

PERFORMANCE OF FORWARD OSMOSIS

USING VARIOUS MEMBRANES

by

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## Abstract

As a result of water scarcity, increasing demand for freshwater, and energy intensive nature of the conventional desalination processes, advancing the science of desalination is crucial in the development of sustainable new technologies. With this in view, this research explores an energy-efficient desalination process, namely forward osmosis (FO). In this thesis, two FO apparatus were constructed for the desalination of brackish and seawater. The first apparatus consisted of a simple U-tube while the second apparatus used a submerged membrane to desalinate saline feed. The water flux performance of two commercial FO membranes was evaluated. The U-tube FO apparatus utilized a cellulose acetate membrane and magnesium sulfate ( $\text{MgSO}_4$ ) draw solution. Using 240,000 ppm of  $\text{MgSO}_4$  draw solution, the membrane achieved an average water flux of  $4.06 \text{ L/m}^2 \text{ h}$  and  $0.60 \text{ L/m}^2 \text{ h}$  in case of brackish and seawater feed, respectively. Pure product water with a salt content of 350 ppm was recovered from the diluted  $\text{MgSO}_4$  draw solution. On the other hand, the submerged membrane apparatus utilized a proprietary FO membrane and copper sulfate ( $\text{CuSO}_4$ ) draw solution. The copper sulfate draw solution was found to be suitable only for desalination of brackish water and an average water flux of  $3.01 \text{ L/m}^2 \text{ h}$  was observed using 200,000 ppm of  $\text{CuSO}_4$  draw solution. Pure water with 100 ppm of dissolved solids was recovered from the diluted  $\text{CuSO}_4$  draw solution. For the first time, metathesis precipitation reaction was used to recover pure product water from the diluted draw solution in the FO process. The magnesium sulfate or copper sulfate draw solution was reacted with stoichiometric amount of barium hydroxide to remove the soluble draw solute as a mixture of precipitates. The use of magnesium sulfate or copper sulfate as draw solute required no energy for product water recovery. Both the draw solutions were completely recovered at the end of the experiments for recycle and reuse in the FO process.

**Search Terms:** Forward Osmosis; Desalination; Metathesis Precipitation; Magnesium sulfate; Copper Sulfate

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## Nomenclature

A – Water permeability coefficient ( $\text{m s}^{-1} \text{Pa}^{-1}$ )

c – Solute number density ( $\text{L}^{-1}$ )

$D_s$  – Diffusion coefficient (m/s)

ECP – External concentration polarization

FO – Forward osmosis

ICP – Internal concentration polarization

$J_w$  – Water flux ( $\text{L m}^{-2} \text{h}^{-1}$ )

$J_{w, sp}$  – Specific water flux ( $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ )

K – Solute diffusion resistance (s/m)

k – Boltzmann's constant ( $1.38 \times 10^{-3} \text{ J/K}$ )

M – Solute molar concentration (mol/L)

n – Moles of solute (mol)

$N_A$  – Avogadro's number

R – Gas constant ( $0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$ )

S – Membrane area available for flux ( $\text{m}^2$ )

t – Thickness of the membrane (m)

$\Delta t$  – Time interval (h)

$\Delta V$  – Volume change (L)

*Greek letters*

$\pi$  – Osmotic pressure (bar)

$\pi_{F,b}$  – Bulk osmotic pressure of the feed solution (bar)

$\pi_{D,b}$  – Bulk osmotic pressure of the draw solution (bar)

$\varphi$  – Osmotic pressure coefficient

$\varepsilon$  – Porosity

$\tau$  – Tortuosity

# Chapter 1: Introduction

## 1.1. Background

Water is an essential input to sustain a healthy environment in our society today. About three quarters of the earth is water and approximately 97 percent of it comes from the sea while 2 percent of it is held within blocks of ice [1]. Although water is available in abundance, fresh water is not easily accessible from its infinite source. Over the past decades, the society has become increasingly aware of the role fresh water plays as a critical resource as well as its vulnerability in terms of quality [2]. Many countries in the world suffer from a scarcity of pure water. In addition, increasing amounts of fresh water will be required in the future as a result of the increase in population as well as enhanced living standards and the expansion in the industrial and agricultural sectors [3].

According to World Health Organization (WHO), a quarter of the world's population live in countries that are unable to access fresh water because of the lack of the infrastructure and resources required to draw and treat water from rivers and aquifers [4]. The Middle East and North Africa is home to 6.3 percent of the world's population while it holds only 1.4 percent of the world's renewable fresh water [5]. With the increasing population, the demand of fresh water has increased but its supply has unvaried. In fact, according to the Worldwatch Institute, more than two-thirds of the world's population may experience water shortages by 2025, thus affecting practically every country in the world, including the developed, unless they reduce demand and/or develop additional water sources [1].

Considering the immense volume of existing seawater in these regions, from a technical point of view, the supply capacity of desalination is virtually infinite. However, seawater must be processed in order to make it suitable for human consumption. Desalination is a method that separates saline water into a stream of pure water with low concentration of salts and another stream of concentrated salt solution.

Statistically, it is estimated that over 75 million people in the world obtain pure water by desalination of brackish or seawater [6]. The IDA Desalting Inventory 2004 Report [7] states that at the end of the year 2002, the number of installed and contracted

brackish and seawater desalination plants worldwide were 17,348 units with a total production capacity of 37.8 million cubic meter of pure water per day. However, the increasing cost of seawater desalination has concerned the scientific community to find efficient methods of desalination. As a result, most of the modern interest in desalination is focused on developing cost-effective ways of providing fresh water for human use in regions where the availability of water is limited [8].

The scarcity of water has been crucially acknowledged all over the world, especially in the Middle East, which is one of the most water scarce region in the world. The United Arab Emirates is home to the world's largest desalination plant that exists in Jebel Ali and uses the method of multi-stage flash distillation to desalinate its water [9]. With growing population and economic development, water resources are facing extensive threats in the UAE [10]. Situated near the equator, the UAE is known to be very dry and arid which leads to a high evaporation rate. Furthermore, the insufficiency of rainfall also adds to the scarcity of water in this country [11]. Dubai gets its water from treating wastewater, desalinating seawater and brackish water and groundwater stored in main aquifers [10]. However, the groundwater has been immensely consumed over the years and is not available in plenty to meet the demands of the population in the UAE, which has unrestrainedly increased owing to its advanced living standards. With the growing demand in water, its production too has vastly increased in the Emirates.

According to statistics provided by Dubai Water and Electricity Authority (DEWA) [12], there has been a continuous increase in the quantity of desalinated water demanded in the UAE over the years as shown in Figure 1. Although this increase in quantity demanded has been successfully met by increasing the capacity of installed desalination plants, yet this has resulted in large economic spending in the desalination sector [13]. In fact, the UAE spends nearly Dh11.8 billion per year on the production of desalinated water to ensure its fast growing potable water demands and to compensate for its declining water reserves [14]. In addition, the demand of fresh water will increase in the future as a result of the growing population, enhanced living standards, and continuous expansion in the industrial and agricultural sectors in the UAE [6].

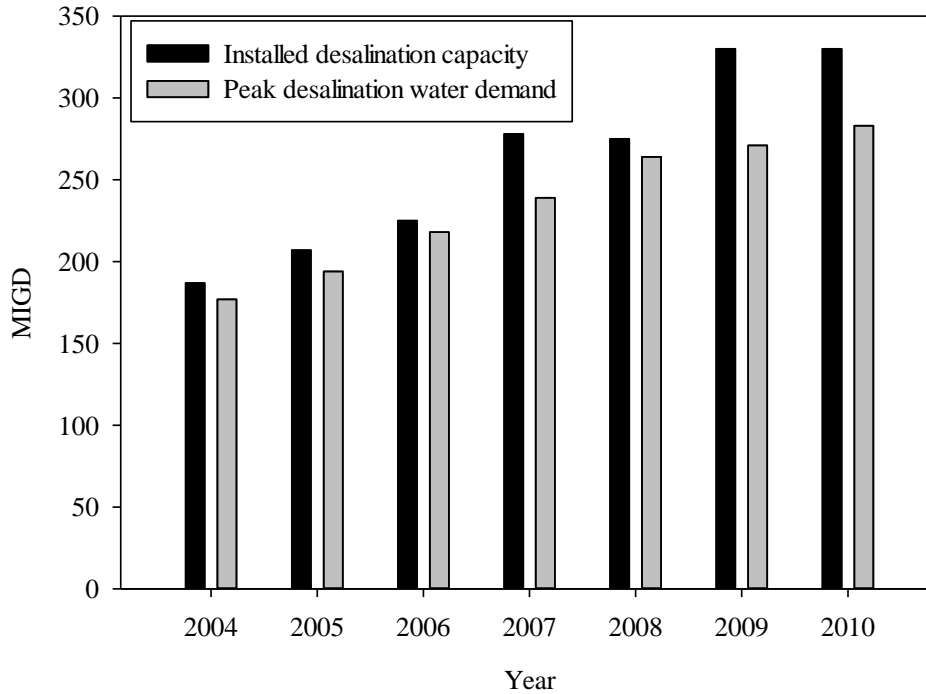


Figure 1: UAE desalinated water demand and supply expressed in MIGD (Million imperial gallons per day) [12]

Unfortunately, the conventional desalination methods such as MSF and RO require large amounts of energy that is costly both in environmental pollution and in terms of money [1]. In order to economically meet the increasing water demands, new energy-efficient and less-costly desalination techniques need to be introduced. As a result, finding efficient desalination technologies becomes an important concern for the scientific community. This thesis work was undertaken to explore an energy-efficient desalination technique namely forward osmosis (FO). The outcomes of this research can be used by the water authorities within the UAE and efforts can be made in order to reduce the cost of desalination and to lower the energy consumption by employing FO on industrial scale. For the semi-arid Arabian Gulf countries such as the UAE, desalination of saline groundwater, brackish waters, and seawater is a vital resource of drinkable water. Desalination using FO is thought to be a promising option. In fact, FO is expected to substantially lower overall cost of water produced and can be employed as the best and low cost desalination process due to the very limited resources of drinkable water in the UAE.



## 1.2. Conventional Desalination Technologies

A number of seawater desalination technologies have been developed over the years to supplement the global supply of water. The development of these desalination technologies is based on membrane separation, thermal vaporization, electrodialysis, etc. [14-20]. In general, desalination processes can be characterized into two major types:

1. Phase-change or thermal processes, and
2. Membrane processes

Some of the phase-change processes include multi-stage flash, multiple effect boiling, vapor compression, freezing, humidification and dehumidification and solar stills [3]. Membrane based processes include reverse osmosis (RO), membrane distillation (MD) and electrodialysis (ED) [21].

However, the multi-stage flash (MSF) distillation and reverse osmosis (RO) processes are the only two desalination techniques of commercial importance [6]. In fact, in the year 1999, approximately 78% of the total seawater desalination capacity consisted of MSF plants. On the other hand, RO accounted for only 10% of the total seawater desalination capacity [22].

**1.2.1. Thermal desalination processes.** The simplest thermal process for desalination is distillation. Saline feed water is heated to generate steam which is eventually condensed to produce distilled water with lower concentration of dissolved salts. The condensed water can be used for industrial, irrigation, or domestic purposes. In thermal desalination processes, the pressure is generally reduced in order to reduce the amount of heat required to vaporize the feed. Thermal desalination processes have the ability to reduce the salt content of saline water to 10 mg/L or less from TDS levels ranging from 60,000-70,000 mg/L. Several methods of distillation are used commercially for desalination, namely [23]:

- Multi-stage flash evaporation/distillation (MSF)
- Multi-effect evaporation/distillation (MED)
- Vapor compression distillation (VCD)

**1.2.1.1. Multi-stage flash distillation (MSF).** Multi-stage flash (MSF) distillation is mostly found in Persian Gulf. It is, in fact, the most well-known technique used for desalination [24]. The following figure shows a simplified schematic of the MSF distillation plant [23]:

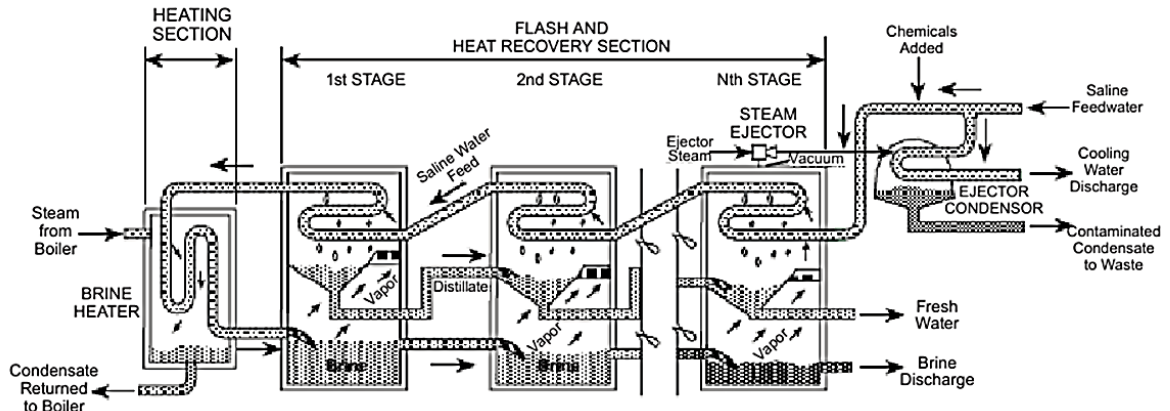


Figure 2: Multi-stage flash distillation plant [23]

MSF distillation is based on the principle of flash evaporation that is followed by condensation. The plant consists of several stages or flash chambers in series containing heat exchangers and condensate collectors. Pressurized seawater passes through closed pipes and exchanges heat with the condensing vapors in the upper section of the flash chambers. Water is then heated using steam to allow vaporization in the lower part of each chamber [25]. The condensed water vapors are collected as pure water in the condensate collectors and are pumped out as the plant product. The latent heat of the condensed vapors is used to preheat the saline feed. The typical energy requirement of the process is 23-27 kWh/m<sup>3</sup> (90 MJ/m<sup>3</sup>) of distilled water produced [26]. Typically, the pure product water from the MSF process has a very low salt content of 2-10 ppm. Therefore, it is usually remineralized by the potabilization step of the process [27-47]. A typical MSF plant may contain from 4 to 40 stages [23]. Although the process is a common one, the operating cost is high if heat is not available for the distillation [25]. As a result, membrane desalination technology, in particular RO, has gained commercial importance.

**1.2.1.2. Multi-effect distillation (MED).** The multi-effect distillation process is similar to the multi-stage flash evaporation with the only difference that steam is used to evaporate seawater in the first stage.

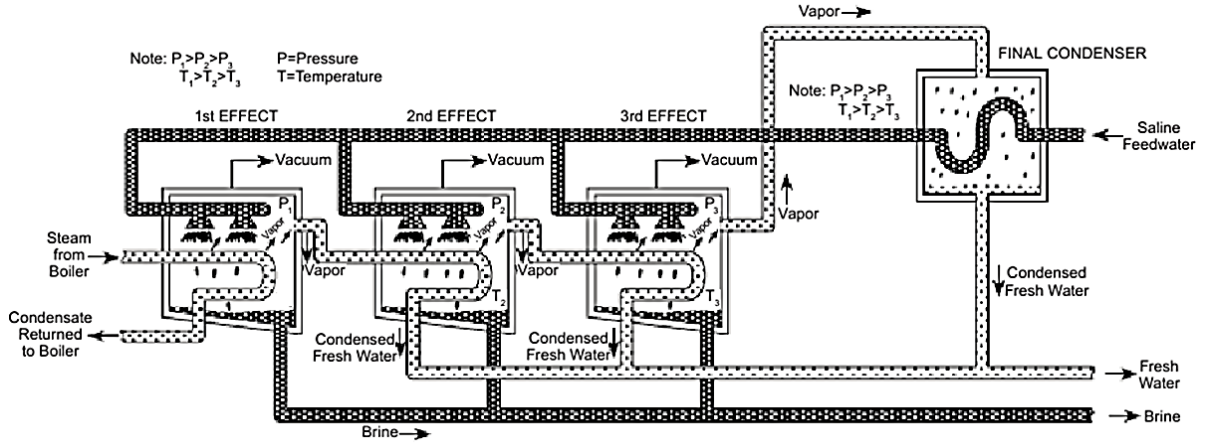


Figure 3: Multi-effect distillation (MED) [23]

The MED process uses multiple vessels or effects arranged in series. The pressure is decreased in each subsequent effect. The resulting vapor is used to evaporate water in each successive stage, while seawater is used to condense the vapors formed. In other words, the vapors formed in each effect are used to heat water entering the next effect. This not only reduces the amount of energy required for distillation but also reduces the amount of electrical energy required. As a consequence, MED desalination process is more cost-effective and less-costly than MSF desalination. Figure 3 shows simplified diagram of the MED process [23].

**1.2.1.3. Vapor compression distillation (VCD).** In this process, steam is generated from seawater using a heating source, which is then compressed using a compressor. The compressed steam is eventually condensed to fresh water by the incoming seawater. Heat required for evaporation is obtained by either mechanical vapor compression or thermo vapor compression. The mechanical vapor compression systems use electricity while the thermo vapor compression systems use high-pressure steam to compress the vapors formed from distillation. The compression leads to an increase in the temperature and pressure of the vapors which can be returned to the evaporator to be used a heat source. The principle of mechanical vapor compression distillation is shown below:

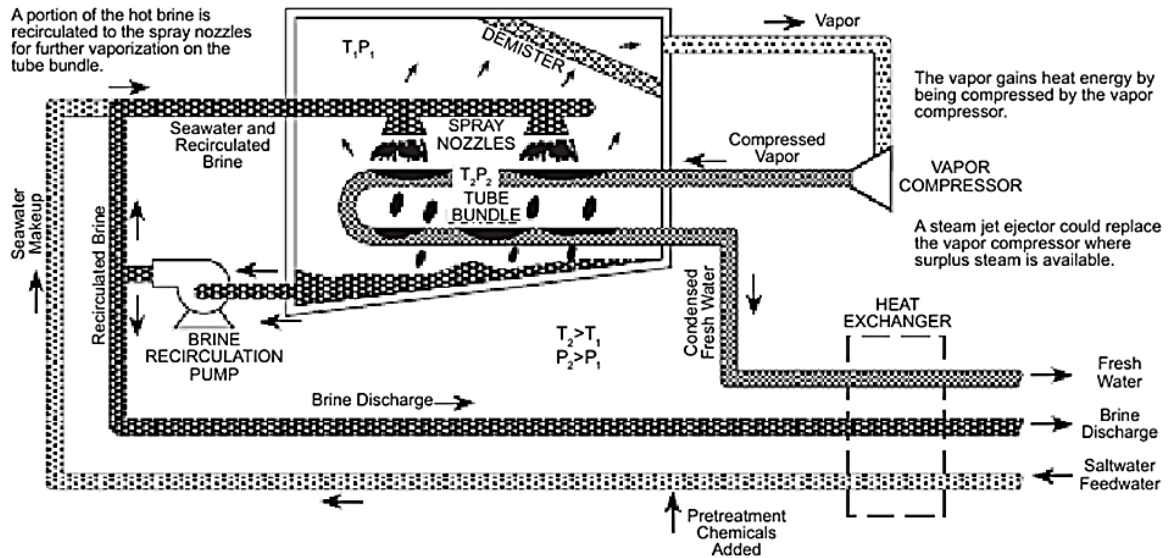


Figure 4: Vapor compression distillation (VCD) [23]

However, VCD is not of commercial importance. It is mainly used in areas where fresh water requirement is relatively low such as in small communities and ships [23].

**1.2.2. Membrane technology in desalination.** Membrane processes are commonly used in desalination of seawater. Perhaps, reverse osmosis (RO) and electrodialysis (ED) are the two commonly used membrane desalination processes, with RO being the most widely used desalination technology. The following figure shows the percentage of world desalinated water production from different processes [48]:

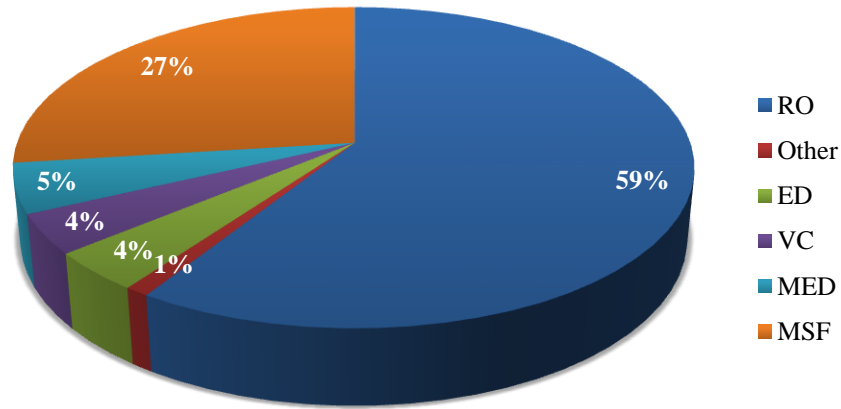


Figure 5: Percentage of world desalinated water production from the different desalination processes [48]

Membrane technology can solve a wide range of separation problems and it may be classified by the range of substances separated and the driving forces employed. The concept of membrane desalination revolves around the ability of semipermeable membranes to selectively allow the passage of water molecules through them.

