 389 (2020): 124452.

62. Wenying, Fu, Chen Jinghu, Li Chengyun, Jiang Lingchang, Qiu Ming, Li Xi, Wang Yangang, and Cui Lifeng. "Enhanced Flux and Fouling Resistance Forward Osmosis Membrane Based on a Hydrogel/Mof Hybrid Selective Layer." *Journal of Colloid and Interface Science* 585 (2021): 158-66.

63. Soheil, Hadadpour, Tavakol Iman, Shabani Zahra, Mohammadi Toraj, Tofighy Maryam Ahmadzadeh, and Sahebi Soleyman. "Synthesis and Characterization of Novel Thin Film Composite Forward Osmosis Membrane Using Charcoal-Based

Carbon Nanomaterials for Desalination Application." *Journal of Environmental Chemical Engineering* 9, no. 1 (2021): 104880.

64. Fozia, T. Minhas, and M. I. Bhanger. "Interfacial Polymerization: A Facile Technique for Developing Solvent Resistant Nanofiltration (Srnf) Membrane." *Procedia Manufacturing* 17 (2018): 680-87.

65. Mariën, Hanne, Lotte Bellings, Sanne Hermans, and Ivo F. J. Vankelecom. "Sustainable Process for the Preparation of High-Performance Thin-Film Composite Membranes Using Ionic Liquids as the Reaction Medium." 9, no. 10 (2016): 1101-11.

66. Mulder, J. *Basic Principles of Membrane Technology.* Springer Netherlands, 1996.

67. Kaifeng, Gu, Wang Shuhao, Li Yunhao, Zhao Xueting, Zhou Yong, and Gao Congjie. "A Facile Preparation of Positively Charged Composite Nanofiltration Membrane with High Selectivity and Permeability." *Journal of Membrane Science* 581 (2019): 214-23.

68. Sanne, Hermans, Mariën Hanne, Dom Elke, Bernstein Roy, and F. J. Vankelecom Ivo. "Simplified Synthesis Route for Interfacially Polymerized Polyamide Membranes." *Journal of Membrane Science* 451 (2014): 148-56.

69. "Responsible Consumption and Production." 2023, accessed 1/9/2023, 2023, https://www.sdgpakistan.pk/web/goals/goal12.