SYNTHESIS AND PERFORMANCES OF POLYAMIDE FORWARD OSMOSIS MEMBRANE FOR HUMIC ACID REMOVAL

MOHAMMAD AMIRUL BIN MOHD YUSOF

Thesis submitted in partial fulfilment of the requirements for the award of the degree of Bachelor of Chemical Engineering (Chemical)

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG
JULY 2014

©MOHAMMAD AMIRUL BIN MOHD YUSOF (2014)
ABSTRACT

Forward osmosis is a one of develop water treatment method that can be used. Forward osmosis is a process that depends on the concentration gradient and also osmotic potential to treat water which is currently, applicable in many industries. This research focuses on the synthesis and performances of polyamide forward osmosis membrane in order to provide the optimum effect in treating wastewater. This research also used sodium chloride as draw solution due to the highest performances recorded by previous researchers on forward osmosis experiment. This research was conducted based on one parameter which will impact the water flux and overall performances of forward osmosis which is the reaction time of polyamide membrane where there are three different polyamide forward osmosis membranes with different reaction time with m-phenylene diamine (MPD) and trimesoyl chloride (TMC). This research also measures the humic acid rejection for each polyamide forward osmosis membrane by using UV-Vis spectrometer. Besides, reverse salt diffusion caused by different type of polyamide membrane was also tested in terms of conductivity to determine the best performing polyamide membrane. This research was conducted by using ultrafiltration membrane that reacted by two monomers which are MPD and TMC with three different reaction times (10s, 30s, and 60s) to separate the feed and draw solution and the permeation module was constructed as the preliminary laboratory work. Based on the results obtained, increase in molarity of draw solution is proportional to the increasing of water flux. In addition, the increasing of polyamide forward osmosis membrane reaction time with monomer also leads to decreasing of water flux. The water flux obtained by using related formula showed the highest results with polyamide membrane with reaction time of 10s at 2.548 L/m²h at 2.5M of draw solution whereas the lowest water flux recorded by polyamide membrane with reaction time of 60s at 1.976 L/m²h at the same concentration of draw solution. Besides that, calculation shows that the increasing of draw solution concentration causes a decreasing in humic acid rejection. However, the data recorded showed that draw solution at concentrations of 0.5M to 2.0M has good humic acid rejection at approximately 95%. Based on the discussion, it is found that this research showed polyamide forward osmosis membrane with reaction time of 30s as the best forward osmosis membrane in treating water using forward osmosis process.
Osmosis kehadapan adalah salah satu kaedah rawatan air yang sedang membangun yang boleh digunakan. Osmosis kehadapan adalah satu proses yang bergantung kepada kecerunan kepekatan dan juga potensi osmosis untuk merawat air sisa pada masa ini, yang terpakai dalam banyak industri. Kajian ini memberi tumpuan kepada penghasilan dan persembahan poliamida membran osmosis kehadapan untuk memberikan kesan yang optimum dalam merawat air sisa. Kajian ini telah dijalankan berdasarkan satu parameter yang akan memberi kesan kepada fluks air dan persembahan keseluruhan osmosis kehadapan yang merupakan masa tindak balas membran poliamida di mana terdapat tiga poliamida berbeza membran osmosis ke hadapan dengan masa tindak balas yang berbeza dengan reaksi terhadap m-phenylene diamine (MPD) dan trimesil klorida (TMC). Kajian ini juga mengukur asid humik penolakan bagi setiap membran osmosis hadapan poliamida dengan menggunakan UV-Vis spektrometer. Selain itu, menterbalikkan penyebaran garam disebabkan oleh jenis yang berbeza membran poliamida juga diuji dari segi kekonduksian untuk menentukan membran poliamida terbaik dari segi persembahannya. Kajian ini dijalankan dengan menggunakan ultrafiltration membran yang disalut oleh dua monomer iaitu MPD dan TMC dengan tiga masa tindak balas yang berbeza (10 saat, 30 saat, dan 60 saat) untuk memisahkan larytan suapan dan larutan penarik dan modul penyerapan dibina ketika kerja makmal preliminari. Berdasarkan keputusan yang diperolehi, peningkatan dalam kemolaran larutan tarikan berkadar dengan peningkatan fluks air. Di samping itu, peningkatan poliamida ke hadapan semasa reaksi osmosis dengan monomer juga membawa kepada penurunan fluks air. Fluks air diperoleh dengan menggunakan formula yang berkaitan menunjukkan angka tertinggi dengan poliamida dengan tindak balas masa 10 saat dengan 2.548 L/m²h pada 2.5m kepekatan larutan manakala fluks air yang paling rendah yang dicatatan oleh poliamida membran dengan tindak balas masa 60 saat dengan 1.976 L/m²h pada kepekatan yang sama larutan tarikan. Di samping itu, pengiraan menunjukkan bahawa peningkatan kepekatan larutan tarikan menyebabkan kurangnya penolakan asid humik. Walau bagaimanapun, data yang direkodkan menunjukkan bahawa setiap larutan tarikan pada kepekatan 0.5M kepada 2.0M mempunyai asid humik penolakan yang baik iaitu pada kira-kira 99%. Berdasarkan perbincangan, didapati bahawa kajian ini menunjukkan poliamida membran osmosis kehadapan dengan tindak balas masa 30 saat sebagai membran osmosis terbaik bagi osmosis kehadapan dalam merawat air menggunakan kaedah osmosis kehadapan.
# TABLE OF CONTENTS