**1.2.2.1. Electrodialysis (ED).** The process of electrodialysis uses ion-exchange membranes which are selective to the cations and anions present in the saline feed water. Application of a direct electrical current in the electrodialysis stack causes the cations to pass through the cation membrane and the anions to pass through the anion membrane. ED was, in fact, the first membrane desalination process to achieve commercial success. However, today it has been taken over by reverse osmosis [23]. Typically, electrodialysis is not used for desalination of seawater since the process becomes less efficient compared to other membrane processes due to high salinity levels. The following figure shows the basic diagram of an electrodialysis cell:

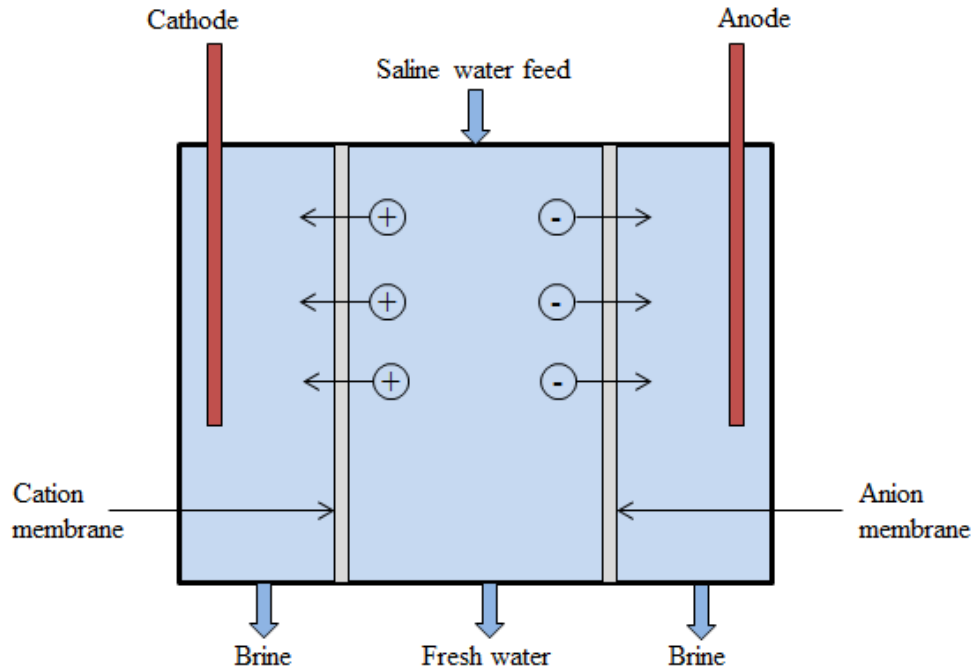


Figure 6: Electrodialysis cell [23]

**1.2.2.2. Reverse Osmosis (RO).** Today, reverse osmosis (RO) is the most widely used desalination technique around the world. It has now overtaken conventional thermal technology such as multi-stage flash (MSF) [49]. The concepts of "osmosis" and "reverse osmosis" have been known to the scientific community for many years. However, the use of RO as a practical desalination process is a relatively new technology [50]. Osmosis is the process in which water passes through a semi-permeable membrane from a low-concentration solution into a high-concentration solution. However, if external pressure is applied to the high-concentration side of the membrane, the reverse process occurs and water diffuses from the high-concentration solution into the low-concentration solution [51]. This reverse process is known as reverse osmosis (RO).

The process of reverse osmosis desalination simply employs a semi-permeable membrane that rejects the salts and only allows pure water to pass through. The feed water is pressurized on one side of a semi-permeable membrane such that the applied hydrodynamic pressure is high enough to exceed the osmotic pressure to cause reversed water flow. This is shown in the following Figure 7 [52]:

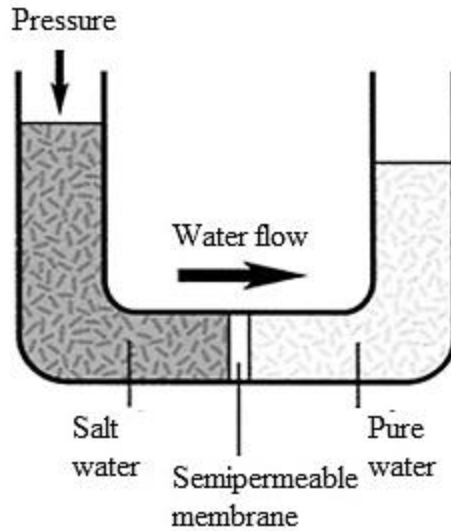


Figure 7: External pressure causes water to diffuse from high to low-concentration solution (Reverse osmosis) [52]

In case of continuous flow industrial reverse osmosis processes, the application of external pressure requires a high-pressure pump. Typically, the saline water feed needs to be pumped to a high pressure before sending it for membrane separation. In case of brackish water, the feeds needs to be pumped to a pressure of 2-17 bar (30-250 psi). On the other hand, in case of seawater the feed needs to be pumped to a pressure of 40-82 bar (600-1200 psi) [53]. A simplified block flow diagram for RO is shown in Figure 8.

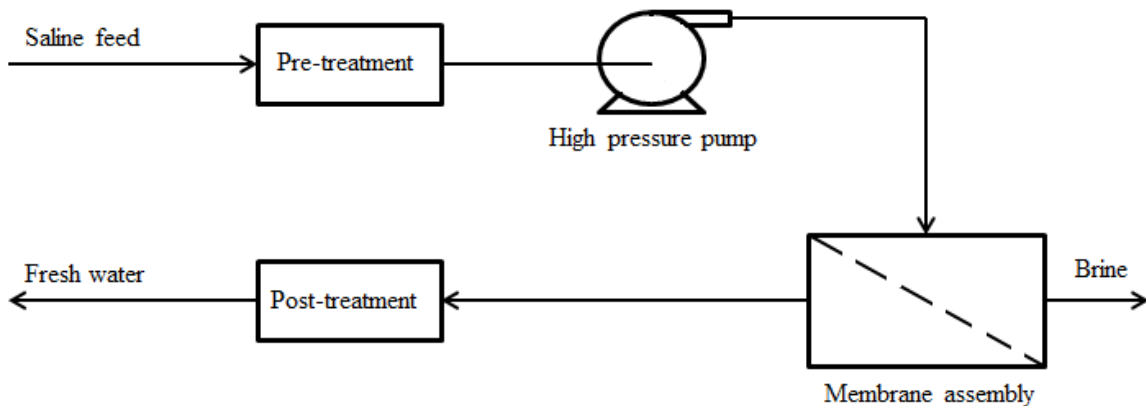


Figure 8: Continuous flow RO process. Applied pressure of 2-17 bar for brackish water, and 40-82 bar for seawater

The salt water feed is first passed through a filter where suspended solids that would foul the membrane are removed. The feed is then pumped to the operating pressure depending on its salinity and finally introduced into the desalination chamber. A portion of water permeates through the membrane and is collected as product after suitable post-treatment. The post-treatment step may consist of addition of minerals and disinfection to ensure drinkability of the pure product water.

### **1.3. Osmotic Membranes**

The preferred materials used for synthesis of osmotic membranes are cellulose acetate and polyamides that are processed to make them reject salts and at the same time pass water at a reasonable rate. Reverse osmosis membrane desalination is, most importantly, governed by the properties and characteristics of the membrane used in the process. The ideal membrane has the following characteristics:

- High water flux
- High salt rejection
- Resistant to biological attack
- Resistant to fouling by suspended material
- Inexpensive
- Mechanically strong
- Chemically stable
- Able to resist high temperatures
- Safe operation at high pressures
- Easy to clean
- No internal leaks

Most currently available RO membranes fall into two categories: asymmetric membranes consisting of only one polymer, and thin-film composite membranes containing two or more polymer layers [50]. Asymmetric RO membranes contain a very thin semipermeable skin layer that is supported on a more porous sub-layer composed of the same polymer. The dense skin layer determines the flux and selectivity while the porous sub-layer acts as a mechanical support for the dense skin layer. On the other hand,



the thin-film composite RO membranes contain a thin polymer layer that is formed on one or more porous support layers. The support layers are almost always a different polymer from the surface layer. The surface layer of the membrane determines the separation characteristics and the water flux through the membrane. The porous support acts only as a support for the surface layer. It has no effect on the separation and transport properties of the membrane [50].

Over the years, different RO membranes have been prepared using a variety of materials and preparation methods. However, the cellulosic polymers (cellulose acetate and cellulose triacetate), aryl-alkyl polyetherurea, and linear and cross-linked aromatic polyamide are among the most important materials for RO membrane synthesis [54-57]. The pore size of the membranes is usually less than 0.6 nm to achieve salt rejection consistently higher than 99% [58].

Cellulose acetate membranes are cast from cellulose diacetate and cellulose triacetate formulations and the blends of the two. With increasing acetyl content, the salt rejection and chemical stability increases but the water flux decreases. Cellulose acetate membranes usually have poor chemical stability and tend to hydrolyze over time depending on the temperature and pH conditions. The operating range of cellulose acetate membranes is 0° to 30 °C and pH in the range 4.0-6.5. As a result of poor stability, cellulose acetate membranes tend to decrease salt rejection with time. However, the popularity of cellulose acetate membranes is attributed to the availability through numerous sources and low cost [50]. On the other hand, asymmetric aromatic polyamide membranes consist of a dense skin, approximately 0.1 to 1.0 μm thick, on the outer surface of the membrane. The remaining structure is a porous support layer approximately 26 μm thick. Salt rejection takes place at the dense layer. These membranes have excellent chemical stability compared to cellulosic membranes. The operating range is 0° to 35 °C and pH in the range 4.0-11. However, asymmetric aromatic polyamide membranes are susceptible to chlorine attack [54].

Reverse osmosis membrane market is dominated by thin film composite (TFC) polyamide membranes that consist of three layers: A polyester web acting as structural support, a micro-porous interlayer, and an ultra-thin barrier layer on the upper surface

[59]. The spiral wound membrane configuration is the most widely used membrane module design in RO desalination applications. A spiral-wound element consists of flat sheets of RO membrane that are separated by spacers and rolled around a perforated collection tube. The brackish or seawater feed is channeled across the rolled membrane sheets, that passes through the membrane, and is collected in the perforated collection tube [57, 60, 61]. This configuration offers high specific membrane surface area, easy scale up operation, low replacement costs and, most importantly, it is the least expensive module configuration to produce from flat sheet TFC membrane [61, 62]. Hollow-fiber membrane configuration is another important RO membrane configuration. The hollow-fiber membrane elements contain large numbers of hollow fiber membranes. These membranes are placed in a pressure vessel. The saline feed flows outside the fibers and passes through these fibers [57, 61, 63]. According to statistics, polyamide spiral wound membranes dominate the RO market with a 91% share in sales. The symmetric cellulose acetate hollow fiber membranes have a distant second spot in the sales [64]. The following table provides a summary of all the major membranes tested in RO applications:

Table 1: *Notable RO membranes*

<b>Membrane Chemical Type</b>	<b>Reference</b>
Cellulose Acetate	65
Aromatic Polyamide	66
Polypiperzine Amide	67
Polybenzimidazoline	68
Polyoxadiazole	69
Polyfurane	70
Polyether-Polyfurane	71
Sulfonated Polysulfone	72
Polyvinylamine	73
Polypyrrolidine	74
Cross linked Aralkyl Polyamide	75

#### 1.4. Need for Improved Desalination Techniques

Ocean desalinated water is among the most expensive ways to supply fresh water for human consumption. In fact, producing fresh water through ocean desalination is three to four times more costly than producing fresh water from traditional supplies. It requires multiple subsidies of both water and electricity to break even, and it involves expensive upfront construction and long-term operation and maintenance costs [76].

All of the aforementioned conventional desalination technologies are energy intensive processes and require large amount of either thermal or electrical energy or both. The most important limitation of the thermal desalination processes is the energy requirement of the vaporization step in the process. The thermal desalination processes are expensive since they require large amount of fuel to vaporize saline water. The typical energy requirements of the thermal desalination processes range from 25-100 kilowatt hour (kWh) per 1000 gallons of fresh water produced [1]. In fact, thermal energy requirement represents the major element in the cost of thermal desalination processes as shown in the following statistics by National Research Council [77].

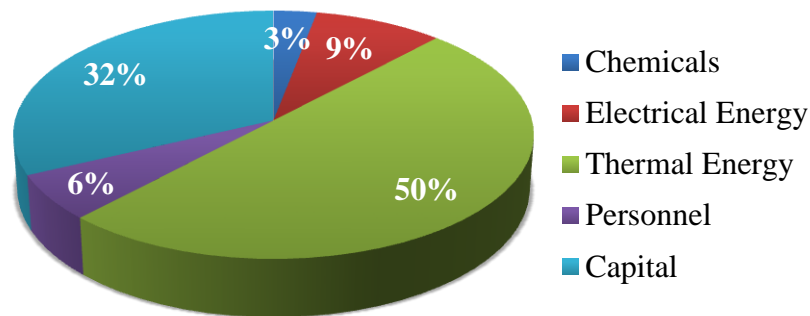


Figure 9: Breakdown of costs in thermal desalination processes [77]

On the other hand, membrane processes, mainly RO, have been found to desalt brackish water economically and therefore, have replaced thermal methods for the desalination of brackish water [78]. However, because of the high cost of membrane

replacement and maintenance cost, membrane processes are less suitable for desalinating seawater [1]. A rough estimate of the costs in RO plants is as follows [23]:

Table 2: *Percentage split of costs for RO plants*

<b>Cost Factor</b>	<b>Percentage (%)</b>
Electrical Energy	23-44
Capital Cost	14-52
Membranes	5-14
Maintenance	5-8
Chemicals	2.5-8
Labor	1-10

In case of RO plants, electrical energy is a major cost factor since the process requires high pressurization of the saline feed using a high-pressure pump [79-86]. Also, membrane fouling in RO requires periodic membrane replacement which increases the membrane cost. The application of high pressure in RO forces the salts, present in the feed, against the membrane resulting in salt deposition and formation of salt gel layer on the membrane surface. This leads to increased membrane fouling in RO [87]. Thus, an effort can be made to decrease the energy requirement in desalination processes in order to minimize the desalination cost and to meet the increasing water demand in an energy efficient manner.

In the Middle East, including the UAE, multi-stage flash distillation (MSF) process dominates the desalination market since the region is rich in energy from the oil and gas sectors. This is shown in Figure 10 [88]. In addition, the MSF plants utilize steam turbines and are one of the primary sources of power generation in the region.

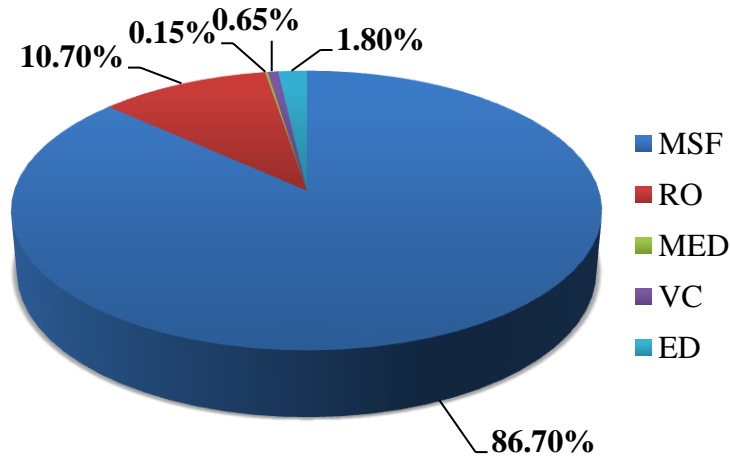


Figure 10: Distribution of desalination production capacity by process technology in Middle East [88]

The power consumption per unit of distillate for the main MSF desalination units installed by the Abu Dhabi Water and Electricity Department (ADWEA) ranges from 3.6 to 5 kWh/m<sup>3</sup> and that the cost of electric power is almost 3 times the cost of the steam [89, 90]. Thus, the use of MSF desalination process requires extensive economic spending on energy. Therefore, there is a space for introduction of energy-efficient and less-costly desalination technologies around the globe, especially in the Middle East including the UAE. This thesis work explores the application of forward osmosis as an efficient desalination technique and aims to study the performance of forward osmosis process with various membranes and draw solutions.

### 1.5. Energy Efficient Desalination Techniques – Forward Osmosis

The increasing demand for fresh water and the high cost of conventional desalination processes require investigation into energy-efficient and less costly desalination processes. Recently, forward osmosis (FO) has been under investigation as an alternative desalination technique [90-96]. In fact, many studies have been done recently to study FO for a range of potential engineering applications including wastewater treatment, water purification and seawater desalination [97]. Unlike hydraulic pressure-driven technologies such as reverse osmosis, FO is an energy effective technology [98]. The application of FO has been studied in various fields such as wastewater treatment [99], water desalination [100] and energy generation [101, 102].

However, very few publications appear in the literature on the use of FO for desalination and water treatment [99].

Forward osmosis is simply a natural osmosis process that involves permeation of water from a low-concentration solution into a high-concentration solution across a semipermeable membrane due to difference in osmotic pressures. The low-concentration solution is called the feed solution and is typically seawater or brackish water that needs to be desalinated. On the other hand, the high-concentration solution is called the draw solution which is prepared in the laboratory using a solute of high osmotic pressure. It is the osmotic pressure difference between the feed and the draw solution that causes water in the feed solution to flow into the draw solution. The salts remain in the feed solution due to the semipermeable nature of the membrane. Figure 11 shows the FO process.

After the flow of water into the draw solution, it must be recovered as pure product water using a suitable energy-efficient technique. As a result, most research on FO focuses on finding suitable draw solutions of high osmotic pressure, suitable membranes that allow high water flux and high salt rejection and energy-efficient techniques for the recovery of product water.

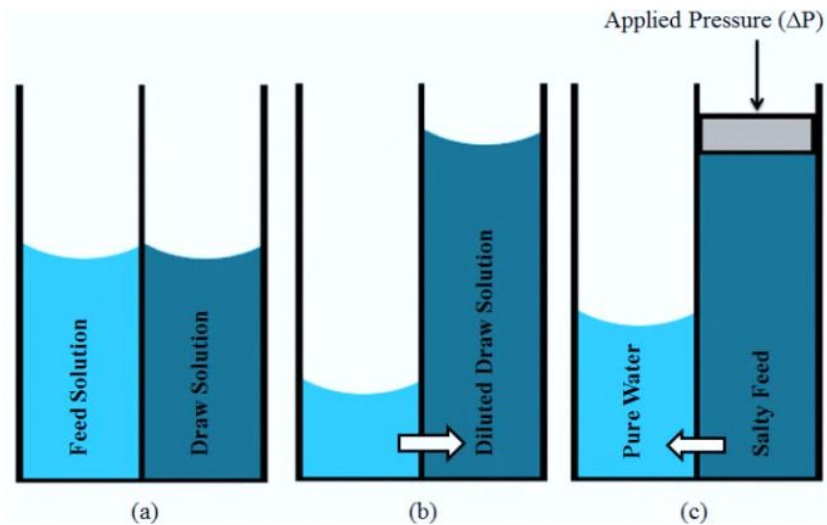


Figure 11: (a) Feed solution separated from a draw solution by a semipermeable membrane (b) FO, water from the feed transfers to the draw solution due to osmotic pressure differential (c) RO, high pressure applied to the salty feed passes water molecules through

The main advantage of FO is that it operates under no hydraulic pressures which results in lower membrane fouling and lower or no energy requirement compared pressure-driven processes such as RO. The flow of water from the feed to the draw solution is a natural process and requires no energy. The recovery of product water may require some energy but the use of proper draw solution can make FO a promising energy-efficient and less-costly process. As a result, continued and more extensive research on FO is needed in order to improve its performance and to implement the process on industrial scale.

Basic research on FO and the development of new engineered applications of FO are progressively growing. However, these developments face the problem of lack of robust membranes and membrane modules for FO [99]. As a result, currently, the most important step to be taken in order to improve the field of FO is the development and testing of new membranes in both hollow fiber and flat-sheet configurations. The membranes need to provide high water permeability, high rejection of salts, substantially reduced internal concentration polarization (CP), high chemical stability, and high mechanical strength.

## **1.6. Forward Osmosis Theory**

**1.6.1. Calculation of Osmotic Pressure.** In case of dilute salt solutions, the osmotic pressure can be estimated using the Van't Hoff equation [103]:

$$\pi = MRT \tag{Eq. (1)}$$

where  $\pi$  is the osmotic pressure in bars,  $M$  is the solute molar concentration in moles/liter,  $R$  is the universal gas constant ( $0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the temperature in Kelvins.

However, for concentrated salt solutions such as the draw solution in FO, the non-ideal solution behavior must be accounted and the osmotic pressure is calculated as follows [103]:

$$\pi = \varphi MRT \tag{Eq. (2)}$$

where  $\phi$  is the osmotic pressure coefficient. In particular, the deviation from ideal solution is compensated by virial equation [104]. According to statistical thermodynamics, the osmotic pressure is related to the solute number density as follows [103-107]:

$$\frac{\pi}{kT} = c + Bc^2 + Cc^3 + \dots \quad \text{Eq. (3)}$$

where  $k$  is the Boltzmann's constant. The virial coefficients ( $B, C, D, \dots$ ) are usually obtained from experimental data. The solute number density is defined as:

$$c = \frac{N_A n}{V} \quad \text{Eq. (4)}$$

where  $N_A$  is Avogadro's number and the term  $n/V$  (moles/volume) represents the molar concentration of the solute.

**1.6.2. Estimation of Water Flux.** The water flux can be calculated from the volume change of the feed or draw solution during the FO experiment. As FO process proceeds, the flow of water from the feed solution to the draw solution results in decrease in volume of the feed solution with a corresponding increase in the volume of the draw solution. The water flux ( $J_w$ ) can be calculated as follows:

$$J_w = \frac{\Delta V}{S \Delta t} \quad \text{Eq. (5)}$$

where  $\Delta V$  is volume change of the feed or draw solution,  $S$  is the area of the membrane available for flux and  $\Delta t$  is the time interval during which the volume changes by amount  $\Delta V$ .

