

**CHARACTERIZATION OF CELLULOSE TRI  
ACETATE (CTA) FORWARD OSMOSIS  
MEMBRANE FOR NOM REMOVAL**

**LAI MEI KEI**

**BACHELOR OF CHEMICAL ENGINEERING  
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# **CHARACTERIZATION OF CELLULOSE TRI ACETATE (CTA) FORWARD OSMOSIS MEMBRANE FOR NOM REMOVAL**

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

**Faculty of Chemical & Natural Resources Engineering  
UNIVERSITI MALAYSIA PAHANG**

JANUARY 2015

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We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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## **STUDENT'S DECLARATION**

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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## ***Dedication***

*I would like to dedicate this research work to my family and my research supervisor, Dr. Mazrul Nizam bin Abu Seman for their guidance and support. Besides that, I dedicate this research work to Universiti Malaysia Pahang for providing me the opportunity in performing a research study as an undergraduate chemical engineering student.*

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## ABSTRACT

Nowadays, to cater for the increasing population in Malaysia, drinking water is taken primarily from surface water sources like rivers, lakes, and reservoirs. These surface water sources need to be treated correctly at low cost and energy before consuming by the citizens. Among all the methods used, forward osmosis (FO) fits the best. In lieu of hydraulic pressure, forward osmosis is separation process which utilizes a highly concentrated draw solution to induce the driving force for water to permeate across the membrane. This research focuses on the characterization of Cellulose Tri Acetate (CTA) Membrane performance in forward osmosis process to treat synthesized river water containing natural organic matter (NOM) which is humic acid with concentration of 15mg/L by using sodium chloride (NaCl) solution as the draw solution. This research was conducted based on the concentration of NaCl draw solution which is a parameter that will impact the water flux and performance of forward osmosis which are humic acid rejection and reverse salt diffusion. In addition, the impact of feed solution pH on the process was investigated. The humic acid rejection was measured by UV-Vis Spectrometer while reverse salt diffusion was measured by conductivity meter. Based on the results obtained, increase in the concentration of NaOH in feed solution increases the pH which ultimately affect the water flux, humic acid rejection and reverse salt diffusion. Besides, it is shown that increase in both draw solution concentration and feed solution pH increase the water flux. The water flux obtained by using related formula showed the highest figure by 2.5M NaCl draw solution with the reading of  $1.580 \times 10^{-6} \text{ m}^3/\text{m}^2.\text{min}$  for feed solution pH of 9.73 and  $2.054 \times 10^{-5} \text{ m}^3/\text{m}^2.\text{min}$  for feed solution pH of 11.65. Furthermore, the increase in draw solution concentration causes a decrease in humic acid rejection for both feed solutions with pH of 11.65 showed a higher solute rejection of more than 97%. It is also shown from the result that the increase in draw solution concentration and water flux causes an increase in reverse salt diffusion for both feed solutions with pH of 9.73 showed a higher reverse salt diffusion. Based on the discussions, it is found that the optimum condition for treating river water by using CTA membrane can be achieved at high concentration of draw solution with high pH of feed solution. By completing this research, the effectiveness of using CTA membrane to treat river water in Malaysia by forward osmosis process can be investigated and the optimum condition of the process will be determined in order to overcome the problem of water depletion in Malaysia.