SUPERVISOR’S DECLARATION .................................................................................. IV  
STUDENT’S DECLARATION .................................................................................. V  
Dedication .............................................................................................................. VI  
ACKNOWLEDGEMENT ............................................................................................. VII  
ABSTRACT ............................................................................................................... VIII  
ABSTRAK ............................................................................................................... IX  
TABLE OF CONTENTS .......................................................................................... X  
LIST OF FIGURES .................................................................................................. XII  
LIST OF TABLES ..................................................................................................... XIII  
LIST OF ABBREVIATIONS ....................................................................................... XIV  
LIST OF ABBREVIATIONS ....................................................................................... XV  

1 INTRODUCTION .................................................................................................. 1  
1.1 Background ....................................................................................................... 1  
1.2 Motivation ......................................................................................................... 3  
1.3 Problem statement ........................................................................................... 5  
1.4 Objective ......................................................................................................... 5  
1.5 Scope ............................................................................................................... 5  
1.6 Organisation of this thesis .............................................................................. 6  

2 LITERATURE REVIEW ....................................................................................... 8  
2.1 Overview ......................................................................................................... 8  
2.2 Membrane Technology in Desalination and Water Reclamation ..................... 8  
  2.2.1 Introduction to Membrane Technology ....................................................... 8  
2.3 Theory of treatment methods ......................................................................... 10  
  2.3.1 Introduction to Forward Osmosis ............................................................... 10  
  2.3.2 Forward osmosis Process ........................................................................ 11  
  2.3.3 Reverse Osmosis ....................................................................................... 12  
  2.3.4 Differences of between forward osmosis and reverse osmosis ................. 14  
2.4 Advantages of forward osmosis ..................................................................... 17  
2.5 Reverse salt diffusion in forward osmosis ....................................................... 17  
2.6 Forward osmosis membranes ........................................................................ 19  
  2.6.1 Previous research on forward osmosis membranes .................................. 19  
  2.6.2 Cellulose triacetate membrane for forward osmosis ................................ 19  
2.7 Humic acid .................................................................................................... 20  
2.8 Recent Applications of forward osmosis ....................................................... 22  
  2.8.1 Forward osmosis for seawater desalination .............................................. 22  
  2.8.2 Forward Osmosis for Water Reclamation ............................................... 24  
  2.8.3 Other applications of forward osmosis ..................................................... 24  
2.9 Summary ....................................................................................................... 25  

3 MATERIALS AND METHODS ......................................................................... 26  
3.1 Overview ....................................................................................................... 26  
3.2 Chemicals ....................................................................................................... 26  
3.3 Preparation of membrane ............................................................................ 26  
3.4 Preparation of draw solution ....................................................................... 28  
3.5 Preparation of feed solution by using humic acid solution ......................... 28  
3.6 Forward osmosis system module ................................................................. 29
LIST OF FIGURES