The specific flux can be calculated by dividing the flux by the driving force, the difference in osmotic pressure ( $\Delta\pi$ ) in this case:

$$J_{w,sp} = \frac{J_w}{\Delta\pi} \quad \text{Eq. (6)}$$



**1.6.3. Water Flux Model.** Based on the classical solution-diffusion model, water flux ( $J_w$ ) in FO can be expressed by the same general equation used in RO or any other membrane driven process [108]:

$$J_w = A(\Delta P - \Delta\pi) \quad \text{Eq. (7)}$$

where  $\Delta P$  is the applied pressure or the hydraulic pressure difference across the membrane and  $\Delta\pi$  is the osmotic pressure difference across the active layer of the membrane. Since the only driving force in FO is the osmotic pressure difference, theoretically, the water flux in FO can be estimated using the following equation:

$$J_w = A(\pi_{D,b} - \pi_{F,b}) \quad \text{Eq. (8)}$$

where  $\pi_{D,b}$  is the bulk osmotic pressure of the draw solution,  $\pi_{F,b}$  is the bulk osmotic pressure of the feed solution and  $A$  is the membrane water permeability coefficient. The equation assumes that the FO membrane is ideally impermeable to the draw solution [109, 110].

Loeb et al. [111] developed a simple equation to describe the water flux during FO:

$$J_w = \frac{1}{K} \ln \left( \frac{\pi_{D,b}}{\pi_{F,b}} \right) \quad \text{Eq. (9)}$$

where  $K$  is the resistance to solute diffusion within the membrane porous support layer. Neglecting any polarization effects within the membrane,  $K$  is defined as follows:

$$K = \frac{t \tau}{\varepsilon D_s} \quad \text{Eq. (10)}$$

where  $t$ ,  $\tau$ ,  $\varepsilon$ ,  $D_s$  represent the membrane thickness, tortuosity, porosity, and diffusion coefficient of the solute respectively. Equation (8) is valid only at low values of water flux.

**1.6.4. External Concentration Polarization (ECP).** The water flux in any osmotic-driven membrane process is given by Equation (7). In this equation,  $\Delta\pi$  represents the

osmotic pressure difference across the active layer of the membrane. The osmotic pressure difference across the active layer is usually much lower than the bulk osmotic pressure difference [112-115]. As a result, actual flux observed in FO is much lower than the flux given by Equation (7). This lower flux in FO is often related to several membrane-associated transport phenomena, the two important of which include internal concentration polarization and external concentration polarization [99].

Usually in pressure-driven processes such as RO, the convective flow of water across the membrane causes a buildup of salts on the active layer of the membrane. This is known as concentration polarization (CP). The effect of concentration polarization is to reduce the flux through the membrane due to osmotic pressure raise [116-118] and increase in resistance to permeation by gel formation and scaling [26]. However, this phenomenon of concentration polarization is not limited to pressure-driven membrane processes but also occurs in osmotic-driven membrane processes [99]. In FO process, the flow of permeate water from the feed solution results in a buildup of solute on the active layer of the FO membrane, which is known as concentrative external concentration polarization. The concept of external concentrative polarization is similar to the concept of concentration polarization in pressure-driven membrane processes. Similarly, the dilution of the draw solution, in contact with the permeate side of the membrane, by the permeating water results in dilutive external concentration polarization.

The net consequence of both concentrative and dilutive external CP is to reduce the osmotic driving force across the membrane resulting in lower water flux. However, the adverse effect of external CP on water flux in osmotic-driven membrane processes can be reduced by increasing the turbulence and flow velocity at the membrane surface [119]. Also, due to low hydraulic pressure used in FO, the effect of external CP is usually negligible [96, 120] and is not of considerable importance.

**1.6.5. Internal Concentration Polarization (ICP).** Internal concentration polarization (ICP) is an important consideration in FO applications that reduces the water flux through the membrane. In the absence of any concentration polarization, the driving force for water or permeate flux is the difference in bulk osmotic pressures of the feed and the draw solutions as shown in Figure 12.

However, the FO membranes are usually asymmetric that are constructed with an active dense layer that is supported on a porous support layer. If the porous support layer of an asymmetric membrane faces the feed solution, a polarized layer is formed along the inside of the dense active layer as shown in Figure 13. As shown, the effective osmotic pressure difference across the membrane is reduced. This is known as concentrative internal CP. The phenomenon of concentrative internal CP is similar to concentrative external CP except that it occurs within the porous layer of the membrane, and thus, cannot be minimized by manipulating the flow rate or turbulence at the membrane surface.

Likewise, if the active layer of the FO membrane faces the feed solution, the draw solution within the porous layer of the membrane becomes diluted. This is referred to as dilutive internal CP. This is illustrated in Figure 14.

As shown in Figures 13 and 14, the bulk osmotic pressure difference  $\Delta\pi_{\text{bulk}}$  is much higher than the osmotic pressure difference across the membrane  $\Delta\pi_{\text{m}}$  and the effective osmotic pressure difference  $\Delta\pi_{\text{eff}}$  is much lower than the two. The bulk osmotic pressure difference  $\Delta\pi_{\text{bulk}}$  is observed when there is no external or internal CP. Similarly,  $\Delta\pi_{\text{m}}$  refers to absence of any internal CP and  $\Delta\pi_{\text{eff}}$  refers to the effective osmotic pressure difference taking into account both the external and internal CP.

Usually in FO desalination and water treatment applications, the active layer of the membrane faces the feed solution and the porous support layer faces the draw solution [26]. Therefore, the effective osmotic pressure difference is very small (as shown in Figure 14) resulting in much lower water flux than ideal flux given by Equation (8).

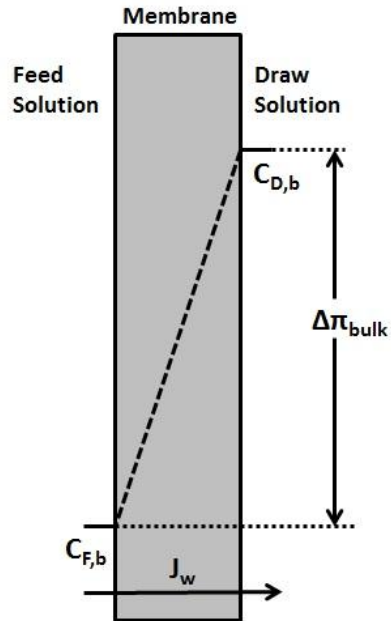


Figure 12: Driving force profile in absence of CP

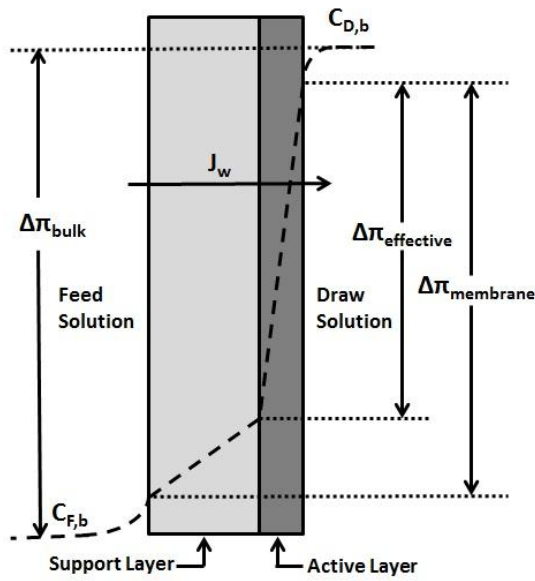


Figure 13: Concentrative ICP in FO with the active layer facing the draw solution

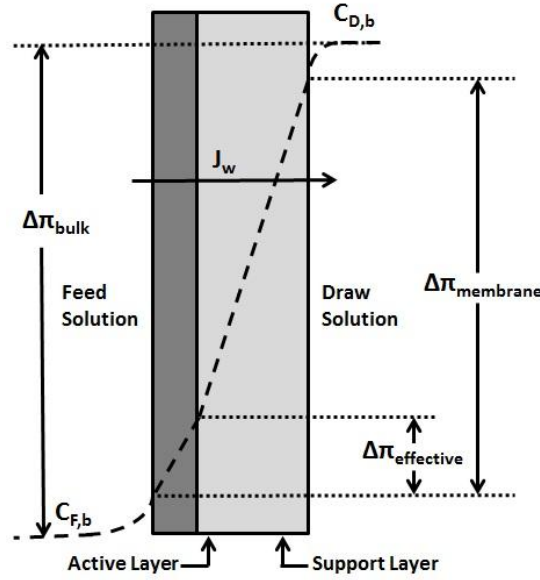


Figure 14: Dilutive ICP in FO with the active layer away from the draw solution

**1.6.6. Modeling Internal Concentration Polarization (ICP).** External CP is usually of little significance and in most cases neglected [96, 99]. However, flux modeling in the presence of internal CP is important since ICP significantly lowers water flux. The effect of ICP on water flux in FO can be modeled by adopting the classical solution-diffusion theory [101, 114]. In case of dilutive ICP, the water flux ( $J_w$ ) can be expressed as follows [108]:

$$J_w = \frac{1}{K} \ln \left[ \frac{A\pi_{\text{Draw}} + B}{A\pi_{\text{Feed}} + B + J_w} \right] \quad \text{Eq. (11)}$$

where  $K$  is called solute resistivity that measures the solute's ability to diffuse into or out of the membrane support layer. Again,  $K$  is given by Equation (10).  $B$  is the solute permeability coefficient of the active layer of the membrane. It can be determined from an RO-type experiment [114] using the following equation:

$$B = \frac{(1 - R)A(\Delta P - \Delta\pi)}{R} \quad \text{Eq. (12)}$$

where  $R$  is the salt rejection.

In case of concentrative ICP, the water flux ( $J_w$ ) can be expressed as follows [108]:

$$J_w = \frac{1}{K} \ln \left[ \frac{A\pi_{\text{Draw}} + B - J_w}{A\pi_{\text{Feed}} + B} \right] \quad \text{Eq. (13)}$$

An analytical model for the effect of both concentrative ICP and dilutive ECP on water flux has been developed to predict water flux in FO [121]:

$$J_w = A \left[ \pi_{\text{Draw}} \exp\left(-\frac{J_w}{K}\right) - \pi_{\text{Feed}} \exp(J_w K) \right] \quad \text{Eq. (14)}$$

## 1.7. Previous Forward Osmosis Desalination Efforts – Literature Review

**1.7.1. Forward osmosis membranes.** Several membranes have been tested in the past for various forward osmosis applications. Any dense and selectively permeable material can be used as a membrane in the forward osmosis process. In addition, for low internal concentration polarization, a thin membrane with minimum porosity of the support layer is preferred. The following are the desired characteristics of a FO membrane:

- High water permeation
- Low reverse salt flux
- High chemical stability
- High mechanical strength
- High salt rejection

The earliest membranes used for forward osmosis were materials such as bladders of pigs, fish skin, natural nitrocellulose, rubber, and porcelain [122]. Loeb and co-workers [123, 124] investigated the use of asymmetric aromatic polyamide RO membranes in FO applications.

In the 1970s, all FO experiments were being carried out using RO membranes and in all cases the researchers observed much lower water flux than expected. Votta et al. [125] and Anderson [122] used different commercial RO membranes to treat dilute wastewater using FO. Kravath and Davis [126] used flat sheet RO membrane supplied by Eastman and cellulose acetate membranes from Dow Chemicals for desalination of seawater using glucose as the draw solution. In addition, in the 1970s, Mehta and Loeb

[127] used DuPont b-9 flat sheet and B-10 Permasep hollow fiber RO membranes in FO applications.

During the 1990s, Hydration Technologies Inc. (HTI, Albany, OR) developed a special FO membrane. Since its development, the membrane has been used extensively in FO applications by various researchers [128-132]. In fact, the HTI's FO membrane is the most popular FO membrane till date.

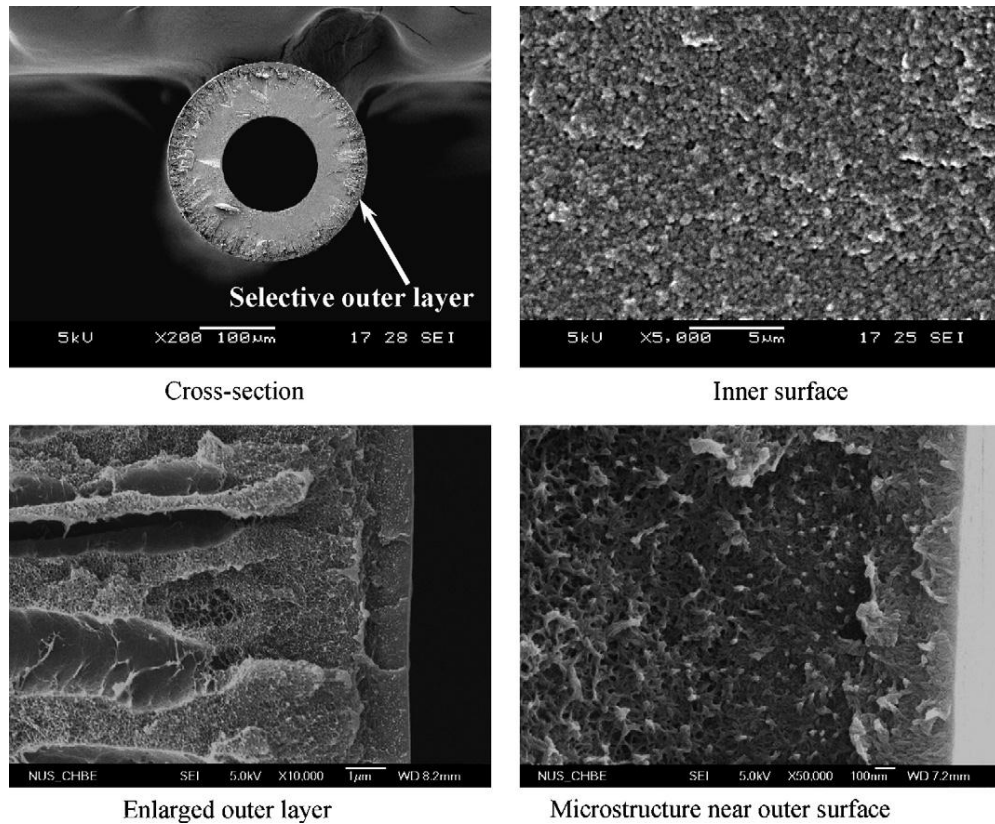


Figure 15: Morphology of PBI membrane used by Wang et al. [134]

Recently, Zhang et al. [133] have studied the application of cellulose ester polymers in FO seawater desalination. Wang et al. [134] for the first time used polybenzimidazole (PBI) nanofiltration membranes for FO desalination. PBI membrane was selected due to its high mechanical strength and excellent chemical stability. Figure 15 shows the SEM of the PBI nanofiltration hollow fiber membranes used by Wang et al. [134]. Although research is being continued to synthesize new polymeric FO membranes with better transport properties, HTI's FO membrane is the most widely used membrane

in FO research due to its commercial success, high salt rejection, and reasonable water flux.

**1.7.2. Forward osmosis draw solutions.** The high osmotic pressure of the draw solution is the source of driving force for water in FO process. The draw solution may also be referred as osmotic agent, osmotic media, osmotic engine, or driving solution. When selecting a draw solution, the main criterion is that it should have a higher osmotic pressure than the feed solution. The higher the osmotic pressure of the draw solution, the more suitable it is in FO applications. In addition, the draw solute must have the following additional characteristics:

- The selected draw solution must require low energy for regeneration or re-concentration and must be easily separated from the pure product water
- The draw solute must be non-toxic
- The selected draw solute must be chemically inert to the membrane
- It must have a high osmotic pressure
- It must be highly soluble

Figure 16 shows the osmotic pressure of various draw solutions as a function of concentration [99]. As depicted in the figure, the osmotic pressure increases with increasing draw solution concentration. Magnesium chloride exhibits the highest osmotic pressure compared to other draw solutes. However, the recovery of pure product water from magnesium chloride draw solution is not possible without use of an RO unit after the FO step. Therefore, magnesium chloride is not considered a good draw solution choice despite of its high osmotic pressure.

In the past few decades, various chemicals have been tested as solutes for draw solutions. Batchelder [135] used volatile solutes, such as sulfur dioxide, for desalination of seawater. In this case, the removal of volatile solutes from the product water requires energy and heating.



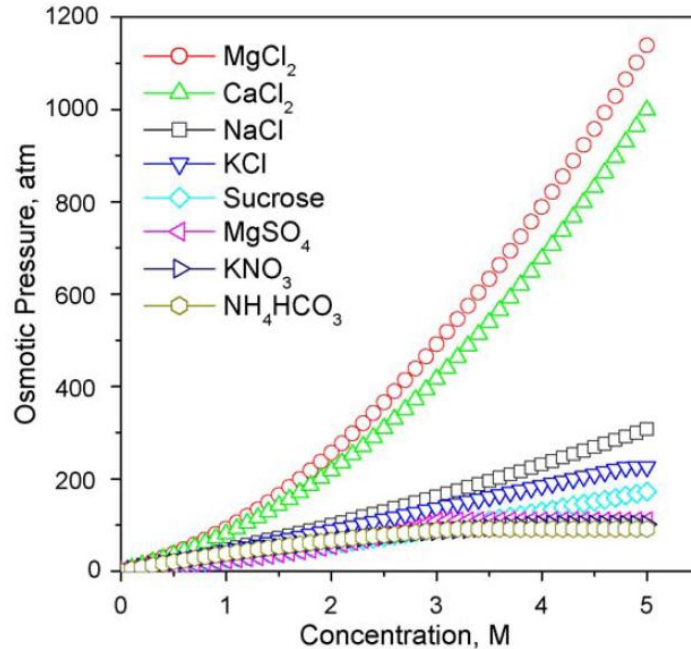


Figure 16: Osmotic pressure of various draw solutes at 25 °C as a function of concentration. Data were calculated using OLI Stream Analyzer 2.0 [99]

McGinnis [136] used a two-stage FO process in which the seawater is first contacted with concentrated  $\text{KNO}_3$  solution. After diffusion of water from the saline feed solution into the  $\text{KNO}_3$  draw solution, a significant amount of  $\text{KNO}_3$  is precipitated by cooling. The remaining diluted  $\text{KNO}_3$  solution is contacted with  $\text{SO}_2$  solution in the second stage of the FO process. Finally, product water is recovered from the  $\text{SO}_2$  solution by heating. Again, in this case, energy in the form of cooling and heating is required to recover pure product water from the draw solution.

Recently, several new types of draw solutions have been suggested for use in FO. Li et al. [137] suggested use of polymer hydrogels as the draw agent. Hydrogels are three-dimensional network of polymer chains that are linked by physical or chemical bonds. The polymer hydrogels are used to drive water across the semipermeable membrane in FO. The polymer hydrogels entrap the water molecules and become swelled. After extraction of water from the feed solution, pure product water is recovered from the swelled hydrogels using temperature, pressure, or solar irradiation as external stimuli.

Stone et al. [138] used phosphazene salts as draw solutes. The water flux through the FO membrane has been reported. However, the recovery of product water from the phosphazene salt draw solution has not been discussed. In another work, Stone and co-workers [139] used a mixture of carbon dioxide, water and tertiary amines as draw solution. This mixture has been named switchable polarity solvent (SPS). The tertiary amines are soluble in water only in the presence of carbon dioxide. After extraction of water from the feed solution into the SPS draw solution, product water is recovered by heating the draw solution to strip carbon dioxide. The removal of carbon dioxide from the SPS draw solution results in separation of tertiary amine from the product water due to increased hydrophobicity of the SPS draw solution (Figure 17).

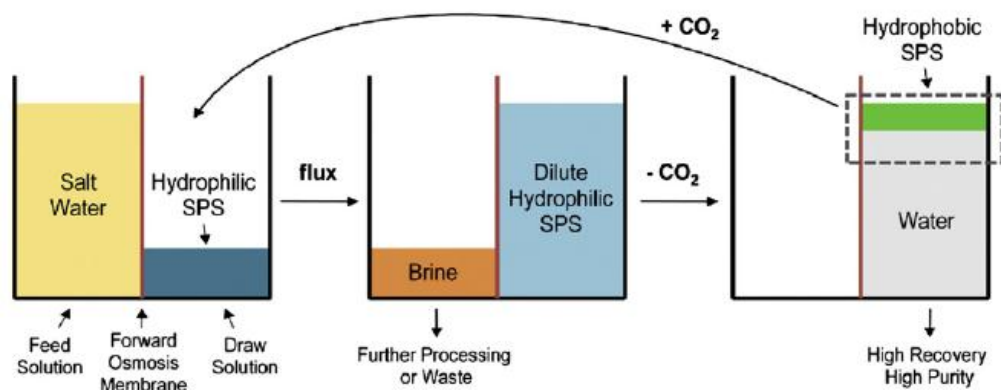


Figure 17: FO system by Stone et al. utilizing SPS draw solution [140]

Yen and co-workers [140] studied the application of 2-Methylimidazole-based organic compounds as draw solutes. In this study, product water is recovered from the draw solution by thermal decomposition of the draw solute.

Ling and Chung [141] used super hydrophilic nanoparticles as the draw solute. Nanoparticles coated with acrylic acid and triethylene glycol were prepared and dissolved in water to be used as draw solution. The separation of nanoparticles from product water was done using an ultrafiltration system.

McCutcheon [100] used highly soluble ammonium bicarbonate as draw solute that resulted in high water flux. The recovery of product water from the draw solution required moderate heating up to 60 °C. Upon heating, the soluble ammonium bicarbonate

draw solute decomposes into ammonia and carbon dioxide gas that escape out of the solution to produce pure product water. In fact, among all the draw solutes used in the past, ammonium bicarbonate is by far the most widely accepted draw solute in FO applications. Ammonium bicarbonate is highly soluble in water which leads to a very high osmotic pressure. Figure 18 shows the schematic of the novel FO process by McCutcheon employing ammonium bicarbonate draw solution.