## ABSTRAK

Pada masa kini, untuk menampung populasi yang semakin meningkat di Malaysia, air minuman diambil terutamanya daripada sumber air permukaan seperti sungai, tasik, dan takungan. Air permukaan ini perlu dirawat pada kos dan tenaga yang rendah sebelum dipakai. Antara kaedah-kaedah yang digunakan, osmosis hadapan merupakan kaedah yang paling sesuai. Sebagai gantian tekanan hidraulik, osmosis hadapan menggunakan larutan penarik pekat untuk mendorong daya penggerak untuk pemisahan melalui membran. Kajian ini memberi tumpuan kepada pencirian prestasi Membran Selulosa Tri Acetate (CTA) dalam proses osmosis hadapan untuk merawat air sungai yang disintesis mengandungi bahan organik semulajadi (NOM) iaitu asid humik dengan kepekatan 15mg/L dengan menggunakan larutan natrium klorida (NaCl) sebagai larutan penarik. Kajian ini dijalankan berdasarkan kepekatan larutan penarik NaCl yang merupakan parameter yang memberi kesan kepada fluks air dan prestasi osmosis hadapan iaitu penolakan asid humik dan penyebaran garam terbalik. Selain itu, kesan pH larutan suapan kepada proses juga dikaji. Penolakan asid humik telah diukur dengan UV-Vis Spektrometer manakala penyebaran garam terbalik diukur dengan meter konduktiviti. Berdasarkan keputusan, peningkatan kepekatan NaOH dalam larutan suapan meningkatkan pH yang memberi kesan kepada fluks air, penolakan asid humik dan penyebaran garam terbalik. Selain itu, ia menunjukkan bahawa peningkatan dalam kepekatan larutan penarik dan pH larutan suapan meningkatkan fluks air. Fluks air yang diperolehi dengan menggunakan formula berkenaan menunjukkan angka tertinggi oleh 2.5M larutan penarik NaCl dengan bacaan  $1.580 \times 10^{-6} \text{ m}^3/\text{m}^2.\text{min}$  untuk pH larutan suapan sebanyak 9.73 dan  $2.054 \times 10^{-5} \text{ m}^3/\text{m}^2.\text{min}$  untuk pH larutan suapan sebanyak 11.65. Peningkatan kepekatan larutan penarik menyebabkan penurunan penolakan asid humik untuk kedua-dua larutan suapan dengan pH 11.65 menunjukkan penolakan bahan larut yang lebih tinggi melebihi 97%. Ia juga ditunjukkan bahawa peningkatan dalam kepekatan larutan penarik dan fluks air menyebabkan peningkatan dalam penyebaran garam terbalik untuk kedua-dua larutan suapan dengan pH 9.73 menunjukkan penyebaran garam terbalik yang lebih tinggi. Berdasarkan perbincangan, didapati bahawa keadaan optimum untuk merawat air sungai dengan menggunakan membran CTA boleh dicapai pada kepekatan larutan penarik dan pH larutan suapan yang tinggi. Dengan kajian ini, keberkesanan penggunaan membran CTA untuk merawat air sungai di Malaysia oleh proses osmosis hadapan boleh disiasat dan keadaan proses yang optimum akan ditentukan untuk mengatasi masalah kekurangan air di Malaysia.

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## LIST OF ABBREVIATIONS

$J_w$	water flux
$A$	water permeability
$n$	Van't Hoff factor
$M$	Molarity
$R$	gas constant
$T$	absolute temperature
$\Delta P$	hydrostatic pressure
$J_s$	reverse flux of the solute
$B$	solute permeability coefficient
$\Delta C$	solute concentration difference across the membrane
$C_F$	bulk feed solution concentration
$t_s$	support layer thickness
$t_A$	active layer thickness
$C_D^m$	draw solute concentration in solution at the support layer side
$C_F^m$	draw solute concentration in solution at the boundary layer side
$\Delta V$	volume of water which permeates through the membrane
$A$	effective area of the membrane
$\Delta t$	time taken for water permeation in minutes
$R$	humic acid rejection
$C_p$	humic acid concentration in permeate
$C_b$	bulk concentration of humic acid

### *Greek*

$\Delta\pi$	Osmotic pressure difference across the membrane
$\pi$	Osmotic pressure
$\pi_D$	Bulk osmotic pressure of the draw solution
$\pi_F$	Bulk osmotic pressure of the feed solution
$\delta$	external boundary layer of thickness

### *Subscripts*

$p$	permeate
$b$	bulk
$D$	draw solution
$F$	feed solution

## LIST OF ABBREVIATIONS

CP	Concentration polarization
CTA	Cellulose Tri Acetate
DS	Draw solution
ECP	External concentration polarization
FESEM	Field Emission Scanning Electron Microscopy
FO	Forward osmosis
FS	Feed solution
HA	Humic acid
HTI	Hydration Technology Inc.
ICP	Internal concentration polarization
MD	Membrane distillation
MF	Microfiltration
NF	Nanofiltration
NMWL	Nominal molecular weight limit
NOM	Natural organic matter
OMBR	Osmotic Membrane Bioreactor
RO	Reverse osmosis
TFC	Thin film composite
UF	Ultrafiltration

# 1 INTRODUCTION

## *1.1 Background*

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 and are unevenly distributed. In highly industrialized countries, 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. In response to these issues in this century, intensive research on finding alternative solutions to supplement insufficient freshwater sources has been carried out, particularly in the field of desalination and water treatment.