Figure 2.1: Membrane process for separation.................................9
Figure 2.2: Direction of solvent flow in forward osmosis (FO) process............11
Figure 2.3: Process of reverse osmosis...........................................12
Figure 2.4: Schematic diagram of membrane fouling mechanisms.................14
Figure 2.5: Water flux direction of forward osmosis, pressure retarded osmosis and reverse osmosis.................................................................15
Figure 2.6: A mechanism of reverse salt diffusion problem............................18
Figure 2.7: Schematic diagram of the ammonia-carbon forward osmosis process....23
Figure 3.1: Plastic frame used to hold membrane during interfacial polymerization method...............................................................27
Figure 3.2: Protocol to prepare polyamide FO membranes.............................28
Figure 3.3: The schematic diagram of lab-scale forward osmosis (FO) system.....30
Figure 3.4: Absorbance standart curve of humic acid (HA).............................31
Figure 4-1: Graph of water flux against concentration of sodium chloride solution....33
Figure 4.2: Absorption against concentration of NaCl solution (draw solution)........36
Figure 4.3: Graph of humic acid rejection against concentration of draw solution......38
LIST OF TABLES

Table 2.1: Comparison of forward and reverse osmosis.................................16
Table 4-1: Table of flux for each membrane..................................................33
Table 4.2: Absorption in Sodium Chloride.....................................................35
Table 4.3: Absorption in Humic Acid Solution................................................35
Table 4.4: Concentration of humic acid in sodium chloride solution...................37
Table 4.5: Concentration of humic acid in humic acid solution........................37
Table 4.6: Table of humic acid rejection.......................................................38
Table 4.7: Table of conductivity for sodium chloride draw solution feed side........40
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_w$</td>
<td>water flux</td>
</tr>
<tr>
<td>$A$</td>
<td>water permeability</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>hydrostatic pressure</td>
</tr>
<tr>
<td>$C_D$</td>
<td>concentration of the solute in the draw solution</td>
</tr>
<tr>
<td>$J_S$</td>
<td>reverse flux of the solute</td>
</tr>
<tr>
<td>$C_F$</td>
<td>bulk feed solution concentration</td>
</tr>
<tr>
<td>$l_S$</td>
<td>support layer thickness</td>
</tr>
<tr>
<td>$l_A$</td>
<td>active layer thickness</td>
</tr>
<tr>
<td>$C_D^m$</td>
<td>draw solute concentration in solution at the support layer side</td>
</tr>
<tr>
<td>$C_F^m$</td>
<td>draw solute concentration in solution at the boundary layer side</td>
</tr>
<tr>
<td>$MW$</td>
<td>molecular weight of solute</td>
</tr>
<tr>
<td>$D_S$</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>$\Delta V$</td>
<td>volume of water which permeates through the membrane</td>
</tr>
<tr>
<td>$A$</td>
<td>effective area of the membrane</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>time taken in hour</td>
</tr>
<tr>
<td>$M$</td>
<td>molarity</td>
</tr>
<tr>
<td>$J$</td>
<td>Van't Hoff factor</td>
</tr>
</tbody>
</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \pi$</td>
<td>Change in osmotic pressure</td>
</tr>
<tr>
<td>$\Delta \pi_m$</td>
<td>Change in osmotic difference across the membrane</td>
</tr>
</tbody>
</table>

**Subscripts**

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>eff</td>
<td>effective</td>
</tr>
<tr>
<td>max</td>
<td>maximum</td>
</tr>
<tr>
<td>min</td>
<td>minimum</td>
</tr>
</tbody>
</table>
LIST OF ABBREVIATIONS

DS  Draw solution
FO  Forward Osmosis
HTI Hydration Technology Ins.
MPD m-phenylene diamine
TMC trimesoyl chloride
RO  Reverse osmosis
NF  Nanofiltration
UF  Ultrafiltration
1 INTRODUCTION