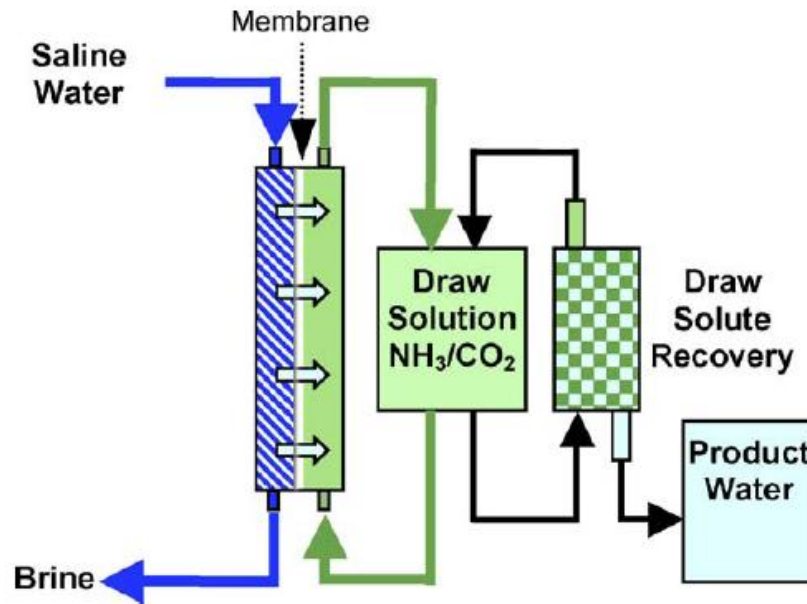


Figure 18: The novel ammonia-carbon dioxide FO process by McCutcheon [100]

### 1.8. Current Limitations of Forward Osmosis Desalination

All of the aforementioned FO efforts mentioned in the previous sections highlight two main limitations in FO desalination. These two limitations are the following:

- Lack of high-performance membranes
- The necessity for an easily separable draw solution

The existing FO membranes result in low water flux due to concentration polarization effects as described in Sections 1.6.4 and 1.6.5. As a result, researchers have been synthesizing new and better FO membranes that allow higher water flux, higher salt rejection, reduced internal concentration polarization, higher chemical stability, and higher mechanical strength.

In addition, all of the previous efforts in FO utilize draw solutions that require energy to recover product water from the diluted draw solution. In any case, after extraction of water from the feed solution into the draw solution, heating or any other form of energy is required to separate the draw solute from the product water. In some cases, the draw solute is separated from the product water using a low-pressure RO unit. In all cases, energy is required for regeneration or separation of the draw solute from the product water. As a result, continuous efforts are being made to find a suitable draw solute that requires less or no energy for separation or regeneration.

### **1.9. Research Methods and Contributions**

Forward osmosis (FO) desalination is a new and emerging technology that can revolutionize freshwater production from brackish and seawater. However, to move FO from laboratory research to real practical applications, there is a pressing need to achieve breakthroughs in the development of both novel FO membranes and draw solutes. As a result, this research aims to make important contributions in the field of FO desalination by investigating the flux performance of different osmotic membranes. In addition, novel draw solutes have been investigated that are easily regenerated and do not require any form of energy for the recovery of product water.

This thesis presents two bench-scale FO apparatus that were used to study the flux performance of two synthetic FO membranes. In addition, the thesis presents two draw solutes that generate high osmotic pressures. In addition, the draw solutes selected in this research can be easily recovered and separated from the pure product water without utilizing any means of energy.

### **1.10. Thesis Objectives**

This thesis explores the following aspects of forward osmosis desalination:

- To construct novel FO laboratory systems for desalination of brackish and seawater
- To study the performance of various commercial FO membranes
- To investigate and present novel draw solutes that require minimum or no energy for regeneration

- To minimize or eliminate the energy use associated with the recovery of pure product water from the draw solution
- To compare the selected draw solutions in terms of osmotic pressures, maximum solubility, and the produced water flux

### **1.11. Thesis Organization**

This thesis presents important contributions in the field of forward osmosis desalination. The background information on the need for energy-efficient desalination technologies, review of conventional desalination techniques and their drawbacks, introduction to forward osmosis and its theory, and literature review on the previous forward osmosis efforts have been presented in Chapter 1. Chapter 2 covers the method and algorithm for the selection of membranes and the draw solutes. Chapter 3 discusses the first laboratory scale FO experimental setup, in the form of a U-tube, for desalination of brackish and seawater. This FO apparatus utilizes a commercial FO membrane provided by Hydration Technologies Inc. (HTI, Albany, OR) and employs magnesium sulfate as the draw solution. The experimental results, performance of the membrane, the observed water flux, and the energy-free recovery of product water from the magnesium sulfate draw solution are highlighted. Chapter 4 presents the second bench-scale FO apparatus for desalination of brackish and seawater. This apparatus utilizes a proprietary FO membrane submerged in copper sulfate draw solution. Chapter 4 also presents the experimental results, the observed water flux using the submerged membrane FO apparatus, and the energy-free recovery of product water from the copper sulfate draw solution. Conclusions from this study and recommendations for improvements and future study are presented in Chapter 5.

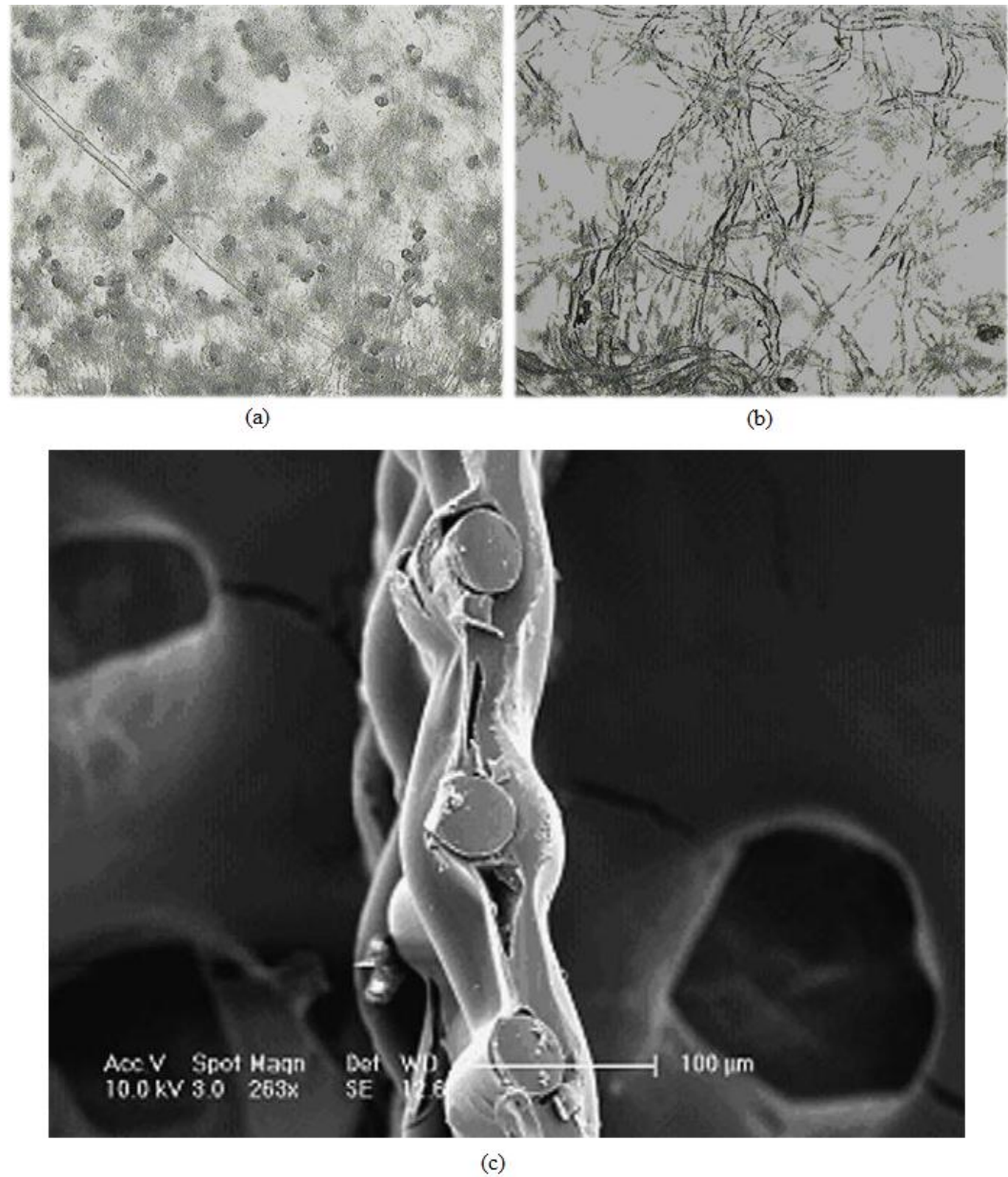
## Chapter 2: Selection of Membranes & Draw Solutions

The operation of a forward osmosis system requires a suitable FO membrane, a suitable draw solution, and an appropriate experimental apparatus. As discussed in Section 1.7.1, the membrane selected for FO must exhibit high water flux, high salt rejection, and mechanical and chemical stability. On the other hand, the draw solution selected for FO desalination must require low or no energy for separation from the pure product water. In addition, the draw solution must be highly soluble and must be able to create a higher osmotic pressure than the feed solution. This chapter highlights the FO membrane and the draw solution selection process and the membranes and draw solutions used in this research.

### 2.1. Membranes Tested

Most of the researches in FO desalination focus on the synthesis of new membranes in the laboratory [92, 97, 127, 134]. However, in this research, two commercial flat-sheet FO membranes were purchased and used in all the experiments. The membranes were selected based on their commercial success, high salt rejection, and high water permeability.

The first FO membrane used in the experiments was a commercial flat sheet cellulose acetate (CA) membrane provided by Hydration Technologies Inc. (HTI, Albany, OR). Hydration Technologies Inc. is the global leader and innovator in the manufacture of commercial FO membranes. The exact composition of this membrane is proprietary. However, it is believed to be composed of cellulose-based polymers with an embedded polyester mesh acting as mechanical support. Cellulose acetate membranes have been widely studied in RO applications [142, 143]. Therefore, the potential application of this cellulose acetate membrane in FO was investigated. The membrane used had an active layer on one side and a non-active layer. The feed solution usually faces the active layer of the membrane in order to reject the salts in the feed. From literature, the salt rejection of the membrane was 95-99% [96] and the membrane water permeability coefficient ( $A$ ) was  $3.07 \times 10^{-12} \text{ m s}^{-1} \text{ Pa}^{-1}$  [144]. Figure 19 shows the microscopic and SEM images of the HTI's FO membrane.



*Figure 19:* (a) (b) Microscopic image of the active and non-active membrane layers, respectively (c) A cross-sectional SEM image of HTI's FO membrane [99]

It can be seen from Figure 19 that the thickness of the HTI FO membrane is less than  $50\ \mu\text{m}$ . In addition, the structure of the membrane is quite different from standard RO membranes [99].

The second membrane used in this research was another commercial flat-sheet FO membrane available in the Chemical Engineering laboratory. The composition of this membrane was unknown. However, the membrane is similar to polyamide thin film

composite RO membranes in texture. The salt rejection was measured using simple RO experiment and was found to be 99-99.5% [59]. The microscopic images of this membrane are shown in Figure 20.

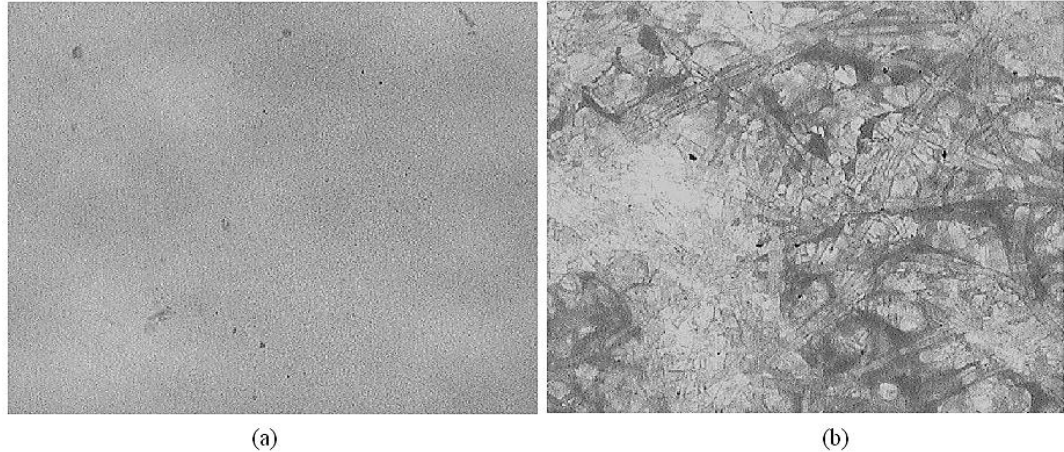


Figure 20: Microscopic image of membrane M-2 (a) Active layer (b) Non-active layer

The following table summarizes the two commercial FO membranes used in the FO experiments:

Table 3: FO membranes used in the experiments

	Membrane 1 (M-1)	Membrane 2 (M-2)
Vendor	Hydration Technologies Inc.	-
Composition	Cellulose acetate	-
Configuration	Flat sheet	Flat sheet
Salt Rejection (%)	95-99	99-99.5
Water Permeability Coefficient ( $\text{m s}^{-1} \text{Pa}^{-1}$ )	$3.07 \times 10^{-12}$	-

The two selected membranes have been named M-1 and M-2 and these notations will be used throughout the text.



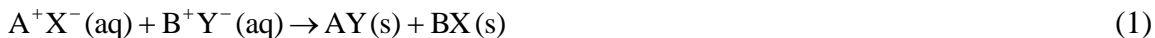
## **2.2. Selected Draw Solutions and Product Water Recovery Method**

Forward osmosis involves permeation of water present in the feed solution (brackish or seawater) into the draw solution across the FO membrane. An important desired characteristic of the draw solute is its high solubility in water. Successful FO operation requires high osmotic pressure of the draw solution. The high solubility and hence high osmotic pressure of the draw solution results in increased water flux across the FO membrane. In other words, the draw solute used in the FO process must be highly soluble in water in order to provide enough osmotic pressure to extract water from brackish or seawater. The typical concentration of brackish and seawater is 5,000 ppm and 40,000 ppm, respectively. Therefore, to desalinate brackish water, the draw solute must be soluble enough to provide a concentration greater than 5,000 ppm on the draw solution side. Similarly, to desalinate seawater, the draw solute must be able to provide a concentration much greater than 40,000 ppm on the draw solution side of the membrane. In short, high solubility is one of the most desired characteristics of the draw solute used in FO desalination. The higher the solubility, the greater is the osmotic pressure and higher is the water flux across the membrane.

However, the most important criterion for the selection of a proper draw solution is the ease of separation of pure product water. In FO, the draw solution becomes diluted after the permeation of water from the feed solution. The diluted draw solution must then be processed to remove the soluble draw solute and produce pure water. As highlighted in Section 1.7.2, all of the previous efforts and researches in FO utilize draw solutions that require energy to recover product water from the diluted draw solution. Therefore, in this research, draw solutes were selected in order to eliminate the energy required to separate pure product water from the diluted draw solution.

The motivation behind the selection of suitable draw solution in this thesis was to eliminate the use of energy required to separate product water from the diluted draw solution. An investigation was made in order to identify highly soluble inorganic salts that can be separated from water by energy-free means such as precipitation by chemical reaction.

Metathesis precipitation reaction was set as the objective method for the separation of product water from the diluted draw solution. A metathesis precipitation reaction is simply a double displacement reaction where the anions and cations exchange partners to produce two solid products.



In other words, soluble chemicals are reacted to produce two non-soluble precipitates. The formation of two precipitates removes all soluble chemicals from the aqueous solution resulting in formation of pure water.

In addition, the toxicity of the draw solute was considered as another selection criterion. Since water is extracted into the draw solution, toxic or hazardous draw solutes are not recommended. Any draw solute with a health hazard factor greater than 2 was rejected according to the Hazardous Materials Identification System (HMIS).

Finally, the recovery and reuse of the draw solute is important. Since the metathesis precipitation reaction will convert the draw solute into a precipitate, the recovery of draw solution must be considered in order to reduce the draw solute chemical cost.

Based on the flow diagram shown in Figure 21, two draw solutes were selected; magnesium sulfate ( $MgSO_4$ ) and copper sulfate ( $CuSO_4$ ). Both of these draw solutes are highly soluble in water and provide high osmotic pressures. Copper sulfate has not been used as FO draw solute in the literature. On the other hand, magnesium sulfate has been used as draw solute by Sairam *et al.* [92] to study the flux performance of the synthesized membrane. However, the recovery of product water from the diluted  $MgSO_4$  draw solution has not been reported. In this research, the recovery of product water from  $MgSO_4$  draw solution has been reported for the first time. After extraction of water from the feed solution, both draw solutes can be precipitated to furnish pure product water. The separation of product water from the diluted draw solutions and the recovery of the draw solutes will be discussed in the subsequent chapters of the thesis (Chapter 4 and 5). Table 4 provides a summary of the selected draw solutes.

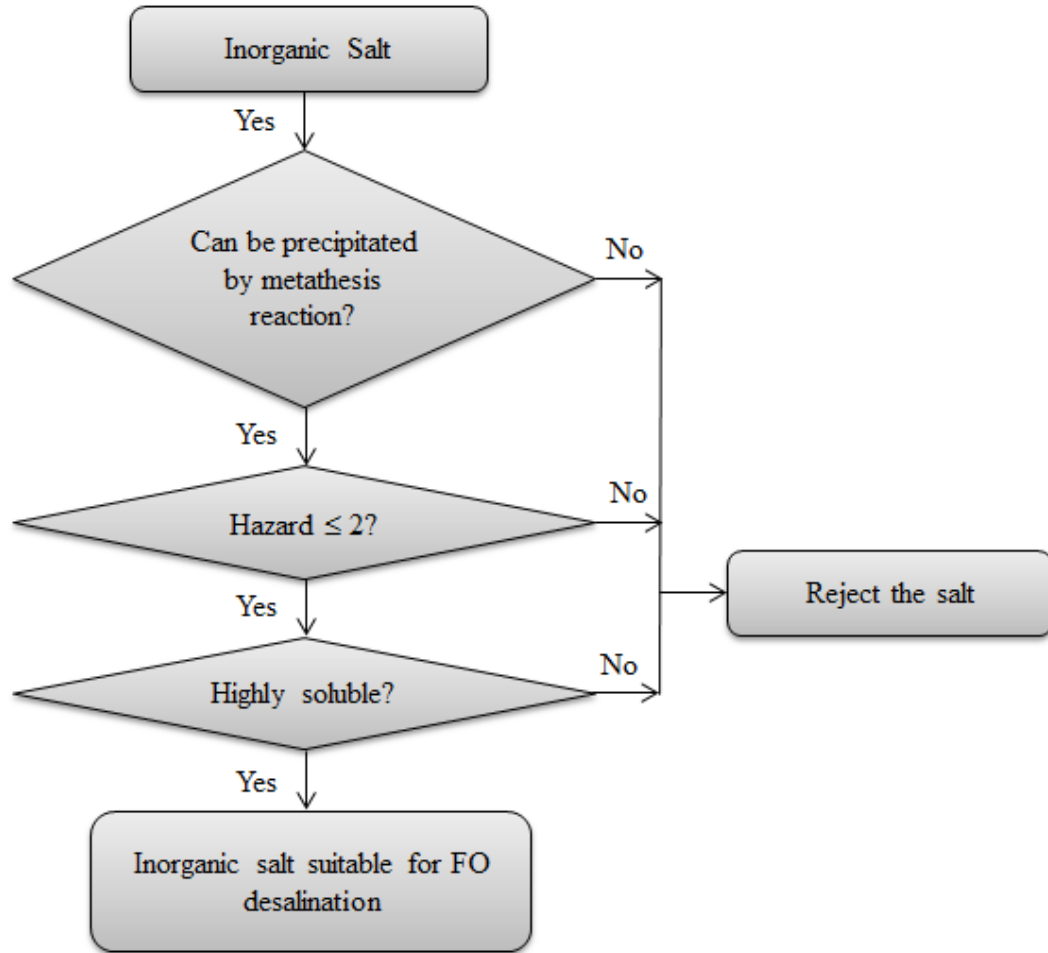


Figure 21: Illustration of flow diagram for draw solution selection

Table 4: Summary of the selected draw solutes

	Magnesium sulfate	Copper sulfate
Maximum solubility (g/100 g H <sub>2</sub> O) [145]	35.7	22.0
Maximum solubility (ppm)	357,000	220,000
Health hazard factor	1	2
Can be precipitated by metathesis reaction?	Yes	Yes
Can be recovered?	Yes	Yes

After selecting the FO membranes and the draw solutions, two laboratory-scale FO apparatus were constructed and the performance of the selected draw solutions and the selected membranes was evaluated.

Figure 22 shows the organization of this research. Membrane M-1 was used with magnesium sulfate draw solution in a batch FO apparatus consisting of a U-tube. On the other hand, membrane M-2 was used with copper sulfate draw solution in a submerged membrane FO apparatus. These are the topics of the subsequent chapters.