In desalination and water reclamation processes, membrane technologies, such as reverse osmosis (RO), have increasingly being adopted to produce freshwater from alternative water resources due to water scarcity. Currently, RO is one of the most commonly used desalination technologies due to the availability of stable and good performance membranes, which are permeable to water but highly impermeable to salts, organic matters and other pollutants. Moreover, RO 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 & Ghaffour, 2007). In the RO process, a high applied pressure (1-10 MPa) is used to force water from a region of high solute concentration to permeate through an RO membrane to a region of low solute concentration, with the solute being retained (Ozaki, 2004). As a result, the requirement for the high applied pressure which leads to high energy consumption as well as the requirement for high strength equipments which can withstand the high applied pressure, leads to a high operational cost and makes RO significantly more expensive than conventional water treatment technologies (Fritzmman et al., 2007). Moreover, limited recovery, typically 35–50% for seawater (Liu et al., 2009), is another drawback of RO.

Forward osmosis (FO), a recently resurgent membrane process, is a membrane process that utilizes a draw solution that can generate high osmotic pressure as a driving force for



separation (Loo et al., 2012). It is developed as a possible alternative technology for desalination and water reclamation at a perceivably reduced cost. In FO, water flows from a low concentration feed water to high concentration draw solution under the concentration gradient across the semi-permeable membrane in FO membrane process. Unlike typical pressure-driven membrane processes where a hydraulic pressure is applied onto the feed water to “push” water through a membrane, forward osmosis occurs spontaneously without the need of externally applied pressure (Cath et al., 2006). FO is highly attractive due to its significantly lower energy demand for pumping. In recent years, FO has been considered as a potential alternative to pressure-driven membrane processes and has attracted much attention from various research groups. Its potential applications may include food processing, water and wastewater treatment, desalination, as well as electricity generation via a derivative pressure retarded osmosis process.

During the last four decades, several reports were published on the FO process. The main focuses were on achieving a better flux performance and on the use of different types of chemicals, such as sulfur dioxide ( $\text{SO}_2$ ), aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ) or glucose, that was either easily removable or consumable as the draw solution (Batchelder, 1965; Frank, 1972; Kravath, 1975; Stache, 1989). Later on, a two-stage FO process was patented, with potassium nitrate ( $\text{KNO}_3$ ) and sulfur dioxide ( $\text{SO}_2$ ) being used as the draw solution in the first and second stage, respectively (McGinnis, 2002). In these attempts, the membrane used was of similar characteristics to the Loeb–Sourirajan type cellulose acetate membrane. In the study of McCutcheon et al. (2005), the performances of the two FO membranes were tested. The membranes are denoted by the manufacturer (GE Osmonics) as AG and CE and are used for brackish water RO. The AG membrane is a polyamide thin film composite membrane formed by interfacial polymerization on a polysulfone backing. The CE membrane is a cellulose acetate asymmetric membrane. However, it was found that severe internal concentration polarization still happened within the FO membranes, which suggested that this FO membrane was not ideal for the FO process. This lack of a suitable membrane, as well as the draw solution, was recognized to be the hindrance for the development of the FO process.

Although the novel concept of forward osmosis was developed as early as 1968 (Popper et al., 1968), it has not been able to advance mainly due to lack of suitable forward osmosis membranes and lack of suitable draw solution. According to the research done by Xu et al. (2010), a higher water flux can be achieved by increasing draw solution

concentration as increase in concentration will also increase the osmotic pressure thus promoting the process of forward osmosis. Therefore, it is important to determine how the FO system performs with respect to the membrane performance criteria (water flux and salt rejection) under a range of osmotic driving forces to advance the FO membrane process technology.