1.1 Background

The increasing of human population throughout the world may increase the demand of basic human needs. Clean water is one of human need for domestic used and commercial used. Then, the increasing of world population will increase the demand for clean water. Nowadays, water treatment is one of the most essential fields to overcome this water shortages problem. As a result, intensive efforts in findings other water sources such as seawater and reuses of wastewater have been made to ensure the reliable supply of fresh water is continuous supply for human population. Other than reliable supply of clean water, the focusing on the minimum uses of cost and energy of the treatment and reducing any negative effects to human and environment also must be considered. Due to these objectives of minimizing costs, energy, and negative impacts to environment, one of the focus alternatives is osmosis. Osmosis is physical separation process that has been research by researchers in various disciplines of sciences and engineering. In started with the natural separation using natural material likes the animal skin and in 90’s, they started osmosis research by using synthetic materials.

Osmosis is a natural phenomenon that has been exploited by human beings since early days of mankind. In preservation, the function of salts has been discovered in early cultures where it is to desiccate foods for a long period of time. Bacteria, fungi, and other pathogenic organisms also can dehydrated and die or inactive because of osmosis. Osmosis is a natural net movement of water through a selectively permeable membrane by differences of osmotic pressure across the membrane (Cath et al., 2006). In-water treatment industry, generally, reverse osmosis (RO) is more familiar process than forward osmosis (FO). RO is where apply a pressure as a driving force for mass transport through membrane whereas in FO, osmotic pressure itself as the driving force for mass transport.

The enhancement of research in membrane filtration technology in the last few decades, especially on reverse osmosis have been spurred the interests of researcher to do a research in engineered applications of osmosis area. The further development in this field of osmosis has brought to a newer form of water treatment process also known as forward osmosis. Osmosis also known as forward osmosis is a water transport across
the selectively permeable membrane from region of higher water chemical potential to a region of lower water chemical potential. Unlike reverse osmosis which uses a hydraulic pressure for water transport across the membrane, forward osmosis is driven by a difference in concentration of solutes across the membrane that allows water passage, but rejects most solute molecules or ions (Cath et al., 2006).

The advantages of using forward osmosis (FO) are that forward osmosis system operates at low or no hydraulic pressure and it has lower membrane fouling propensity (Holloway et al., 2005). Recent studies indicate that, the membrane fouling may not be a significant issues for forward osmosis process although literatures on forward osmosis membrane fouling are still scarce. This advantage on membrane fouling shows that the differences between forward osmosis and reverse osmosis. Even though the concept of forward osmosis has been applied as early as 1968 (Popper et al., 1968); it has not been able to advance due to lack of suitable forward osmosis membranes and reverse salt diffusion problem.

The type of membrane plays a big role in the filtration process including forward osmosis area. The current asymmetrical membranes used for pressure based filtration results in concentration polarization effects that severely decrease the net osmotic pressure between the two solutions and hence lower the water flux across the membrane (Tang et al., 2010). While the external concentration polarization that occurs on the membrane surface can be mitigated using crossflow, similar to pressure based membrane filtration system such as reverse osmosis, internal concentration polarization occurs within the porous support layer of the asymmetrical membranes and therefore cannot mitigated (Cath et al., 2006). Internal concentration polarization is exclusive to forward osmosis process and is said to be mainly responsible for much lower water flux obtained in forward osmosis process than the expected or theoretical water flux (Gray et al., 2006). Several significant research breakthroughs have been however reported recently in the forward osmosis membrane fabrication particularly with thin film composites membranes that may provide a lower concentration polarization effects (Yip et al., 2010).

The development of high performance forward osmosis membranes is one of the priority that must be concern in the forward osmosis area. Current asymmetric membrane performances are generally limited by their relatively low water permeability and salt
rejection (Wei et al., 2011). Previous research demonstrated that the reaction between membranes with polymers may significantly enhance membrane properties such as permeability, selectivity, or stability in various membrane separation processes. Research by Ma et al. (2012) indicated that the thin film nanocomposite reverse osmosis membrane that development from the polysulfone membrane with composite material has shown the improvement in water permeability and salt rejection during reverse osmosis process.