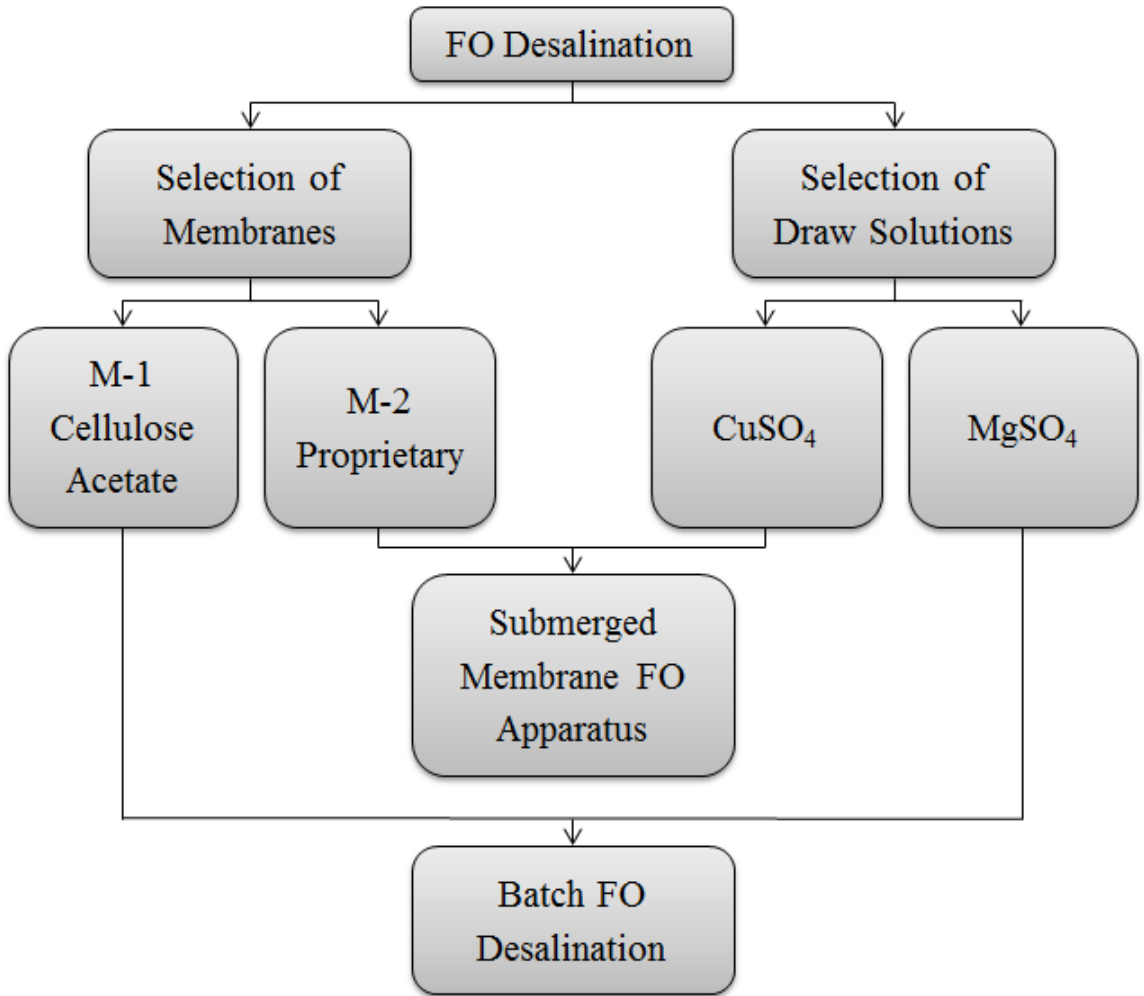
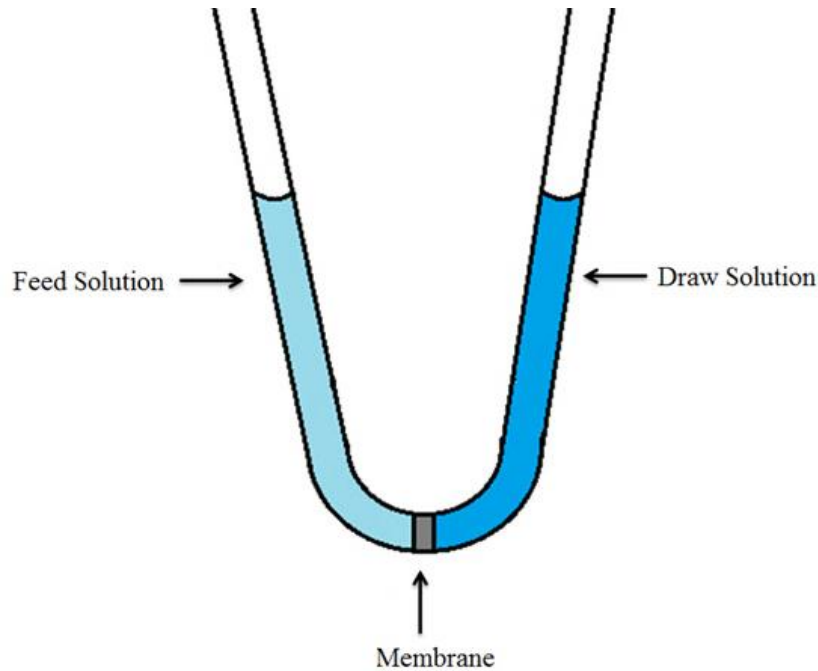


Figure 22: FO desalination research organization

## Chapter 3: Batch Forward Osmosis Desalination Using Membrane M-1 & MgSO<sub>4</sub> Draw Solution

### 3.1. Experimental Setup

The batch FO experiments were carried out in a simple U-tube as shown below:



*Figure 23:* U-tube FO apparatus

The cellulose acetate membrane provided by Hydration Technologies Inc. (membrane M-1) was placed in the middle of the circular U-tube. The feed solution of low salt concentration (low osmotic pressure) was fed to one side of the membrane. The other side of the U-tube was filled with a highly concentrated draw solution of high osmotic pressure and having higher salt concentration than the feed solution. The initial level of the feed and the draw solution in the U-tube was kept the same by placing equal volumes of the feed and the draw solution on each side of the U-tube. The feed and draw solution sides were kept open to the atmosphere to allow natural FO to take place. The area of the membrane available for the flux was 6.157 cm<sup>2</sup>.

Naturally, due to osmotic pressure gradient, water in the feed solution flows to the draw solution. The U-tube was calibrated on both sides to measure the changes in volume

of the solutions with time. From the measured values of volume change, water flux through the membrane can be calculated using Equation 5.

### **3.2. Chemicals & Materials**

Unless otherwise specified, all chemicals and reagents used in the FO experiments were of analytical grade. Deionized water with negligible dissolved solid content (50 ppm) was used as solvent for preparation of the feed and the draw solutions. The feed solution was prepared using analytical grade sodium chloride (NaCl) purchased from Fisher Scientific, UK. Sodium chloride was used to simulate brackish and seawater feeds since the major component in these feeds is NaCl. The draw solution was prepared using analytical grade magnesium sulfate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) purchased from Merck Group, Germany. Barium hydroxide octahydrate ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ) was purchased from Panreac, Spain.

### **3.3. Concentration Measurement**

The flow of water from the feed to the draw solution results in a change in concentration of both the feed and the draw solution. The change in concentration of the NaCl feed solution was measured using a standard TDS meter. The TDS meter by HACH is used in the laboratory. On the other hand, gravimetric analysis was used for quantitative determination of  $\text{MgSO}_4$  draw solution concentration.

### **3.4. Experimental Conditions & Procedure**

All the U-tube FO experiments were conducted at a laboratory temperature of  $25 \pm 3^\circ\text{C}$ . The following is a summary of the procedure for conducting the experiments:

- Clean the U-tube prior to running the experiment. Small amount of salts or solids in the U-tube may introduce errors in the concentration measurements.
- Fix the cellulose acetate membrane (M-1) in the middle of the U-tube. Check for any leakages by performing a simple leak test using deionized water.
- Fill the U-tube with the feed solution facing the active side of the membrane and the  $\text{MgSO}_4$  draw solution on the other side.

- Keep the same initial level of solutions on both sides of the membrane by pouring equal volumes of solutions on each side of the U-tube.
- From the calibrated scale on the U-tube, measure the change in volume of the feed or the draw solution after suitable time intervals for flux calculations.
- Measure the concentration of the feed solution with time using a TDS meter.
- Measure the final concentration of the  $\text{MgSO}_4$  draw solution using gravimetric analysis as follows:
  - Obtain a sample of the diluted  $\text{MgSO}_4$  draw solution and measure its volume in mL.
  - Measure the mass (in grams) of an empty crucible using a weighing balance. Place the sample on the crucible and heat it on an electric heater.
  - Measure the mass of the crucible after vaporizing all the water.
  - Find the mass of  $\text{MgSO}_4$  by subtracting the mass of crucible after heating and the mass of empty crucible.
  - Divide the mass of  $\text{MgSO}_4$  in the draw solution sample by the volume (in liters) to find the concentration in g/L.

### 3.5. Basic Performance Using NaCl Draw Solution

The first part of the experiments conducted consisted of checking the basic performance of membrane M-1 in the FO process. For this case, deionized water was used as feed with dissolved solid content of approximately 50 ppm. A draw solution of 8,000 ppm NaCl was used. Initially, 500 mL of the feed and the draw solution was added to each side of the membrane. The change in volume of the draw solution and the concentration of the draw solution was measured at different intervals of time. As the FO process proceeded, the flow of water from the feed to the draw solution resulted in a decrease in NaCl concentration in the draw solution. Therefore, the flux is expected to decrease with time. From the change in volume of the draw solution, flux was calculated for each time interval of measurement using Equation (5). The data collected is summarized in the following table:

Table 5: Data collected and calculated flux using deionized water (100 ppm) as feed and 8,000 ppm NaCl draw solution

Start Time (min)	End Time (min)	Volume Change $\Delta V$ (mL)	Draw Solution Concentration (ppm)	Water Flux ( $L/m^2 h$ )
0	-	-	8,000	-
0	31.08	11.0	7,490	34.49
0	79.00	27.0	7,340	33.30
0	60.37	18.0	7,120	29.05
0	32.00	10.0	7,240	30.45
0	31.53	9.0	7,030	27.81
0	60.38	17.0	6,950	27.44
0	30.85	7.0	6,740	22.11

Figure 24 shows the change in water flux through the membrane with the changing draw solution concentration with time.

As the concentration of the draw solution decreased with time due to the flow of water from the feed solution, the flux decreased linearly with time ( $R^2=0.9701$ ).



Therefore, water flux through the cellulose acetate membrane in the U-tube was observed to decrease with time since the draw solution becomes diluted.

From this basic performance test of membrane M-1, it was observed that the membrane M-1 worked well in FO process and the maximum observed flux was 34.49 L/m<sup>2</sup> h when the draw solution concentration was 7,490 ppm NaCl. After the performance test, the membrane was tested for real FO brackish and seawater desalination.

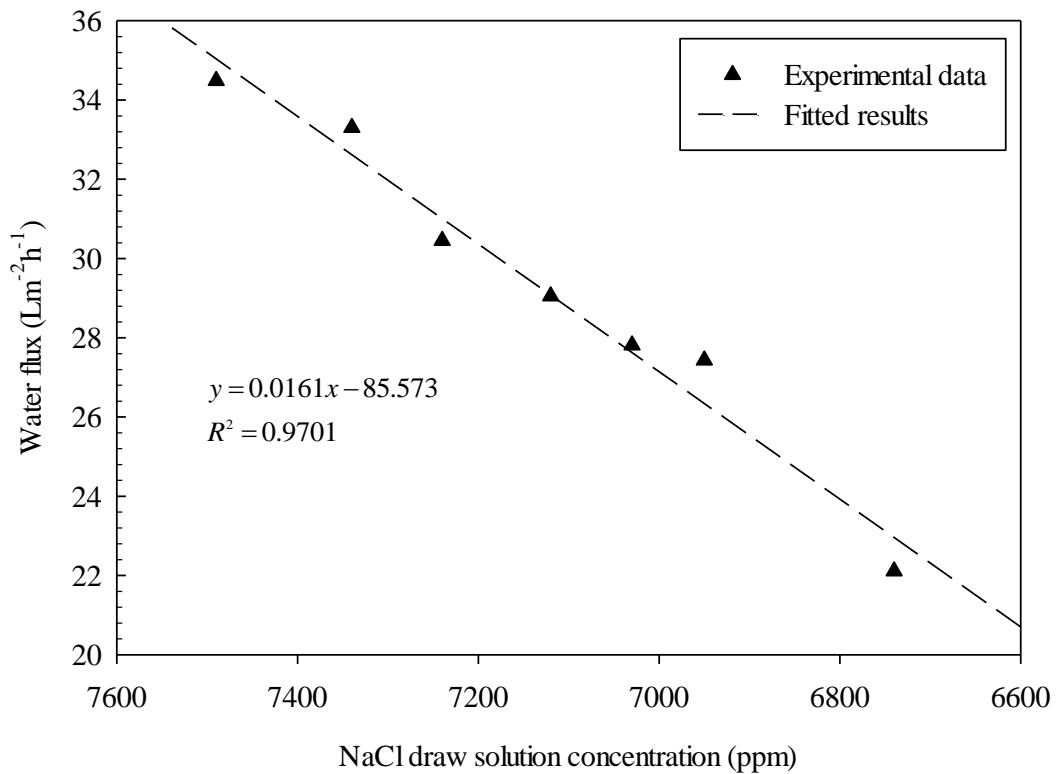


Figure 24: Water flux through the cellulose acetate membrane as a function of draw solution (NaCl) concentration using deionized water (50 ppm) as the feed solution. Initial draw and feed solution volume: 500 mL, initial draw solution concentration: 8,000 ppm NaCl

### 3.6. Effect of Feed Solution Concentration

After testing the application in the FO process, the membrane M-1 was utilized for real desalination applications. Different feed solutions were prepared with concentrations ranging from approximately 5,000 ppm (corresponding to brackish water) to approximately 40,000 ppm (corresponding to seawater). Then, the effect of feed solution concentration on the flux was studied. Feed solutions were prepared by dissolving NaCl in deionized water. Each time the concentration of the draw solution used was kept constant at 80,000 ppm NaCl.

Table 6: Average flux obtained for different feed solution concentrations. Draw solution concentration constant at 80,000 ppm NaCl

Feed Solution Concentration (ppm)	Average Water Flux (L/m <sup>2</sup> h)
5,030	9.744
10,150	5.594
19,500	2.806
31,300	1.369
39,000	1.042

The active side of the cellulose acetate membrane faced the feed solution. Each time from the measured volume change, the average flux was calculated over a period of time. The results are summarized in the Table 6 and Figure 25 shows the graphical representation of the results.

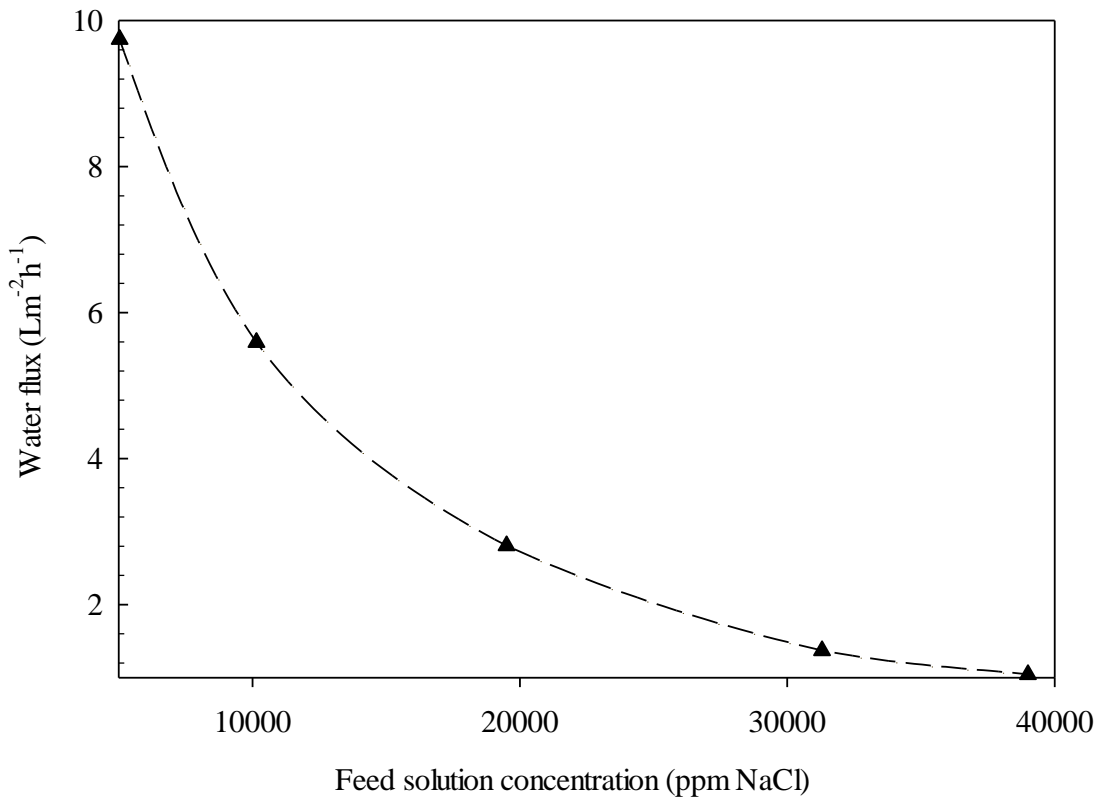


Figure 25: Average water flux through the cellulose acetate membrane as a function of feed solution concentration. Initial draw and feed solution volume: 500 mL, initial draw solution concentration: 80,000 ppm for all cases. (▲: experimental results, dotted line: fitted results).

It was observed that increasing the NaCl concentration in the feed solution results in an asymptotic decrease in the average water flux through the FO membrane M-1 at a constant draw solution concentration of 80,000 ppm NaCl. This is due to the fact that greater the concentration difference between the feed and the draw solution, the greater the osmotic pressure difference, and hence higher the flux. At feed solution concentration of 5,030 ppm, corresponding to typical brackish water concentration, an average water flux of 9.74 L/m<sup>2</sup> h was observed using 80,000 ppm of NaCl draw solution. Similarly, for the feed solution concentration of 39,000 ppm, which corresponds to typical seawater concentration, an average flux of 1.04 L/m<sup>2</sup> h was observed using 80,000 ppm of NaCl draw solution. In short, the cellulose acetate membrane M-1 was found to be suitable for desalination.

### 3.7. Effect of Draw to Feed Solution Concentration Ratio

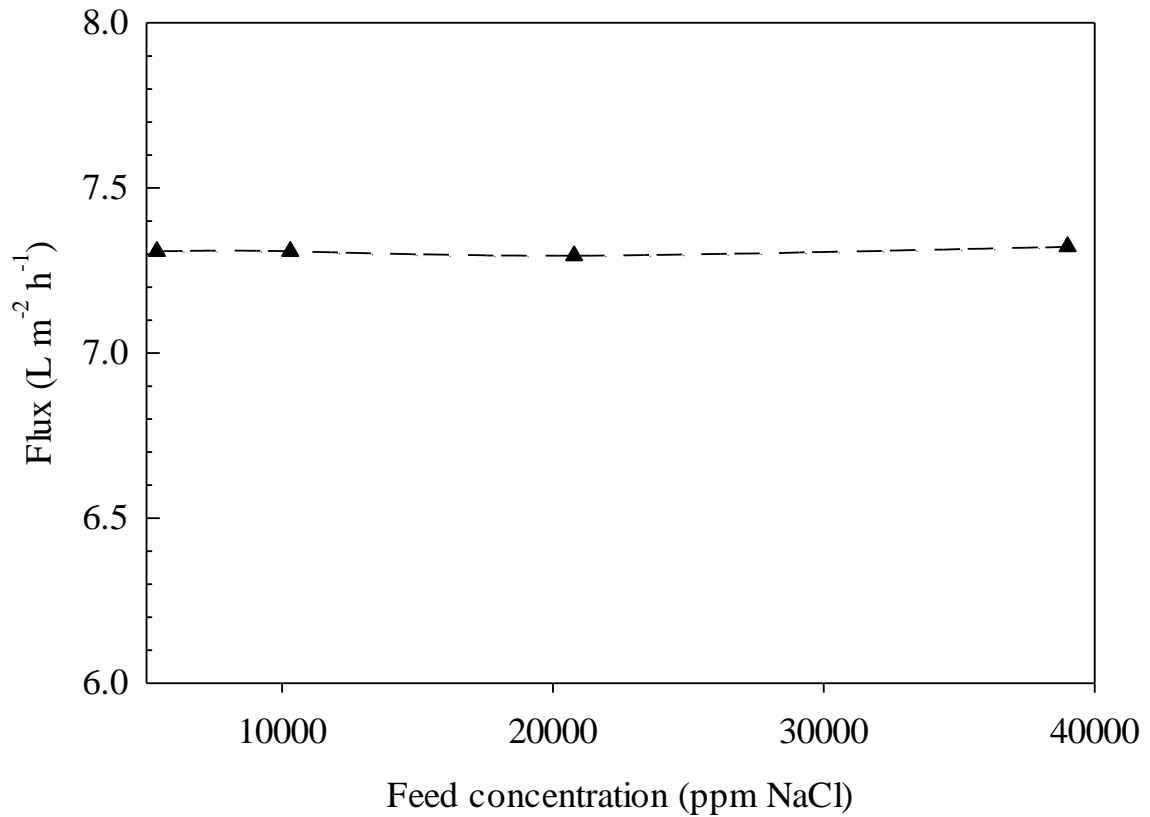
The next step was investigating the effect of changing the ratio of draw to feed solution concentration on the flux through the membrane. The motivation behind this investigation was the high flux obtained when deionized water was used as feed solution. As depicted in Figure 24, the water flux through the membrane was very high. In this case, a draw solution of 8,000 ppm NaCl was used and the ratio of draw solution concentration to feed solution concentration (50 ppm for deionized water) was 160. However, when the membrane was tested at higher feed concentrations, a draw solution of 80,000 ppm NaCl was used. In this case, the draw to feed solution concentration ratio was varied from 16 to 2.05 by using feed solutions ranging from 5,000 ppm to 39,000 ppm, respectively. As result, a lower flux was obtained due to lower draw to feed concentration ratio used. Also, using deionized water as feed, the effect of internal concentration polarization is expected to be of much less significance than in cases of high feed and draw solution concentrations resulting in higher water flux in the former case. Nevertheless, the ratio of draw to feed solution concentration played a significant role in controlling the water flux through the membrane.