## ***1.2 Motivation***

Water is generally known as an important necessity for all activities such as living consumption, industries, agricultural washing and bathing. Clean drinking water is essential to human and other living things. For increasing population in Malaysia nowadays, drinking water is taken primarily from surface water sources like rivers, lakes, and reservoirs. However, the sources of the clean drinking water are contaminated by chemical constituents (organics, inorganics and gases) and physical contaminants (colour, odour and solid) (Srivastava, 2011). In rivers, about 50 % of the dissolved organic materials are humic substances that affect pH and alkalinity (Kile & Chiou, 1989). The principal constituent of humic substances is humic acid which is a natural organic matter (NOM) that causes the colour of fresh water to turn dark brown at high concentration. As a result, the river water in Malaysia needs to be treated correctly at low cost and energy before consuming by the citizens.

Among many water treatment methods, osmosis is the most common method used in desalination of water. For this research, forward osmosis was chosen over reverse osmosis as the process to treat river water due to the fact that the process of reverse osmosis has high cost, high energy consumption and has limited recovery which is roughly about 30%-50% (Chekli et al., 2012; Liu et al., 2009). On the other hand, the process of forward osmosis can be done at lower cost, energy and also has higher recovery rate (McGinnis & Elimelech, 2008). Although FO has a number of advantages, one of its challenges is the lack of optimized membrane to produce high water flux. The current only available commercial FO membranes are developed by HTI (Hydration Technologies Inc., OR) using cellulose triacetate (CTA) as the membrane material (Herron, 2008). It is suitable to be used to treat river water as it is not prone to biodegradation and hydrolysis compared to other fabricated membranes (Ong & Chung, 2012).

There are a lot of studies have been done related to desalination of seawater particularly by using RO techniques. However, researches based on river water treatment by using membrane processes are scarce especially by using FO membrane process. In order to produce high quality drinking water that is conforming to drinking water quality standard in Malaysia, the application of FO in river water treatment is needed to be examined. In addition, the performance of CTA membrane in NOM removal of river water using FO membrane process is worth studying. This technique is believed to be able to help the citizens who live in rural areas without clean water and far away from the city's water pipes.

### ***1.3 Problem statement***

The following are the problem statements of this research:

- 1) RO is the benchmark in membrane-based water treatment but its efficiency and sustainable operation are hampered by membrane fouling & high energy consumption.
- 2) FO can be a sustainable alternative membrane system for humic acid removal to minimize energy consumption and lower membrane fouling. However, one of the challenges of FO is the reverse salt diffusion which could affect its performance.
- 3) FO process is a recently resurgent membrane process, therefore it is lack of suitable membrane and draw solution to optimize the process.

### ***1.4 Objective***

The objective of this research is to characterize cellulose triacetate (CTA) forward osmosis membrane based on its performance in humic acid removal by using NaCl as draw solution with different concentrations and humic acid as feed solution with different pH.

### ***1.5 Scope of research***

To achieve the objective of the current work, three main scopes of research had been identified. First of all, the CTA membrane was characterized in terms of pure water permeability. This is done by determining the water flux of desired solution across the membrane from feed solution to the draw solution by using draw solution at different

concentrations and feed solution at different pH. The results will help in determining the optimal concentration of draw solution to be used in forward osmosis process for river water. In addition, CTA membrane was characterized in term of physical properties by using Field Emission Scanning Electron Microscopy (FESEM). The surface morphology and properties of the membrane were determined.

The second scope of this research is to study the ability of FO CTA membrane for humic acid removal. This is done by checking the absorption value of draw solution after the experiment by using UV-vis spectrophotometer to determine the presence of humic acid that will probably be found in the product draw solution. It can also determine how acceptable the product is to be consumed by human being.

Last but not least, to study the effect of different concentration draw solution (i.e. NaCl) on reverse salt diffusion. This is completed by determining the conductivity value of the feed solution before and after the experiment to check the existence of salt that will possibly backflow to the feed solution through the membrane. Different humic acid feed solution pH and NaCl draw solution concentrations were used to determine how it affects the amount of reverse salt diffusion.

## ***1.6 Organisation of this thesis***

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

Chapter 2 introduces the membrane technology used in water treatment and the fundamental principles of osmosis and forward osmosis (FO). Besides that, this chapter discusses on the advantages of using FO method and its applications. The differences between FO and the current most popular membrane process RO are also compared. In addition, this chapter provides a description on the different method of membrane technologies currently used in this era. Furthermore, this chapter discusses on the common membrane used for forward osmosis process known as cellulose triacetate (CTA) membrane and the discussion on the humic acid is also done as it is the feed solution for this research. The selection of NaCl draw solution and its properties that could influence the FO performance is also discussed on this chapter. Lastly, this chapter also looks into the current challenges of FO that can gravely affect the efficiency of the process which are concentration polarization, reverse salt diffusion of draw solution and draw solution recovery.