1.2 Motivation

The increasing of human population throughout the world may increase the demand of basic human needs. Clean water is one of human need for domestic and commercial used. Then, the increasing of world population will increase the demand for clean water. Other than for domestic used, clean water also very important in energy, food production, industrial output, and the quality of our environment ultimately undermining the economies of the world at large (Whetton et al., 1993). Water also plays a very important role for improving the productivity of agricultural and others sector to meet the world’s needs to improve into a better life.

River are very important to human life. In world history also stated the role of river to human civilization, where river be a source of human civilization in transportation, agriculture, foods and beverages and others (StudyMode.com, 2012). In Malaysia, river also plays an important role in providing water to Malaysians and also to environment. However, according to Katimon et al. (2010), despite holding such important role in providing water consumeable to Malaysian citizens, rivers in Malaysia was researched and found to have a lower pH value which shows that the river water in Malaysia mostly is acidic. It is important to treat the water correctly before it can be distributed to Malaysians. Among many water treatments, osmosis is the most common method to used in desalination of water. In this study, forward osmosis was chosen over other methods as the process to treat the river water. Reverse osmosis for example use a lot of energy to pressurized the water to pass through the membrane. The consumption of energy will lead to high cost. On the other hand, forward osmosis process can be done
in lower cost because lower energy consumption used in the process of forward osmosis (Ng et al., 2006).

Other than that, forward osmosis has attracted growing interest in others treatments area such as wastewater treatment, seawater/brackish water desalination, food processing, and power generation (McGinnis & Elimelech, 2007) where the treatment process occurs as accordance to the differences in osmotic pressure between feed solution and draw solution which is separated by a semi permeable membrane (Zhao et al., 2012). This further brings forward osmosis to another advantage where the absence of hydraulic pressure could potentially reduce membrane fouling and toxicity effects of product water (Suh & Lee, 2013). Besides that, the research on polyamide forward osmosis membranes used to treat river water was scarce because more researcher used only a ordinary membrane like ultrafiltration membrane as forward osmosis membrane.

Eventhough osmosis field have been discovered since 60’s in the desalination of seawater but the problem in reverse salt diffusion still the main challenges of forward osmosis area. The reverse salt diffusion from draw solution into feed solution become a issues in forward osmosis process thus this problem give an attention in this study to study the relationship of polyamide forward osmosis membrane with the reverse salt diffusion problem. The success of forward osmosis desalination in the future especially for drinking purposes, will rely mainly on how easily and efficiently the draw solution can be separated and recovered from the desalinated water. Under all these circumstances, the performances of polyamide forward osmosis membrane for the process of forward osmosis where humic acid solution acts as Malaysia river as the feed solution remains skeptical to the industries, researches, and students until today.
1.3 Problem statement

The following are the problem statements of this research:

1) The common drinking water treatment, reverse osmosis is promising technology but too expensive.

2) Alternatively, the new technology in water treatment named forward osmosis could be used. However, there are least researches of forward osmosis process using polyamide forward osmosis membrane.

3) Since that in this study, we used humic acid as synthetic river water and as a feed solution with contain higher amount of humic acid solute, it will have a problem within the humic acid removal that will accumulate on the membrane surface that will cause the fouling problem.

4) On top of that, the salt solute also will reverse it movement from draw solution into the feed solution with will affect our efficiency of membrane performances.

1.4 Objective

In this study, we are focusing on the synthesis and performances of polyamide forward osmosis membrane. The performance is show by determination of water flux of three different of polyamide forward osmosis membrane in five different concentration of draw solution, to determine the reverse salt diffusion of forward osmosis process, and to determine the humic acid removal or rejection in this forward osmosis process.

1.5 Scope

The research was done based on differences of osmotic pressure creates by differences concentration of two solution which are feed solution and draw solution. In this study, we used sodium chloride as our draw solution due to the highest performances shown in forward osmosis treatment process (Achilli et al., 2010). Humic acid solution was used as feed solution and as synthetic river water due to the fact that it is the main and most abundant acidic component present in Malaysia’s river water. It supported by Campinas et al. (2010) research where he stated that humic acid is a large composition of organic matter present in surface or ground waters.
This research discussed on the preparation of polyamide membrane by reaction between \( m \)-phenylene diamine (MPD) and trimesoyl chloride (TMC) which affect the efficiency of forward osmosis process. Polyamide forward osmosis membrane was synthesized using interfacial polymerization method between MPD and TMC with ultrafiltration membrane with three different reaction times (10s, 30s, and 60s). The characteristics of membrane in term of degree of cross link between the polymers reaction and membrane charge ion will be discussed more in literature review and discussion part. Apart from that, the synthesis and performances of polyamide membrane in reverse osmosis also was discussed in the literature reviews part.