Table 7: Feed and draw solution concentrations at constant concentration ratio

Feed Solution Concentration (ppm NaCl)	Draw Solution Concentration (ppm NaCl)	Ratio	Average Water Flux (L m <sup>-2</sup> h <sup>-1</sup> )
5,380	25,600	4.8	7.31
10,300	50,000	4.9	7.31
20,780	99,680	4.8	7.29
39,000	198720	5.1	7.32

In order to study the effect of the draw to feed solution concentration ratio on water flux, a constant ratio of approximately 5 was used. The concentrations of the feed and draw solutions used and the average flux observed in this part of experimental study are summarized in Table 7.

The maximum draw to feed solution concentration ratio was limited by the solubility of NaCl in water at room temperature. The maximum solubility of NaCl in water at 25 °C is 360,000 ppm [145]. This indicates that the maximum ratio of draw to feed solution concentration of 9 can be used with a feed solution concentration of 40,000 ppm. However, a ratio of 5 was chosen in order to avoid reaching the saturation limit of NaCl. Using a saturated NaCl draw solution may cause precipitation in the draw side of the membrane and is, therefore, not recommended. The precipitation of NaCl will result in fouling of the FO membrane. Therefore, to avoid precipitation of NaCl, the maximum concentration of the draw solution was limited to 200,000 ppm or less.



*Figure 26:* Average water flux through the cellulose acetate membrane at constant draw to feed solution concentration ratio of 5. Initial draw and feed solution volume: 500 mL (▲: experimental results, dotted line: fitted results).

The feed solution concentration was varied from 5,380 ppm to 39,000 ppm with a corresponding 5 times more concentrated draw solution. For each trial, the flux through the membrane remained constant at 7.3 L/m<sup>2</sup>h approximately. Therefore, the water flux through the membrane was observed to be a function of the draw to feed concentration ratio. The higher the ratio used, the greater the water flux and vice versa. Thus, the average water flux was found to be constant when the ratio of draw to feed solution concentration was kept constant at 5. This is shown in Figure 26.

### **3.8. Desalination Using MgSO<sub>4</sub> Draw Solution**

Sodium chloride (NaCl) was used as draw solute in the previous sections in order to evaluate the flux performance of the membrane M-1. However, the use of NaCl as draw solution in FO is not the best choice despite its high solubility, non-toxic nature and low membrane fouling characteristic. This is because the recovery of pure product water from the diluted NaCl draw solution requires use of energy consuming processes such as RO or distillation. In order to avoid the use of any energy-intensive product water recovery method, magnesium sulfate was tested as the draw solute.

Compared to sodium chloride, magnesium sulfate has a lower osmotic pressure, especially at higher concentrations as shown in Figure 16 [99]. This is because the osmotic coefficient ( $\phi$ ) of NaCl is higher than that of MgSO<sub>4</sub>. Therefore, in cases where the NaCl and MgSO<sub>4</sub> concentrations are the same, the MgSO<sub>4</sub> draw solution will result in a lower flux compared to NaCl draw solution of the same concentration to due lower osmotic pressure of MgSO<sub>4</sub> draw solution as indicated by Equation (2). However, the use to magnesium sulfate as draw solute in FO is useful in terms of product water recovery. Magnesium sulfate is highly soluble in water and pure water can be recovered from the diluted draw solution by metathesis reaction with barium hydroxide to precipitate all soluble chemicals as insoluble magnesium hydroxide and barium sulfate.

The membrane M-1 was tested in the U-tube using magnesium sulfate as the draw solute. A 240,000 ppm of MgSO<sub>4</sub> draw solution was prepared by dissolving 491.4 g of magnesium sulfate heptahydrate in 1 L of water. In order to simulate real desalination applications, two feed solutions were used; brackish water (5,050 ppm NaCl) and seawater (40,000 ppm NaCl). The initial concentration of magnesium sulfate in the draw

solution was 240,000 ppm in both cases. The procedure for conducting the experiments in highlighted in Section 3.4.

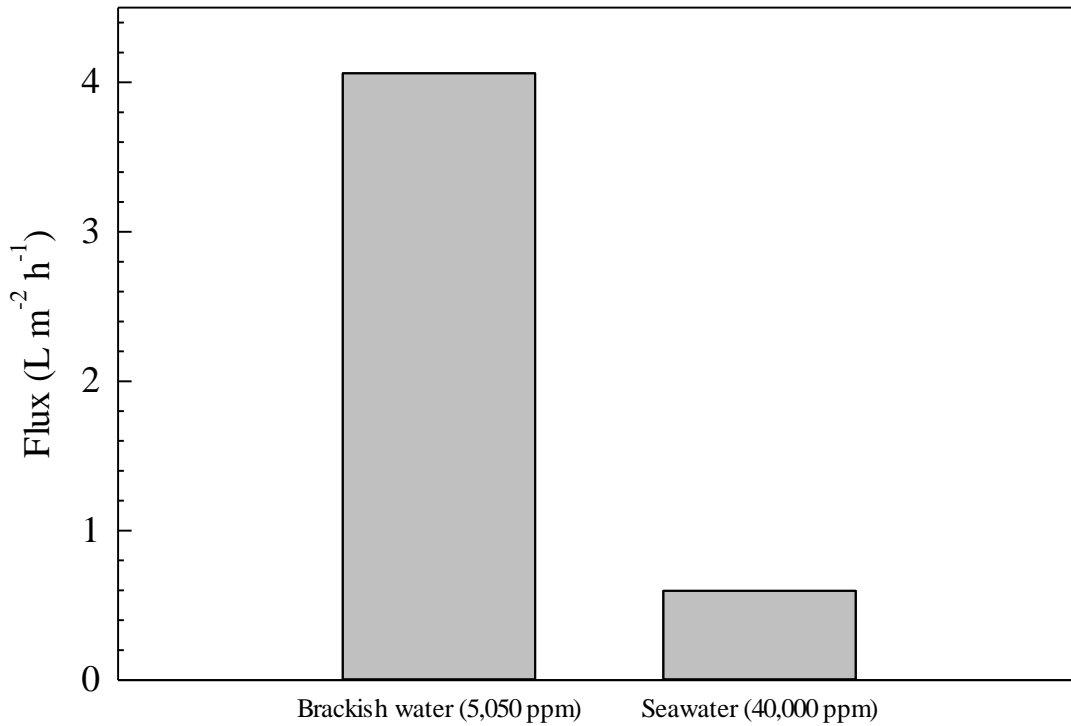


Figure 27: Average water flux using brackish and seawater and MgSO<sub>4</sub> draw solution. Initial draw and feed solution volume in the U-tube: 400 mL, initial draw solution concentration: 240,000 ppm.

Using 240,000 ppm of magnesium sulfate draw solution, an average water flux of 4.06 L/m<sup>2</sup> h was achieved using a feed solution concentration of 5,050 ppm corresponding to typical brackish water concentration. Similarly, for the feed solution concentration of 40,000 ppm, which corresponds to typical seawater concentration, an average flux of 0.60 L/m<sup>2</sup> h was observed using 240,000 ppm of magnesium sulfate draw solution. The water flux at 40,000 ppm of feed solution was found to be low. The flux may be increased by increasing the concentration of magnesium sulfate in the draw solution. The maximum concentration of magnesium sulfate heptahydrate in water is 357,000 ppm [145]. Increasing the draw solution concentration will result in higher osmotic pressure and thus, higher water flux through the membrane.

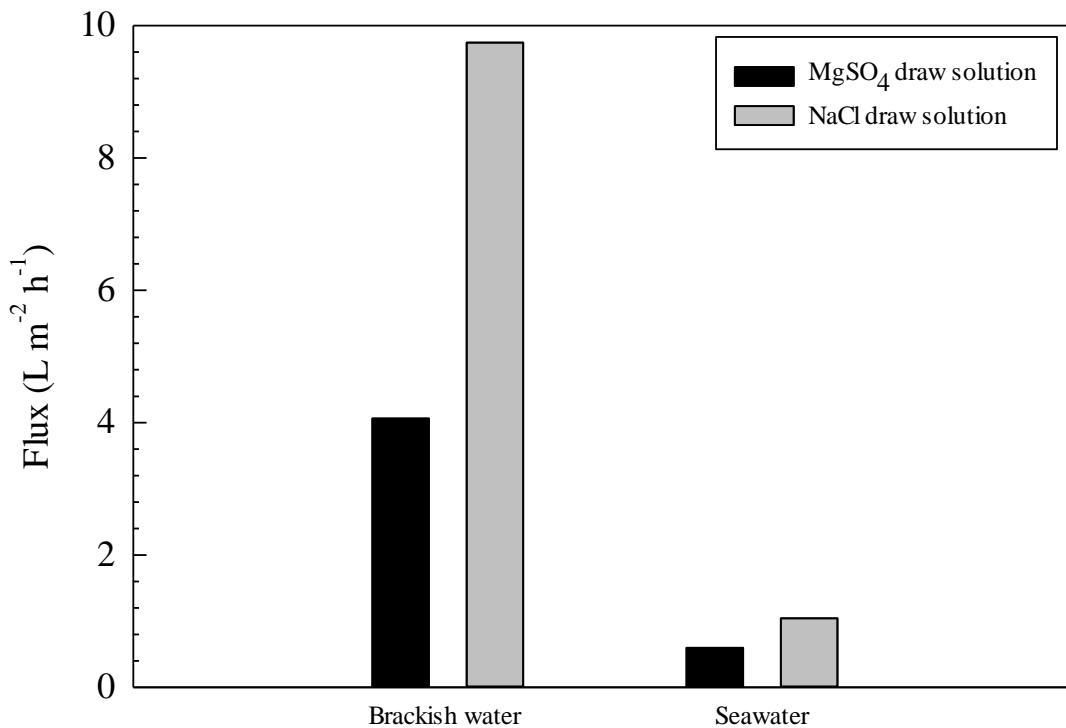


Figure 28: Comparison of flux obtained using NaCl and MgSO<sub>4</sub> draw solutions.

As depicted in Figure 28, using magnesium sulfate as draw solute resulted in a lower water flux compared to the water flux obtained using NaCl draw solution even though the draw solution concentration of magnesium sulfate was much higher. This is attributed to the fact that magnesium sulfate has much lower osmotic pressure compared to NaCl as explained earlier.

Therefore, it was found that the magnesium sulfate draw solution and the membrane M-1 (cellulose acetate) can be successfully used to extract water from brackish and seawater. The water flux performance was satisfactory since a small membrane area was used. The water flux can be increased by increasing the membrane area that is available for flux. This can be done using a U-tube with larger diameter. In addition, the flux can further be increased by increasing the concentration of the magnesium sulfate draw solution. The higher the concentration of the draw solution, the greater is the osmotic pressure and hence higher the water flux across the membrane.



### 3.9. Method of Product Water Recovery

The diluted draw  $\text{MgSO}_4$  solution was collected from the U-tube at the end of the experiment using seawater as feed and its concentration was measured. Based on the concentration of magnesium sulfate in the diluted draw solution, stoichiometric amount of barium hydroxide solution was added. This metathesis reaction resulted in formation of two insoluble precipitates namely magnesium hydroxide and barium sulfate. The reaction is as follows:

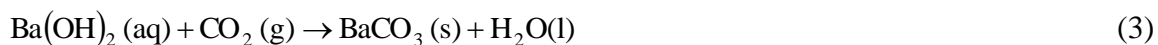


Both magnesium hydroxide and barium sulfate have negligible solubility in water compared to barium hydroxide and magnesium sulfate as indicated in Table 8.

Table 8: Solubility values of the chemicals used and the products [145]

Compound	Solubility (g/100 g $\text{H}_2\text{O}$ )
Magnesium sulfate heptahydrate	35.7
Barium hydroxide octahydrate	4.91
Magnesium hydroxide	$6.90 \times 10^{-4}$
Barium sulfate	$3.10 \times 10^{-4}$

The precipitates containing a mixture of magnesium hydroxide and barium sulfate were allowed to settle. The top water layer was filtered using standard filter paper supplied by Whatman Ltd. to remove the suspended precipitates. In case if excess barium hydroxide solution is added, carbon dioxide can be bubbled through the solution using a diffuser in order to convert excess soluble barium hydroxide to insoluble barium carbonate according to the following reaction:



Finally, filtration may be performed once again to ensure removal of any suspended precipitates.

### 3.10. Product Water Recovery From the Diluted MgSO<sub>4</sub> Draw Solution

At the end of the FO run using seawater as feed, the diluted draw solution was collected from the U-tube. The concentration of magnesium sulfate was measured using gravimetric analysis. Two trials were performed and the average concentration was found to be 130,500 ppm (130.5 g/L).

Table 9: Concentration measurement of diluted MgSO<sub>4</sub> draw solution using gravimetric analysis (at the end of FO run using seawater as feed)

	Trial 1	Trial 2
Mass of empty crucible (g)	36.548	36.551
Volume of draw solution sample (mL)	1	1
Mass of crucible after evaporation of water (g)	36.676	36.684
Concentration of MgSO <sub>4</sub> (g/L)	128	133
Average concentration (g/L)	130.5	

Based on the amount of magnesium sulfate present in the draw solution, stoichiometric amount of barium hydroxide octahydrate (dissolved in water) was added to the diluted draw solution. In this case, 171 g of barium hydroxide octahydrate dissolved in water was added to 500 mL of the diluted magnesium sulfate draw solution. Magnesium hydroxide and barium sulfate precipitates formed were allowed to settle as shown below:



*Figure 29:* Reaction of magnesium sulfate with barium hydroxide to produce magnesium hydroxide and barium sulfate precipitates.



*Figure 30:* Settlement of precipitates, top layer is the product water.

The top water layer was collected and filtered twice to remove the suspended precipitate particles. Since, barium hydroxide was added in stoichiometric amount, subsequent treatment with carbon dioxide was not required to remove excess barium hydroxide.

### 3.11. Product Water Analysis

Finally, the salt content of the product water was found using gravimetric analysis. Two trials were performed as indicated in the following table:

Table 10: *Measurement of salt concentration of the final product water by gravimetric analysis*

	Trial 1	Trial 2
Mass of empty crucible (g)	36.551	36.551
Volume of draw solution sample (mL)	10	10
Mass of crucible after evaporation of water (g)	36.554	36.555
Concentration of salts (g/L)	0.3	0.4
Average concentration (ppm)	350	

According to Table 8, the maximum solubility of magnesium hydroxide and barium sulfate in water is 6.90 ppm and 3.10 ppm, respectively. However, the salt content of the product water was found to be 350 ppm. This may be attributed to the fact that the salt rejection of the FO membrane was 95-99% and some of salt present in the feed flow with the water diffusing through the membrane. The turbidity and pH of the final product water was 1.19 NTU and 7.25, respectively. The results are summarized below:

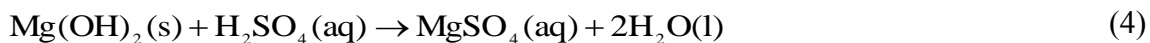
Table 11: *Analysis of product water after desalination of seawater (40,000 ppm NaCl)*

	pH	Turbidity (NTU)	Salt content (ppm)
Product water	7.25	1.19	350

### 3.12. Recovery and Reuse of MgSO<sub>4</sub> Draw Solution

The mixture of magnesium hydroxide and barium sulfate precipitates can be processed to recover the MgSO<sub>4</sub> draw solution. The insoluble magnesium hydroxide can be converted to soluble MgSO<sub>4</sub> to be reused as draw solution. This can be achieved by addition of sulfuric acid in stoichiometric amount with magnesium hydroxide. The insoluble magnesium hydroxide reacts with sulfuric acid according to the following

reaction:



The solution can be filtered to separate the insoluble barium sulfate from the recovered magnesium sulfate draw solution. The recovered draw solution can be reconcentrated by addition of more solute and can be used again in the FO process.

Barium sulfate is obtained as a side product of the process. It can be dried and used in standard applications such as thickener in oil well drilling fluids for crude oil and natural gas exploration. It can also be used as a filler and extender and as a contrast agent in X-ray diagnosis. In addition, barium sulfate can also be used as a coating of photographic paper to increase reflexivity of the image [146].

### **3.13. Summary of Batch FO Desalination Using MgSO<sub>4</sub> Draw solution**

Figure 31 shows the schematic of the batch FO desalination process utilizing the cellulose acetate membrane M-1 and magnesium sulfate draw solution. The membrane is placed in the middle of a graduated U-tube. The feed solution (brackish or seawater) is fed to one side of the U-tube while 240,000 ppm of MgSO<sub>4</sub> draw solution is fed to the other side. Water is extracted to from the feed solution into the MgSO<sub>4</sub> draw solution. The salts present in the feed are rejected by the membrane. After extraction of all the water present in the feed, the diluted MgSO<sub>4</sub> draw solution is reacted with barium hydroxide solution to precipitate all soluble chemicals as magnesium hydroxide and barium sulfate precipitates. The precipitates are allowed to settle and the top water layer is filtered to furnish pure product water. Using this method, seawater (40,000 ppm NaCl) was successfully desalinated to produce pure water with a salt content of 350 ppm. Furthermore, the MgSO<sub>4</sub> draw solution can be recovered by reaction of the precipitate mixture, containing magnesium hydroxide and barium sulfate, with stoichiometric amount of sulfuric acid. Insoluble magnesium hydroxide reacts with sulfuric acid to form soluble magnesium sulfate. The soluble magnesium sulfate solution is separated from insoluble barium sulfate by filtration. The recovered magnesium sulfate draw solution can be reconcentrated and reused in the FO desalination process. Barium sulfate is obtained as a side product of the desalination process and can be used for standard applications.

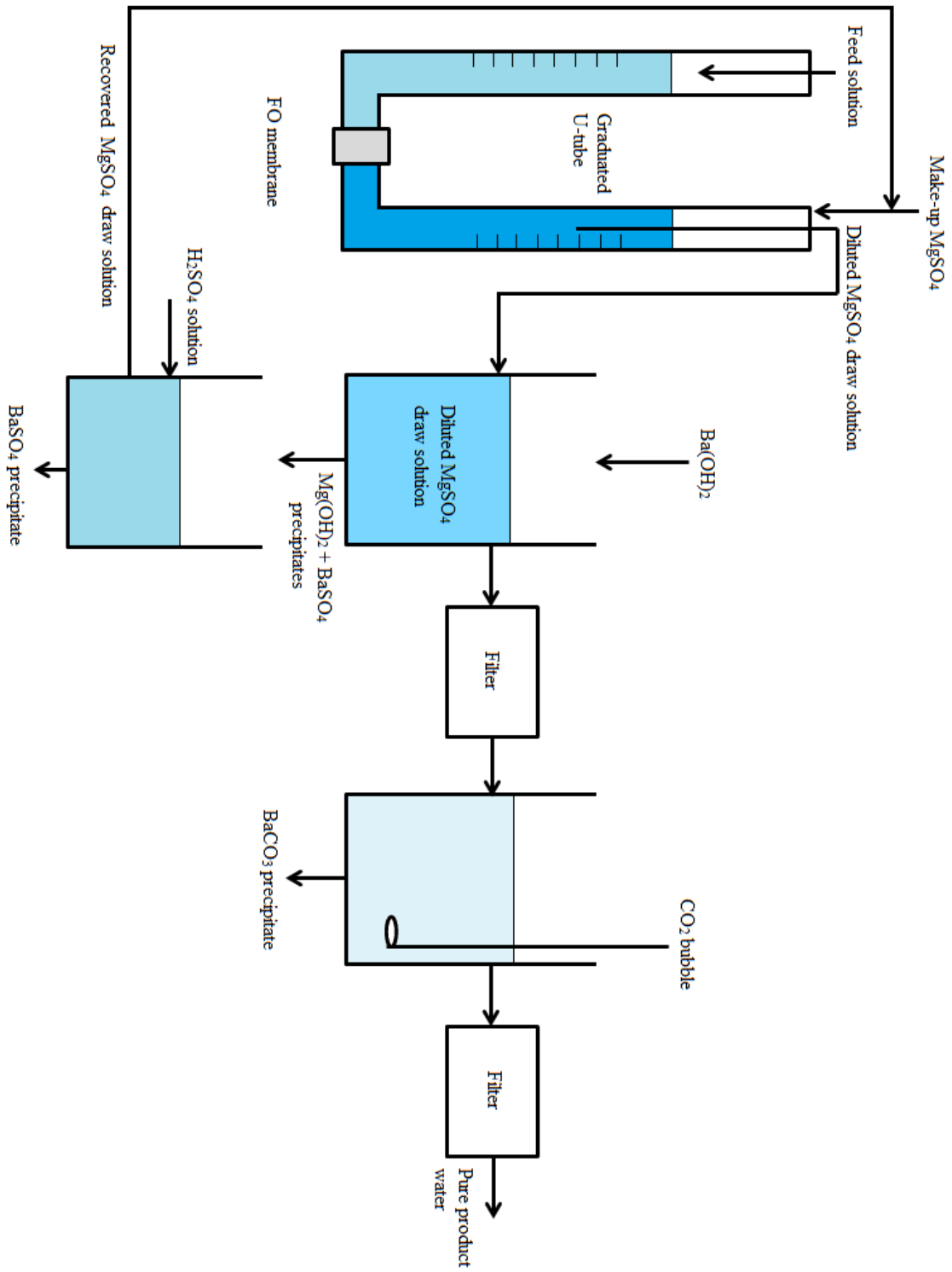


Figure 31: Schematic diagram of bench-scale forward osmosis system utilizing NaCl feed solution and MgSO<sub>4</sub> draw solution

## **Chapter 4: Forward Osmosis Desalination Using Submerged Membrane M-2 and CuSO<sub>4</sub> Draw Solution**

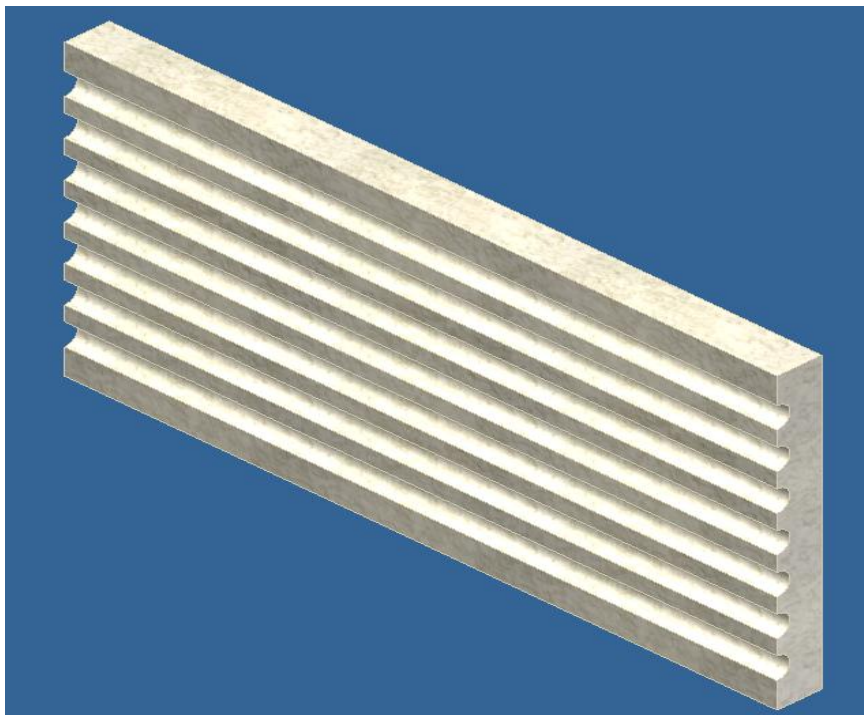
The second part of the research dealt with FO desalination using a novel experimental apparatus. In this part of the research, a submerged-membrane FO apparatus was used that utilized membrane M-2 and copper sulfate draw solution. The basic desalination and water flux performance of membrane M-2 was tested using NaCl draw solution. Finally, copper sulfate draw solution was used and the product water was recovered from the diluted copper sulfate draw solution by metathesis precipitation.