Chapter 3 provides description on the chemicals used and methodology of this research which includes the procedures to characterize CTA FO membrane in terms of physical and chemical properties. The preparation of draw solution and feed solution will be described and the permeation module of the experiment will be demonstrated.

Chapter 4 discusses on the experimental data which was obtained. This chapter discusses on the performance of different draw solution concentrations by means of water flux from feed to permeate side, humic acid rejection and also reverse salt diffusion. In addition, the impact of pH on CTA membrane performance at different draw solution concentrations is discussed too. Lastly, determination of the optimal draw solution concentration and feed solution pH in treating river water is completed.

Chapter 5 draws together a summary of the thesis and provides some recommendations to improve the research.

## **2 LITERATURE REVIEW**

### ***2.1 General overview***

First of all, this chapter introduces the membrane technology used in water treatment and the fundamental principles of osmosis and forward osmosis (FO). This chapter also discusses on the advantages of using FO in water treatment over the current most popular membrane process which is the reverse osmosis (RO). The applications of FO are also will be discussed. Besides that, this chapter discusses and compares the other pressure-driven membrane processes, namely reverse osmosis (RO), nanofiltration (NF) ultrafiltration (UF), and microfiltration (MF). Apart from that, this chapter also reviews on the properties of cellulose triacetate (CTA) membrane which makes it a suitable membrane for forward osmosis membrane. A review on humic acid is also present in this chapter as it is the main feed solution which was used for this study. Moreover, the selection of sodium chloride (NaCl) draw solution will be discussed. This chapter also discusses the properties of draw solution that will affect FO performance which are concentration and temperature. Lastly, the current challenges of FO that can gravely affect the efficiency of the process which are concentration polarization, reverse salt diffusion of draw solution and draw solution recovery are also present in this chapter.

### ***2.2 Introduction to membrane technology in water treatment***

Under the threats of freshwater shortage, many engineers and researchers have been dealing with reclaiming polluted water, while others try to find other alternative 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 water treatment. Membrane technology is the application of a positive barrier or film in the separation of unwanted particles, microorganisms and substances from water and effluents. Membrane technology is gaining popularity due to its ability to remove organic and inorganic substances, micropollutants and some harmful chemicals which cannot be removed by conventional water treatment system.

A membrane is a thin, typically planar structure or material that selectively controls the mass transport between two environments or phases. Organic polymers, metals, ceramics, layer of chemicals, liquids and gases can be membrane (Khulbe, 2008). In this separation process, a semi-permeable membrane acts as a highly 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 (Strathmann, 2001). A schematic representation of membrane separation is given in Figure 2-1.

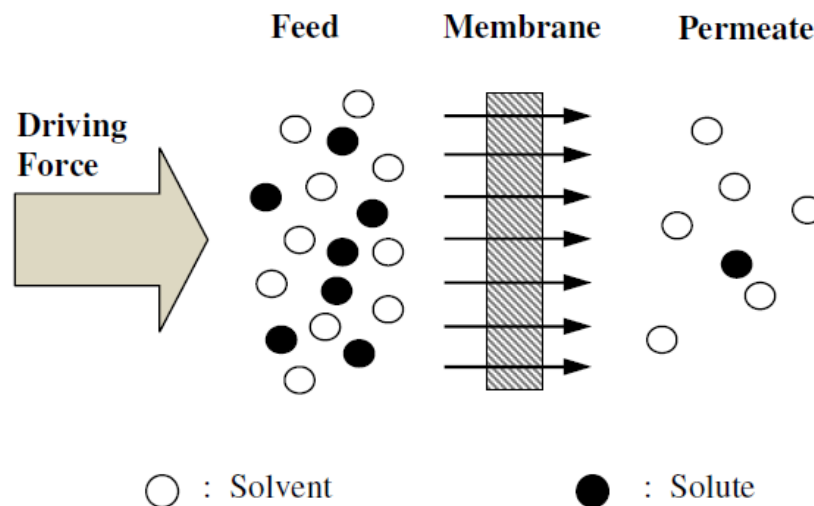


Figure 2-1: Schematic representation of a membrane process for separation (Khulbe, 2008).