Besides that, this research was also completed by performing experiments with provided the water flux across the membrane to study the performances shown by polyamide forward osmosis membrane. Other than water flux, this research also focused on the reverse salt diffusion problem where it also will affect the performances of forward osmosis. These two parameters will lead to the efficiency of polyamide membrane to be used in forward osmosis process for river water. Thus, the performances analysis will further tested using UV-vis spectrometer and conductivity meter for humic acid removal and reverse salt diffusion problem, respectively.

1.6 **Organisation of this thesis**

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description on the differences method of osmosis currently used this era. Besides that, this chapter also discusses on the differences between all these three osmosis method and the advantages of using forward osmosis method. This chapter also discusses on the problems faced by forward osmosis known as reverse salt diffusion and removal of humic acid. In addition, this chapter also discusses on the common membrane used for forward osmosis process known as cellulose triacetate membrane and also the discussion on the humic acid is also done as it is feed solution in this study. The characterization of polyamide forward osmosis membrane to the forward osmosis performances also will be discusses in this chapter. Lastly, common applications of forward osmosis are also discussed in this chapter.
Chapter 3 gives description on the chemical which was used during the experiment and the preparation on polyamide forward osmosis membrane. Besides that, this chapter also discussed on the preparation of membrane which was used using three different reaction time to study the performances of the membrane to the forward osmosis process. In addition, this chapter also provide the description on the preparation of draw solution and feed solution using sodium chloride and humic acid solution, respectively. Besides that, the methodology on the process of forward osmosis will be discussed in this chapter and the method of evaluating and analysing the polyamide forward osmosis membrane performances for humic acid removal.

Chapter 4 discusses on the experimental data which was obtained from the experiment. This chapter will discussed on the performances of polyamide forward osmosis membrane in term of water flux from feed to permeate side, humic acid removal and reverse salt diffusion analysis. Besides, this chapter will briefly determine the best polyamide forward osmosis membrane to treat river water using forward osmosis method treatment.
2 LITERATURE REVIEW

2.1 Overview

This chapter is about the discussion and comparison between two types of membrane technology treatments between forward osmosis treatment and another treatment that relatively close to the concept of forward osmosis, called reverse osmosis. Besides that, this chapter also discusses briefly the reverse osmosis process and discusses also the advantages of forward osmosis in water treatment compared to reverse osmosis. Other than that, this chapter also will discuss the main problems faced by forward osmosis which is reverse salt diffusion and humic acid removal which can gravely affect the performances and efficiency of forward osmosis process. Apart from that, this chapter also discusses the contribution of polyamide forward osmosis-membrane compared to cellulose triacetate membrane which generally used in forward osmosis research as forward osmosis membrane in term of it properties such as the degree of crosslink polymers and membrane charge properties to feed solution. In addition, a review on humic acid is also present in this chapter it is the main feed solution which was used for this study. Lastly, this chapter reviews on the recent application of forward osmosis in the field on desalination, wastewater treatment and also food concentration.

2.2 Membrane Technology in Desalination and Water Reclamation

2.2.1 Introduction to Membrane Technology

With the rapid increase in global population and the development of industries, the demands for freshwater have increased drastically whereas the available water sources have remained limited. In developing countries and industrial countries like Malaysia, there are growing problems of providing adequate water supply and properly disposing of municipal and industrial used water. In developing countries, particularly those in arid parts of the world, there is a need to develop low-cost methods of acquiring new water supply while protecting existing water sources from pollution.

Under the threats of freshwater shortage, many engineers and researchers have been dealing with reclaiming polluted water, while others try to find other alternatives sources. Nowadays, desalination for seawater and other water sources, as well as water
reclamation, is becoming a more and more attractive method to produce high quality water for both industrial and domestic usage. With this rapid development, membrane technology has become economically attractive for desalination and water reclamation.