### **4.1. Membrane Preparation**

The membrane M-2 was a flexible flat-sheet membrane. In order to submerge it in a draw solution bath, the membrane was wrapped around a ceramic support as shown in Figure 32. The salts present in the saline feed were not rejected by the ceramic support. In other words, the salts present in the feed solution were able to pass through the pores in the support. Salts present in the feed solution were only rejected by the membrane M-2.



*Figure 32: Ceramic support*



*Figure 33:* A cross-section of the ceramic support showing the internal channels for feed solution flow

The ceramic support consisted of internal channels for the flow of the feed solution as shown in Figure 33. The feed solution entered through holes provided at the side of the support as shown in Figure 34. While flowing through the internal channels in the ceramic support, a portion of the water present in the feed solution diffuses into the draw solution after passing through the wrapped membrane M-2. The remaining feed solution leaves the support channels through the holes provided at the other end of the support.



*Figure 34:* Holes at the side of the ceramic support for the flow of feed solution

In order to prepare the membrane and ceramic support assembly, a rectangular portion of the flat-sheet membrane M-2 was taken and the edges of the membrane were glued to the ceramic support. Inflow and outflow pipes for the feed solution were



connected to both sides of the support. These pipes covered the holes on both sides of the membrane and support assembly. Figure 35 shows the membrane and the ceramic support assembly.

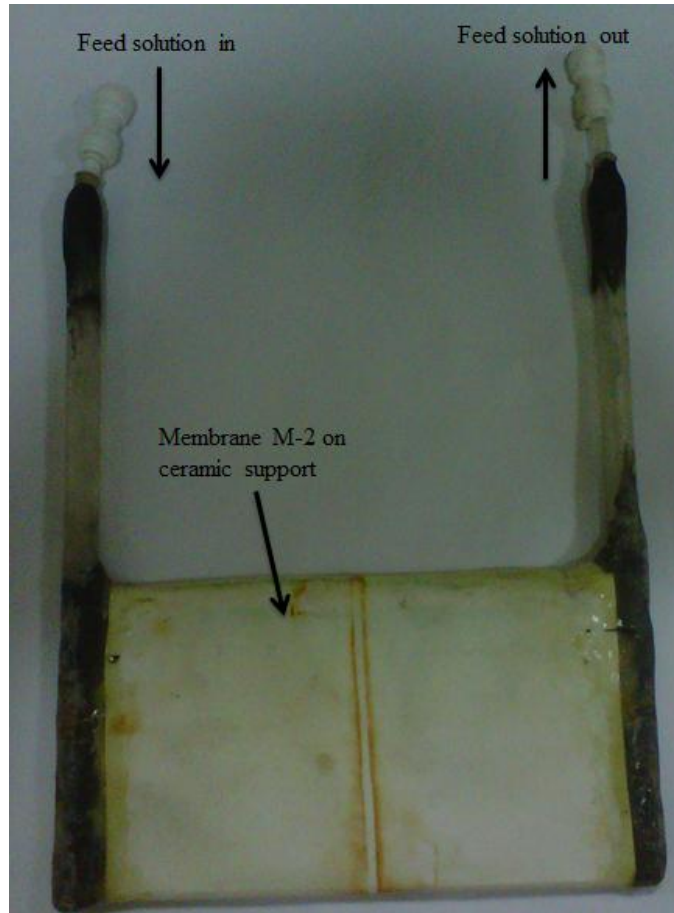


Figure 35: Membrane M-2 wrapped on a ceramic support

After the preparation of the membrane, a simple leak test was performed. Deionized water was pumped through the membrane to ensure absence of any leaks.

#### 4.2. Experimental Setup & Working Principle

Figure 36 shows the schematic of the submerged membrane FO desalination apparatus. The feed solution tank is calibrated to read the change in volume of the feed solution with time. The volume change can then be used to estimate the water flux by using Equation (5). The membrane M-2 wrapped on the ceramic support is submerged inside a draw solution bath.

Initially, a portion of the feed solution is pumped into the membrane in order to remove entrapped air bubbles present in the channels of the ceramic support. This is achieved using a laboratory metering pump with a flow rate of 1.5 L/min.

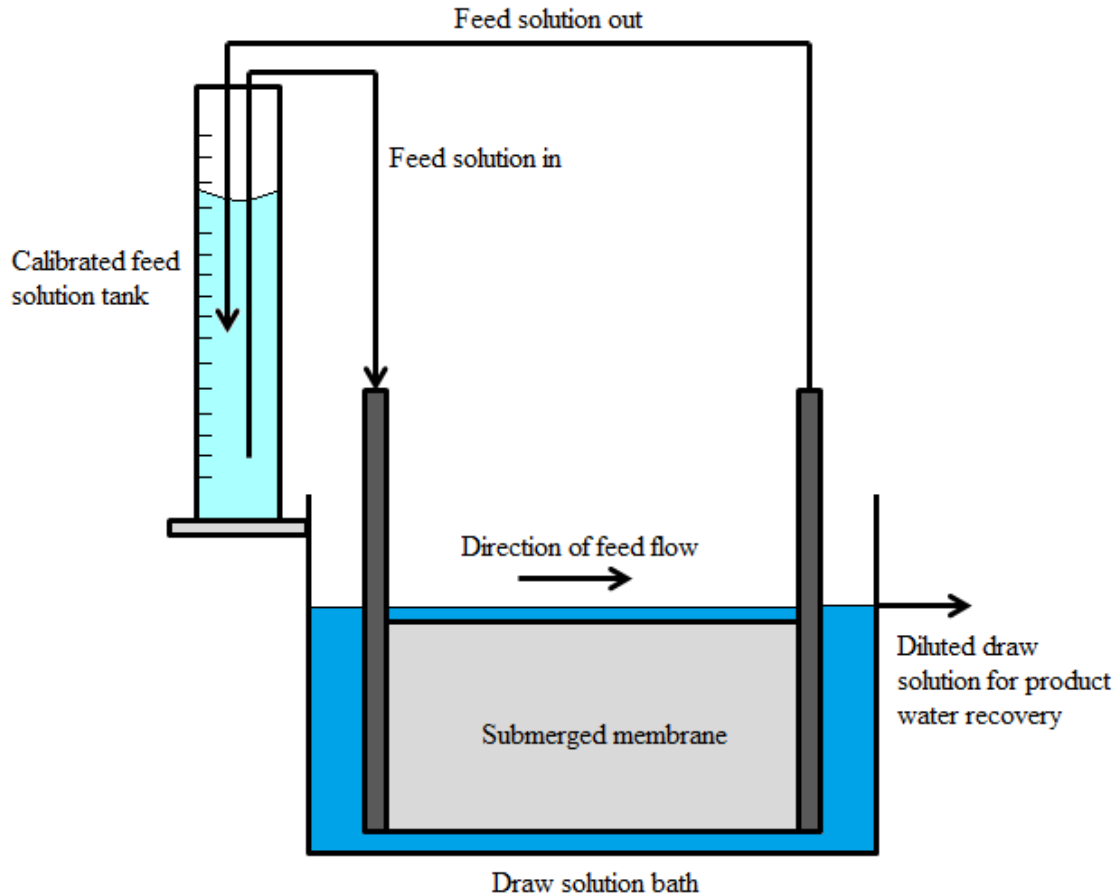


Figure 36: Submerged membrane FO desalination apparatus

The pumping of the feed solution causes swelling of the wrapped membrane due to water flowing out of the porous ceramic support. After removal of entrapped air bubbles, the pump is disconnected and the feed solution is allowed to flow into the membrane under the action of gravity as shown in Figure 36. For this purpose, the feed solution tank is placed at a higher level than the draw solution bath. The swelled membrane is placed in the draw solution bath for FO process to occur. The swelled submerged membrane now contains the feed solution between the ceramic support and wrapped membrane M-2.

Water in the feed solution present within the channels of the swelled membrane diffuses into the draw solution due to a difference in osmotic pressures. As water diffuses into the draw solution, more feed solution flows into the membrane under the action of gravity. The salts are rejected by the membrane M-2 which is wrapped on the ceramic support.

As the FO process takes place, the volume of the feed solution decreases with time. On the other hand, the volume of the draw solution increases with time with a corresponding decrease in the concentration of the draw solute. At the end of the experiment, the diluted draw solution can be collected and processed for the recovery of pure product water. The submerged membrane FO apparatus presented does not require use of any energy to pump the feed solution. The feed flows into the membrane under the action of gravity and water present in the feed diffuses across the membrane into the draw solution.

The rectangular submerged membrane was 16.5 cm wide and 11.8 cm in height. The thickness of the membrane was 1 cm. The total surface area (available for water flux) of the two faces of the membrane was 422.4 cm<sup>2</sup>.

### **4.3. Chemicals & Materials**

All chemicals and reagents used in this part of the research were of analytical grade. Deionized water with negligible dissolved solid content (50 ppm) was used as solvent for preparation of the feed and the draw solutions. The feed solution was prepared using analytical grade sodium chloride (NaCl) purchased from Fisher Scientific, UK. Sodium chloride was used to simulate brackish and seawater feeds since the major component in these feeds is NaCl. The draw solution was prepared using analytical grade copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) purchased from BDH Laboratory Supplies, UK. Barium hydroxide octahydrate (Ba(OH)<sub>2</sub>·8H<sub>2</sub>O) was purchased from Panreac, Spain.

#### **4.4. Concentration Measurement**

In these set of experiments, the concentration of NaCl feed solution was measured using the same technique as highlighted in Section 3.3. Gravimetric analysis was used for quantitative determination of CuSO<sub>4</sub> draw solution concentration.

#### **4.5. Experimental Conditions & Procedure**

The experiments were conducted at a laboratory temperature of  $25 \pm 3$  °C. The main steps to operate the submerged membrane FO apparatus are as follows:

- Prepare the feed and the draw solutions.
- Submerge the membrane M-2 inside the draw solution bath.
- Remove any air bubbles entrapped inside the channels and connection pipes of the membrane. This can be done by pumping a portion of the feed solution into the membrane. A metering pump with a flow rate of 1.5 L/min can be used.
- Disconnect the pump and arrange the apparatus a shown in Figure 36.
- Place the feed solution tank above the draw solution bath to allow the flow of feed solution by gravity.
- Measure the change in volume of the feed solution with time to computer the water flux.
- Measure the concentration of the feed solution (NaCl) using a TDS meter.
- Measure the concentration of copper sulfate draw solution using gravimetric analysis using the steps highlighted in Section 3.4.

#### 4.6. Basic Performance of the Submerged Membrane Using NaCl Draw Solution

After preparation of the membrane, simple experiments were conducted to check the applicability of membrane M-2 in the FO process. The basic flux performance of the membrane M-2 was investigated using NaCl draw solution.

Again, as in case of the U-tube apparatus in Chapter 3, different feed solutions were prepared with concentrations ranging from 5,000 ppm (corresponding to brackish water) to 40,000 pm (corresponding to seawater). The combinations of the feed and the draw solution concentrations used and the average flux observed are shown in Table 12.

Table 12: *Combinations of feed and draw solution concentrations used*

Trial No.	NaCl Feed Solution Concentration (ppm)	NaCl Draw Solution Concentration (ppm)	Water Flux ( $\text{L m}^{-2} \text{h}^{-1}$ )
1	5,220	80,000	3.89
2	9,390	80,000	3.69
3	25,000	80,000	3.15
4	40,000	80,000	2.84

For each case, the submerged membrane apparatus was operated according to the procedure highlighted in Section 4.5.

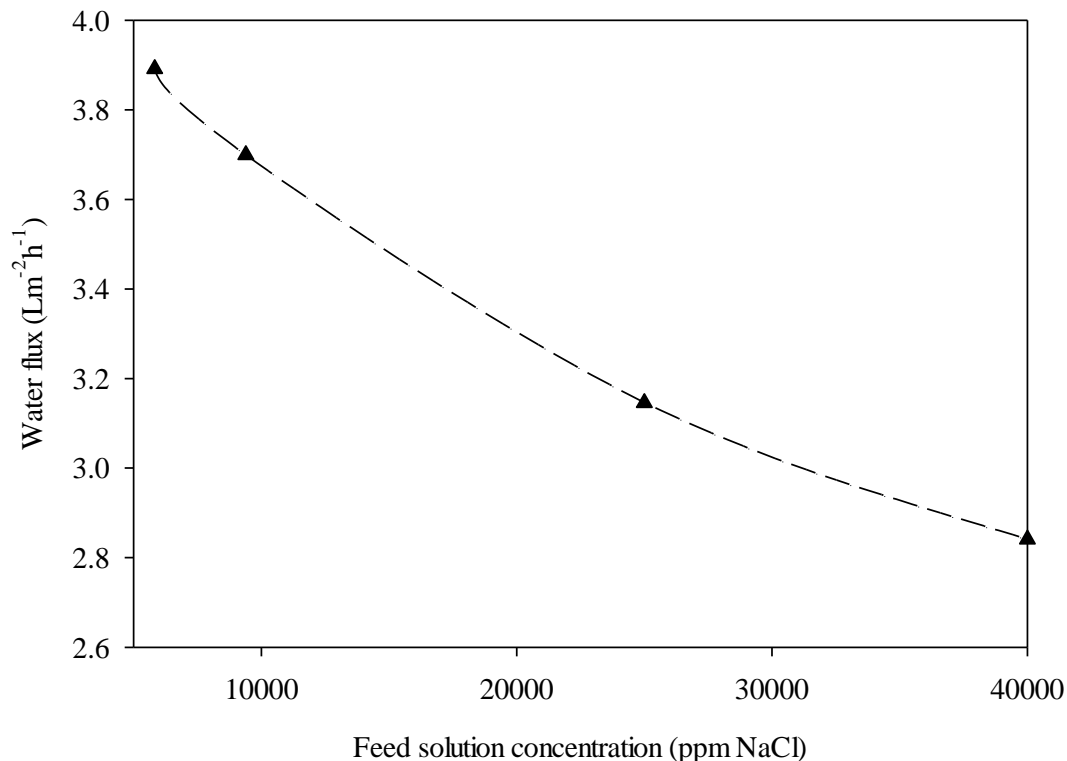


Figure 37: Average water flux through membrane M-2 as function of feed solution concentration

The average water flux, as expected, decreased as the NaCl feed solution concentration was increased at a constant draw solution concentration as depicted in Figure 37. Increasing the feed solution concentration increases the osmotic pressure of the feed. As a result, the osmotic pressure difference between the feed and the draw solution decreases resulting in a decreased water flux.

In case of submerged membrane, the decrease in average water flux was not significant as the feed solution concentration was increased. Increasing the NaCl feed solution concentration from 5,220 ppm to 40,000 ppm resulted in a decrease in water flux from 3.89 to 2.84 L/m<sup>2</sup>h. As a result, it can be concluded that the membrane M-2 did not suffer from high internal concentration polarization compared to membrane M-1. In case of membrane M-1, as depicted in Figure 25, increasing the feed solution concentration resulted in significant decrease in water flux through the membrane.

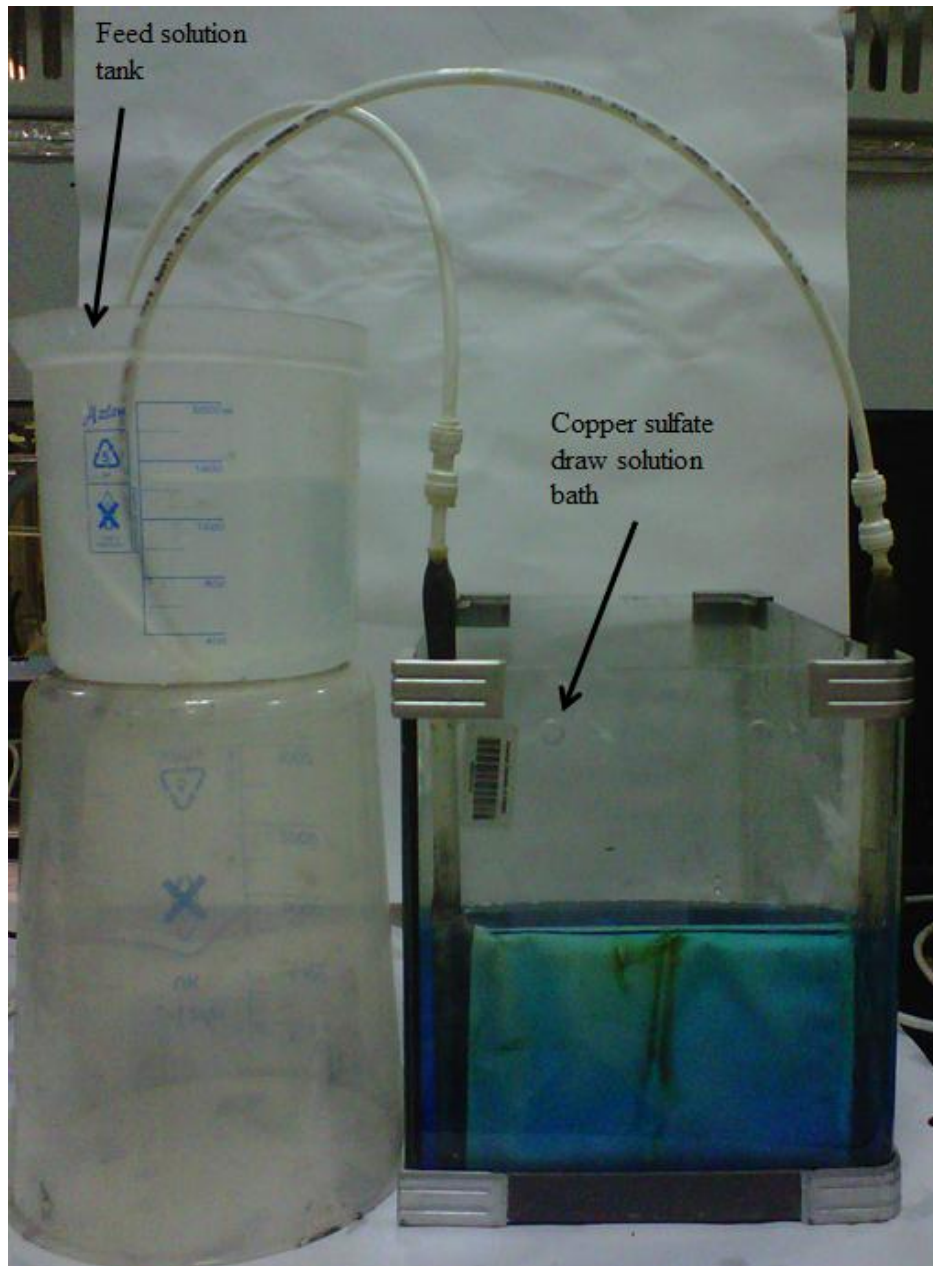
At feed solution concentration of 5,220 ppm, corresponding to typical brackish water concentration, an average water flux of 3.89 L/m<sup>2</sup> h was achieved using 80,000 ppm NaCl draw solution. Similarly, for the feed solution concentration of 40,000 ppm, which corresponds to typical seawater concentration, an average flux of 2.84 L/m<sup>2</sup> h was observed using 80,000 ppm draw solution.