## 2.3 Types of pressure-driven membrane processes

### 2.3.1 Reverse Osmosis

The current state-of-the-art for desalination and water purification is RO process, for it can remove salts, hardness, turbidity and most of potable water contaminants known today. Reverse osmosis is a pressure-driven membrane-based process, where the membrane (almost always polymers) acts as the heart of the process in separating the undesired constituents from a feed to obtain the desired pure product (Matin et al., 2011). Figure 2-4 shows the process model of reverse osmosis process (Chekli et al., 2012). Nowadays, the most popular membrane processes for saline water treatment are Reverse

Osmosis (RO), Microfiltration (MF), Ultrafiltration (UF) and Nanofiltration (NF). Membrane permeability and the size of constituents rejected by each process decrease in the order presented (MF > UF > NF > RO) (Coday et al., 2014). Table 2-2 shows the general description of these four membrane processes. RO process enjoys a number of advantages which make it an attractive technology for seawater desalination because of its reliability, high water recovery rate and salt rejection rate, and its ability to treat a wide range of seawater concentrations. At present, more than 50% of the world's desalination water is produced by RO process (Altaee et al., 2014).

Although RO process has a number of advantages, the high power consumption is the process's main disadvantage. With the Energy Recovery Instrument (ERI), an average of 3.5 kWh/m<sup>3</sup> is required for seawater desalination (seawater TDS 35,000 mg/L). Indeed, reducing power consumption in the process of reverse osmosis was the objective of many research studies (Altaee et al., 2014). Other than that, RO is highly susceptible to inorganic scaling and to particulate, biological, and organic fouling. These foulants can become compacted and difficult to clean, leading to low water permeability, increased pressure loss, and considerable chemical consumption for cleaning (Coday et al., 2014). In addition, designing an efficient RO desalination system involves many complicated and interacting choices to meet the technical, environmental and economic requirements. One of the main problems in reverse osmosis plants is concentration polarization. Prediction of solute concentration on the membrane surface in crossflow membrane processes has vital role in the design of reverse osmosis processes and in estimating their performances (Sassi & Mujtaba, 2011). All these problems can compromise membrane performance and surface chemistry.

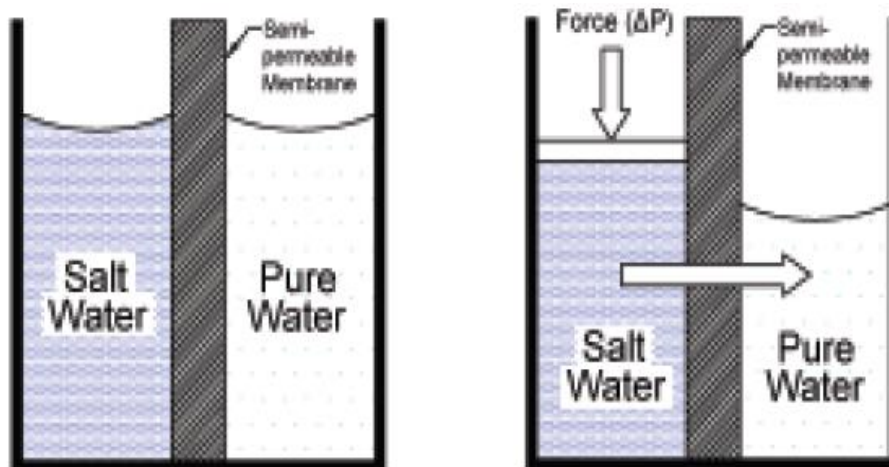


Figure 2-2: Process model of reverse osmosis (Duranceau, 2012).