Membrane technology is the application of a positive barrier of film in the separation of unwanted particles, micro-organisms and substances from water and effluents. In this separation process, a semi-permeable membrane acts as a high specific filter that is capable of separating substances because of differences in their physical and chemical properties under a variety of driving forces. Examples of these driving forces are the application of high pressure, the introduction of electric potential and the maintenance of concentration gradient across a membrane. A schematic representation of membrane separation is given in Figure 2.1.

![Membrane process for separation](image)

**Figure 2.1: Membrane process for separation**

In the early 1960s, two US scientists, Sidney Loeb and S. Sourirajan, discovered a way of making mechanically strong, defect-free, ultra-thin RO membranes with excellent performances. Their works made RO a commercial reality and contributed significantly towards the development of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), electrodialysis (ED) and other membrane processes. Moreover, this development has transformed membrane separation from a laboratory process into an industrial
technology. From then on, interest in membrane processes for water and used water treatment has grown steadily. The main advantages of membrane technology, which make it competitive to conventional techniques, are that it works with relatively low energy requirement compared to thermal process, ease of application and well-arranged process setup, and without the need for the addition of chemicals.

2.3 Theory of treatment methods

2.3.1 Introduction to Forward Osmosis

Nowadays, desalination for seawater and other water sources is becoming a more attractive method to produce good quality water for both industrial and domestic usage. However, current desalination technologies are prohibitively expensive and energy intensive. Reverse osmosis (RO), one of the most common used desalination technologies, has a relatively lower overall cost compared to traditional thermal processes, which make use of excessive thermal energy while achieving a low feed-water recovery (Reddy and Ghaffour, 2007). However, RO generally requires more energy to apply hydrodynamic pressure to push water through the membrane. When there were used of high pressure, it lead to use of heavy duties pressurizing pumps, and all of these mean more energy and cost needed for the RO process, and thus make it more expensive than standard treatment of freshwater for potable use.

Upon the need for a less expensive technology, forward osmosis (FO) process is a possible alternative technology for both desalination and brine treatment due to its lower energy requirement. Forward osmosis (FO) known also as osmosis is the transport of water across a selectively permeable membrane from a region of higher concentration of solution to a region of lower concentration of solution (Cath et al., 2006). FO process utilizes an osmotic pressure gradient that generated by a highly concentrated draw solution to allow passage of water across the membrane from feed water solution which is relatively less concentrated. One example of direct usage of the diluted draw solution is “hydration bag” used by backpacker or soldier which is used their recycle urine as their fresh water to survive in arid environments (Salter, 2005).
2.3.2 Forward osmosis Process

Osmotic pressure plays an important role in forward osmosis process. Osmotic pressure \( (\pi) \) is the pressure which, if applied to the more concentrated solution would prevent transport of water across the membrane. Moreover also forward osmosis uses osmotic pressure differential \( (\Delta \pi) \) across the membrane, rather than hydraulic pressure differential which is the concept was used same like reverse osmosis, as driving force for water transport through the membrane (Cath et al., 2006). The process of forward osmosis occur in two compartment which are compartment for draw solution and feed solution. The draw solution is a concentrated solution, to generate an osmotic pressure gradient across a semi permeable membrane for the FO process, while the feed solution is more dilute than draw solution. The water is transport from draw solution solution into the feed solution based on the differential concentration of these two solution. The direction of solvent in forward osmosis process is illustrate in the Figure 2.2.