In short, the membrane M-2 was found to be suitable for FO desalination. In addition, the basic FO experiments showed that the submerged membrane FO desalination apparatus was working successfully. After the preliminary experimental runs, the membrane M-2 and the submerged membrane apparatus was used for real desalination purposes using copper sulfate draw solution.

#### **4.7. Desalination Using CuSO<sub>4</sub> Draw Solution**

The applicability and basic flux performance of membrane M-2 in FO desalination was first tested using NaCl draw solution. After finding that the membrane M-2 was suitable for FO desalination and the submerged membrane apparatus was working successfully, real desalination experiments were conducted using copper sulfate draw solution.

Copper sulfate draw solution with a concentration of 200,000 ppm was prepared by dissolving 312.9 g of copper sulfate pentahydrate in 1 L of water. In order to simulate real desalination applications, two NaCl feed solutions were prepared. The first experiment was conducted using brackish water (5,000 ppm NaCl) while the second experiment used seawater (39,500 ppm NaCl) as the feed solution. The initial concentration of copper sulfate in the draw solution was 200,000 ppm in both cases. The procedure for conducting the experiments is highlighted in Section 4.5.



*Figure 38: Submerged membrane M-2, FO desalination using  $\text{CuSO}_4$  draw solution*



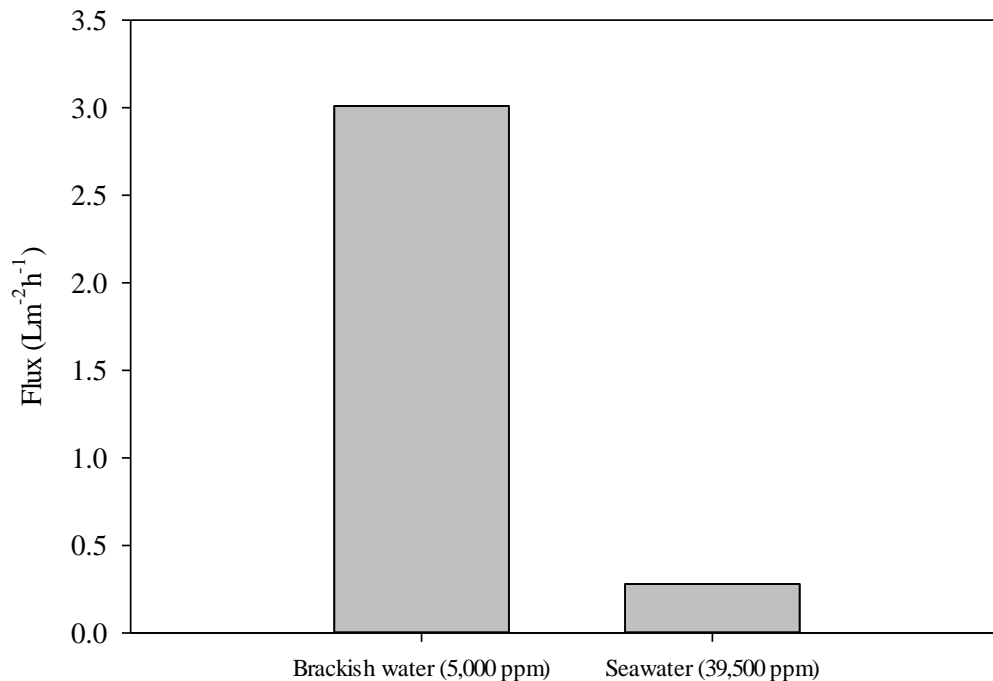


Figure 39: Average water flux using brackish and seawater and 200,000 ppm of CuSO<sub>4</sub> draw solution.

Figure 38 shows the submerged membrane FO desalination apparatus utilizing CuSO<sub>4</sub> as draw solute. Using 200,000 ppm of copper sulfate draw solution, an average water flux of 3.01 L/m<sup>2</sup> h was achieved using a feed solution concentration of 5,000 ppm corresponding to typical brackish water concentration. Similarly, for the feed solution concentration of 39,500 ppm, which corresponds to typical seawater concentration, an average flux of 0.28 L/m<sup>2</sup> h was observed using 240,000 ppm of copper sulfate draw solution. The water flux at 39,500 ppm of feed solution was found to be low. The maximum concentration of copper sulfate pentahydrate in water is 220,000 ppm [145]. A copper sulfate draw solution of 200,000 ppm can be taken as the maximum draw solution concentration since a saturated draw solution is not recommended. A saturated draw solution will result in precipitation and fouling of the FO membrane can possibly occur.

Therefore, it was found that copper sulfate draw solution was only suitable for brackish water desalination. In case of seawater, a very low flux of 0.28 L/m<sup>2</sup> h was observed using a 200,000 ppm of CuSO<sub>4</sub> draw solution. The flux cannot be improved by

increasing the draw solution concentration since the concentration is limited by the maximum solubility of copper sulfate pentahydrate in water at room temperature (220,000 ppm).

#### 4.8. Method of Product Water Recovery

The use of  $\text{CuSO}_4$  draw solution was investigated since pure product water can be recovered from this draw solution without use of any means of energy. As the FO process proceeds, water present in the feed solution flows across the membrane M-2 to the  $\text{CuSO}_4$  draw solution. As a result, the  $\text{CuSO}_4$  draw solution becomes diluted with time. The diluted  $\text{CuSO}_4$  draw solution is then collected and stoichiometric amount of barium hydroxide solution is added. Upon addition of barium hydroxide solution, the soluble copper sulfate reacts to form two insoluble products (copper hydroxide and barium sulfate). The chemical reaction is as follows:



Both copper hydroxide and barium sulfate have negligible solubility in water compared to barium hydroxide and copper sulfate as indicated in Table 13.

Table 13: Solubility values of the chemicals used and the products [145]

Compound	Solubility (g/100 g H <sub>2</sub> O)
Copper sulfate pentahydrate	22.0
Barium hydroxide octahydrate	4.91
Copper hydroxide	None
Barium sulfate	$3.10 \times 10^{-4}$

The precipitate containing a mixture of copper hydroxide and barium sulfate is allowed to settle. The top water layer is filtered using standard filter paper supplied by Whatman Ltd. to remove the suspended precipitates. In case if excess barium hydroxide solution is added, carbon dioxide can be bubbled through the solution using a diffuser in order to convert excess soluble barium hydroxide to insoluble barium carbonate according to the chemical reaction indicated by Equation 17.

Finally, filtration may be performed once again to ensure removal of any suspended precipitates. After removal of all the suspended particles, pure product water is obtained with negligible salt content.

#### 4.9. Product Water Recovery From the Diluted CuSO<sub>4</sub> Draw Solution

At the end of the FO experiment using membrane M-2 and brackish water as feed solution, the diluted copper sulfate draw solution was collected from the draw solution bath. The concentration of the diluted draw solution was then measured by gravimetric analysis using similar procedure as highlighted in Section 3.4. Three trials were performed. The results are indicated in the following table:

Table 14: Concentration measurement of diluted CuSO<sub>4</sub> draw solution using gravimetric analysis (at the end of FO run using brackish as feed)

	Trial 1	Trial 2	Trial 3
Mass of empty crucible (g)	36.159	36.127	36.142
Volume of draw solution sample (mL)	1	1	1
Mass of crucible after evaporation of water (g)	36.272	36.279	36.268
Concentration of CuSO <sub>4</sub> (g/L)	113	152	126
Average concentration (g/L)	130		

After performing the gravimetric analysis, the concentration of copper sulfate in the diluted draw solution was found to be 130 g/L (130,000 ppm). Based on this concentration, stoichiometric amount of barium hydroxide, dissolved in water, was added to the diluted draw solution. In this case, 128.5 g of barium hydroxide octahydrate dissolved in water was added to 500 mL of the diluted copper sulfate draw solution. Copper hydroxide and barium sulfate precipitates formed were allowed to settle as shown in Figure 40.



*Figure 40:* Formation of copper hydroxide and barium sulfate precipitate mixture

The top water layer was collected and filtered twice to remove the suspended precipitate particles. Since, barium hydroxide was added in stoichiometric amount, subsequent treatment with carbon dioxide was not required to remove excess barium hydroxide. After removal of all suspended solids pure water was obtained as the final product. Figure 41 shows the final product water sample after removal of soluble copper sulfate draw solute by metathesis precipitation.



*Figure 41:* Pure product water recovered from copper sulfate draw solution

#### 4.10. Product Water Analysis

The step in the recovery of pure product water was to find the concentration of salts and soluble chemicals in the final product. Gravimetric analysis was used for this purpose. A single trail of gravimetric analysis showed that the salt content of the product water sample was 100 ppm as shown below:

Table 15: *Measurement of salt concentration of the final product water by gravimetric analysis*

	Trial 1
Mass of empty crucible (g)	36.134
Volume of draw solution sample (mL)	10
Mass of crucible after evaporation of water (g)	36.135
Concentration of salts (g/L)	0.1

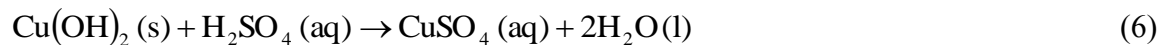
Therefore, pure product water with 100 ppm of dissolved solids was obtained from a diluted draw solution with a concentration of 130,000 ppm of CuSO<sub>4</sub>. The turbidity and pH of the final product water was 0.44 NTU and 7.61, respectively. The results are summarized below:

Table 16: *Analysis of product water after desalination of brackish (5,000 ppm NaCl)*

	pH	Turbidity (NTU)	Salt content (ppm)
Product water	7.61	0.44	100

#### 4.11. Recovery and Reuse of CuSO<sub>4</sub> Draw Solution

The mixture of magnesium hydroxide and barium sulfate precipitates can be processed to recover the CuSO<sub>4</sub> draw solution. The insoluble magnesium hydroxide can be converted to soluble CuSO<sub>4</sub> to be reused as draw solution. This can be achieved by addition of sulfuric acid in stoichiometric amount with copper hydroxide. The insoluble copper hydroxide reacts with sulfuric acid according to the following reaction:



The solution can be filtered to separate the insoluble barium sulfate from the recovered copper sulfate draw solution. The recovered draw solution can be reconcentrated by addition of more solute and can be used again in the FO process.

Barium sulfate is obtained as a side product of the process. It can be dried and used in standard applications as mentioned in Section 3.12.

#### **4.12. Summary of Submerged Membrane FO Desalination Using CuSO<sub>4</sub> Draw Solution**

The submerged membrane FO apparatus was constructed using membrane M-2. The basic flux performance of membrane M-2 was evaluated using NaCl draw solution. After successful initial operation of the apparatus, 200,000 ppm of copper sulfate draw solution was used to desalinate brackish (5,000 ppm NaCl) and seawater (39,500 ppm NaCl). An average water flux of 3.01 L/m<sup>2</sup> h was achieved using brackish water while an average flux of 0.28 L/m<sup>2</sup> h was observed using seawater. The copper sulfate draw solution was found to be suitable only for desalination of brackish water. The diluted CuSO<sub>4</sub> draw solution was collected after extraction of water from brackish water feed. Stoichiometric amount of barium hydroxide solution was added to precipitate the draw solute in the form of copper hydroxide and barium sulfate. Pure water with 100 ppm of dissolved solids was obtained as the final product after filtration. The CuSO<sub>4</sub> draw solution was recovered by addition of sulfuric acid in stoichiometric amount with copper hydroxide. The recovered copper sulfate draw solution is separated from insoluble barium sulfate by simple filtration. The recovered draw solution can then be reconcentrated and reused in the FO desalination process. Figure 42 shows the complete FO desalination technique utilizing membrane M-2 and copper sulfate draw solution.

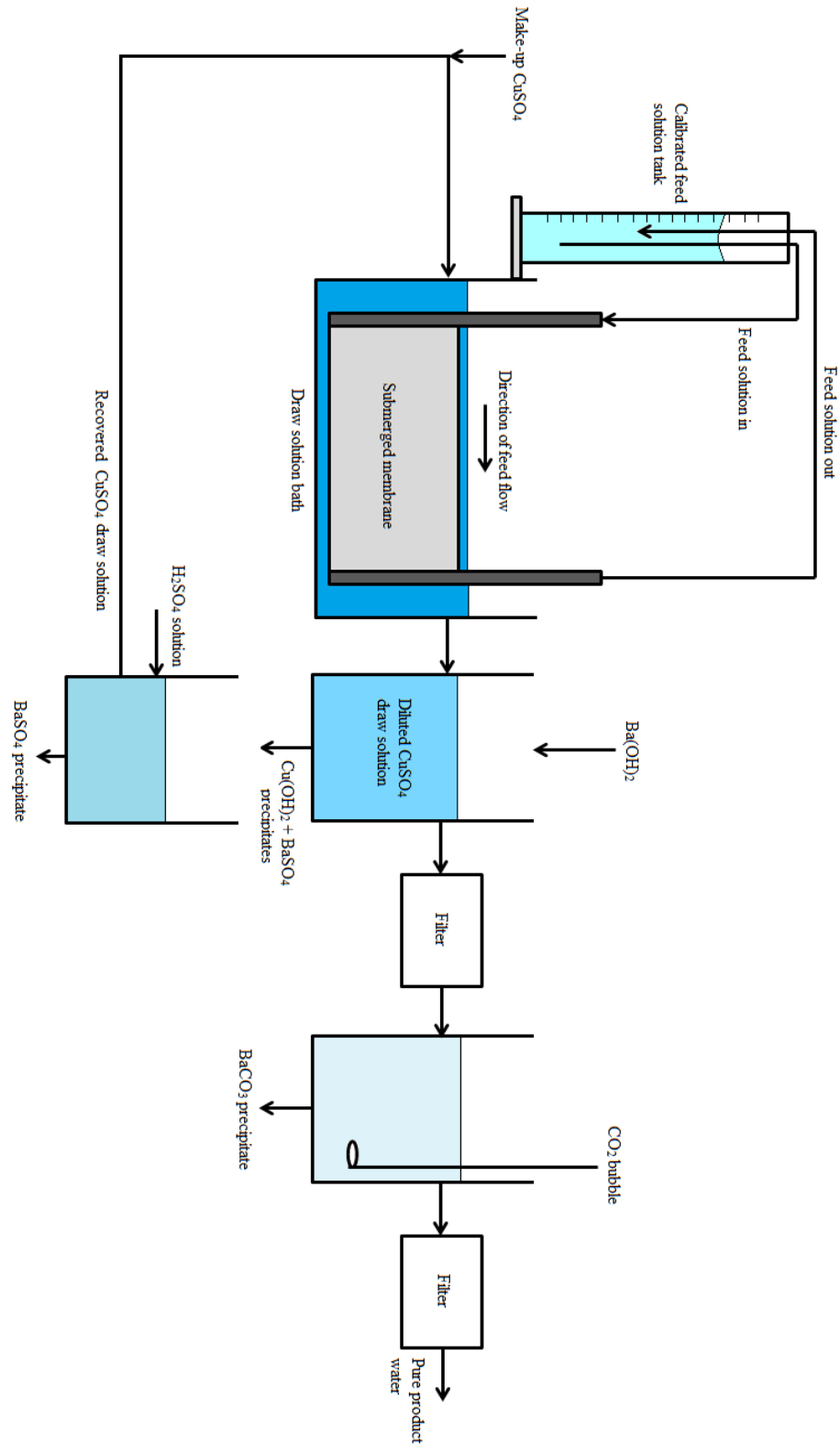


Figure 42: Schematic of submerged membrane FO desalination apparatus utilizing  $\text{CuSO}_4$  draw solution

## Chapter 5: Conclusions and Recommendations

Forward osmosis (FO) desalination is a new and emerging technology that can revolutionize freshwater production. However, to move FO from laboratory research to real practical applications, there is a pressing need to achieve breakthroughs in the development of both novel FO membranes and draw solutes. Desalination using forward osmosis (FO) is thought to be a promising option. In fact, FO is expected to substantially lower the energy requirement and the overall cost of water produced and can be employed as the best and low cost desalination process in semi-arid countries such as the UAE. The outcomes of the research can be used by the water authorities within the UAE and efforts can be made in order to reduce the cost of desalination and to lower the energy consumption by employing FO on industrial scale.

In this research, two novel FO desalination apparatus were constructed. The first experimental apparatus consisted of a simple U-tube with the feed and the draw solution fed to each side of the membrane. This apparatus utilized cellulose acetate membrane M-1 and magnesium sulfate draw solution. The apparatus was used successfully to desalinate brackish and seawater with a water flux of 4.06 L/m<sup>2</sup> h and 0.60 L/m<sup>2</sup> h, respectively. A magnesium sulfate draw solution of 240,000 ppm concentration was used in both cases.

In the second part of the research, a submerged membrane FO apparatus was constructed using membrane M-2. The membrane was submerged in a copper sulfate draw solution bath. In this case, the apparatus was found to be suitable only for desalination of brackish water. The water flux obtained using brackish water feed was 3.01 L/m<sup>2</sup> h using 200,000 ppm of copper sulfate draw solution. In case of seawater feed solution, a very low water flux of 0.28 L/m<sup>2</sup> h was observed. It was concluded that the copper sulfate draw solution was not suitable for desalination of seawater since the observed flux was very low and the flux cannot be further improved by increasing draw solute concentration due to solubility limit of the copper sulfate in water.

It was observed, for both the membranes, that the water flux decreases as the feed solution concentration increases keeping the draw solution concentration constant. The membranes performed well in FO desalination. The performance of the membranes was satisfactory in terms of water flux and the salt rejection.



The research presented the novel idea of using magnesium sulfate and copper sulfate as draw solutes in FO desalination. In addition, novel product water recovery method was presented. Pure product water was obtained from the diluted draw solution by metathesis precipitation reaction where the draw solute (magnesium sulfate or copper sulfate) was reacted with barium hydroxide solution to precipitate all solutes chemicals.

Compared to the previous FO efforts, the use of magnesium sulfate or copper sulfate as draw solute requires no energy for the recovery of product water. The metathesis precipitation reaction can be performed at room temperature to remove all soluble chemicals as precipitates to furnish pure water. However, the process requires use of additional chemical in the form of barium hydroxide and additional filtration cost. The recovery of pure water from magnesium sulfate or copper sulfate draw solution eliminates the need of high-pressure pump as in case of RO.

The FO process in this study was found to be slow with respect to water flux. As a part of the future work, it is recommended that new FO membranes should be synthesized in the laboratory in order to further improve water flux. In addition, the performance of other commercial membranes must be studied following the procedures and methods presented in this study. The experimental data presented in this study must be compared with theoretical models (described in Section 1.6.6) in order to compare the experimental flux with the model equations. Finally, it is recommended to construct a pilot plant with employing a continuous FO process. The use of FO eliminates the need of energy required for pressurization as in RO. Additionally, the use of magnesium sulfate and copper sulfate draw solutes require no energy to separate product water from the diluted draw solution.

It is also recommended to study hybrid desalination techniques employing FO. Forward osmosis can be used for osmotic dilution of the saline feed entering the RO plant. Since the energy required for desalination is a function of the salinity of feed water, therefore, dilution of the feed using FO results in lower energy requirements in RO [147, 148]. In addition, hybrid forward osmosis-nanofiltration [149] and forward osmosis-membrane distillation [150] processes must be investigated to potentially reduce the energy consumption of the desalination process, and thus, lower the current limitations and barriers to FO desalination.

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## Appendix

### Publications

1. R. Alnaizy, A. Aidan, M. Qasim, “Draw Solute Recovery by Metathesis Precipitation in Forward Osmosis Desalination”, accepted for publication in *Desalination & Water Treatment*, 2013.

### Conferences

1. Raafat Alnaizy, Ahmed Aidan and M. Qasim Rafiq, “Applied Aspects of Forward Osmosis Desalination”, *International Conference of Water and Environmental Engineering*, UAE, Feb. 14-17, 2012.
2. Ahmed Aidan, Raafat Alnaizy, M. Qasim Rafiq, “Fruit Juice Concentration Process using Different Kinds of Membranes in Forward Osmosis”, *International Conference of Water and Environmental Engineering*, UAE, Feb. 14-17, 2012.
3. Raafat Alnaizy, Ahmed Aidan and M. Qasim Rafiq, “Applied Aspects of Forward Osmosis Desalination”, *American Institute of Chemical Engineers (AIChE Conference)*, Texas, April 1-4, 2012.
4. Raafat Alnaizy, Ahmed Aidan and M. Qasim Rafiq, “Potable Water by Metathesis Precipitation in Forward Osmosis Desalination”, *UAE-Swizz Research Day*, Nov. 11-12, 2012.
5. Raafat Alnaizy, Ahmed Aidan and M. Qasim Rafiq, “Cellulose Acetate Hollow Fiber Membranes for Forward Osmosis Processes”, *Technology Conference and Exposition by American Membrane Technology Association Membrane*, Feb. 25-26, 2013.

## **Vita**

Muhammad Qasim was born on September 22, 1988, in Abu Dhabi, United Arab Emirates. He joined the American University of Sharjah in 2006, from which he graduated magna cum laude, in 2010. His degree was a Bachelor of Science in Chemical Engineering.

In January 2011, Mr. Qasim began a Master's program in Chemical Engineering at the American University of Sharjah. He received a full-time scholarship as a graduate teaching assistant at the Chemical Engineering department. He was awarded the Master of Science degree in Chemical Engineering 2013.