Figure 2.2: Direction of solvent flow in forward osmosis (FO) process (Millat, 2011)
2.3.3 Reverse Osmosis

The current state technology that used nowadays for desalination and water purification is reverse osmosis (Baudequin et al., 2014), for it can remove salts, hardness, pathogens, turbidity, disinfection by-product (DBP) precursors, synthetic organic compounds (SOCs), pesticides and most of potable water contaminants known today. According to Penate (2011), reverse osmosis is a separation of dissolved solids from water by applying a pressure differential across a membrane that is permeable to water but not to the dissolved solids. This process also known as a opposite of the natural phenomena of osmosis. In osmosis, water molecules flow through a semi-permeable membrane from less concentrated solution to the more concentrated solution without external influence. This will continue until the process reach a equilibrium concentration or zero pressure differential for both solution, feed and draw solution. In reverse osmosis, hydraulic pressure is applied to the more concentrated solution (draw solution) to pressurized the water molecules that pass through membrane to the dilute solution (feed solution). Besides, as stated by Paul (2004), the membrane, made either cellulose acetate or polyamide, rejects most of the solids creating two streams, one of pure water, product or permeate, and one with dissolved solids, concentrate or reject. Figure 2.3 shows the reverse osmosis process.

Figure 2.3: Process of reverse osmosis (Chekli et al., 2012)
2.2.2.1 Effect of Concentration Polarization

As freshwater diffuses through the semi permeable membrane, the concentration of dissolved impurities increases in the remaining feed water. Consequently, the osmotic pressure increases, which reduces the effective driving force and results in a flux declination. Moreover, some of the impurities will accumulate on the membrane surface and they are subject to movement backward to the bulk feed water due to diffusion. As a result of equilibrium between the permeate flow and back diffusion, a dynamic elevated concentration layer will be formed near the membrane surface. This phenomenon is called concentration polarization (CP).

2.2.2.2 Effect of Membrane Fouling

Another phenomenon that significantly weakens the membrane performance is membrane fouling. Fouling is the deposition of suspended or dissolved substances on the membrane surface, on the membrane pores, or within the membrane pores (Xie et al, 2014). Membrane fouling process may be attributed to a number of mechanisms, which increases the actual membrane resistances. These mechanisms include biofouling by the unwanted adsorption and growth of microorganisms and their microbial products, pore blocking by solutes that are of similar diameter to the pores, formation of a cake layer from retentate solutes (i.e., solutes unable to permeate through the membrane pores) by precipitation or gelation of inorganic and organic particulates at the membrane surface as a result of the localized high concentrations that occur at the membrane solution interface (as illustrated in Figure 2.4). While interactions between foulants and the membranes are poorly understood, it is thought that effects like charge interactions, bridging, and hydrophobic interactions may play important roles in fouling.
2.3.4 Differences of between forward osmosis and reverse osmosis

Forward and reverse osmosis have huge differences that can be differentiate between this two water treatment processes. The differences can be seen by the water flux and energy consumption of these processes. According to Chou et al. (2012), theoretically, the water flux in an osmosis process can be described as shown in equation (1).

\[ J_w = A \times (\Delta \pi - \Delta P) \] (1)

Where \( J_w \) is the water flux, \( A \) is the water permeability while \( \Delta \pi \) and \( \Delta P \) is the osmotic and hydrostatic pressure respectively across the semi permeable membrane. Whereas, for osmosis, according to Chou et al. (2012), the energy consumption in an osmosis process can be described in the equation as shown in equation (2).

\[ W = A \times (\Delta \pi - \pi P) \times \Delta P \] (2)

Where \( W \) is the energy consumption or power density, \( A \) is the water permeability while \( \Delta \pi \) and \( \Delta P \) is the osmotic and hydrostatic pressure respectively across the semi-permeable membrane. The Figure 2.5 below graphically shows the differences between these 3 processes in terms of water flux.
Figure 2.5: Water flux direction of forward osmosis, pressure retarded osmosis and reverse osmosis (Chou et al., 2012)

Based on the Figure 2.4, in order to forward osmosis process to achieve high water flux value, it does not require hydrostatic pressure differential, where $\Delta P = 0$. However, for reverse osmosis process, hydrostatic pressure is needed to be higher than osmotic pressure in order to let the process occur. In addition, based on the graph, the higher the hydrostatic pressure, the higher the water flux, which is supported by the concept of reverse osmosis (Afonso et al., 2004). Hence, it can concluded that the process of forward osmosis does not require any hydrostatic pressure in order to achieve water flux required while the reverse osmosis required high hydrostatic pressure to work effectively with high water flux. Then, table 2.1 shows the summary of comparison between forward and reverse osmosis.