### **2.3.2 Nanofiltration**

NF membranes have a nominal pore size of approximately 2-5nm (Ozaki, 2004). Pushing water through these smaller membrane pores requires a higher operating pressure than either MF or UF. Operating pressures are usually near 600 kPa (90 psi) and can be as high as 1,000 kPa (150 psi) (Rautenbach et al., 1996). These systems can remove virtually all the cysts, bacteria, viruses, and humic materials. They provide excellent protection from disinfection byproducts formation if the disinfectant residual is added after the membrane filtration step. Because NF membranes also remove alkalinity, the product water can be corrosive, and measures, such as blending raw water and product water or adding alkalinity, may be needed to reduce corrosivity (Greenlee et al., 2009). NF also removes hardness from water, which accounts for NF membranes sometimes being called “softening membranes”. Hard water treated by NF will need pretreatment to avoid precipitation of hardness ions on the membrane (Rautenbach et al., 1996). More energy is required for NF than MF or UF, which has hindered its advancement as a treatment alternative.

### **2.3.3 Ultrafiltration**

Ultrafiltration (UF) is the process of separating extremely small particles and dissolved molecules from fluids. The primary basis for separation is molecular size, although in all filtration applications, the permeability of a filter medium can be affected by the chemical, molecular or electrostatic properties of the sample (Basile & Nunes, 2011). Ultrafiltration can only separate molecules which differ by at least an order of magnitude in size. Molecules of similar size cannot be separated by ultrafiltration. Materials ranging in size from 1,000 to 1,000,000 molecular weight are retained by ultrafiltration membranes, while salts and water will pass through (Khaled, 2013). Colloidal and particulate matter can also be retained. Ultrafiltration membranes can be used both to purify material passing through the filter and also to collect material retained by the filter. Materials significantly smaller than the pore size rating pass through the filter and can be depyrogenated, clarified and separated from high molecular weight contaminants. Materials larger than the pore size rating are retained by the filter and can be concentrated or separated from low molecular weight contaminants (Schwab & Moore, 2012).

Ultrafiltration is typically used to separate proteins from buffer components for buffer exchange, desalting, or concentration. Ultrafiltration are also ideal for removal or exchange of sugars, non-aqueous solvents, the separation of free from protein-bound ligands, the removal of materials of low molecular weight, or the rapid change of ionic and/or pH environment. Depending on the protein to be retained, the most frequently used membranes have a nominal molecular weight limit (NMWL) of 3 kDa to 100 kDa (Khaled, 2013). Ultrafiltration is far gentler to solutes than processes such as precipitation. UF is more efficient because it can simultaneously concentrate and desalt solutes. It does not require a phase change, which often denatures labile species, and UF can be performed either at room temperature or in a cold room (Basile & Nunes, 2011).

### **2.3.4 Microfiltration**

Microfiltration (MF) is the process of removing particles or biological entities in the 1.5  $\mu\text{m}$  to 10.0 $\mu\text{m}$  range from fluids by passage through a microporous medium such as a membrane filter. Although micron-sized particles can be removed by use of non-membrane or depth materials such as those found in fibrous media, only a MF membrane having a precisely defined pore size can ensure quantitative retention (Ozaki, 2004). MF membrane can be used for final filtration or pre-filtration, whereas a depth filter is generally used in clarifying applications where quantitative retention is not required or as a pre-filter to prolong the life of a downstream membrane. MF membrane and depth filters offer certain advantages and limitations. They can complement each other when used together in a microfiltration process system or fabricated device (Basile & Nunes, 2011). The retention boundary defined by a MF membrane can also be used as an analytical tool to validate the integrity and efficiency of a system. For example, in addition to clarifying or sterilizing filtration, fluids containing bacteria can be filtered to trap the microorganisms on the membrane surface for subsequent culture and analysis. Microfiltration can also be used in sample preparation to remove intact cells and some cell debris from the lysate (Rautenbach et al., 1996). Membrane pore size cut-offs used for these types of separation are typically in the range of 10 to 1000 nm.

Table 2-1: General descriptions of RO, NF, UF and MF membrane processes (Ozaki, 2004).

<b>Particulars</b>	<b>Reverse Osmosis (RO)</b>	<b>Nanofiltration (NF)</b>	<b>Ultrafiltration (UF)</b>	<b>Microfiltration (MF)</b>
<b>Pore size (nm)</b>	No-detectable pore size	2 - 5	3 - 10	10 – 1000
<b>Retain Particulars (MW)</b>	< 350	> 150	1,000 - 300,000	> 300,000
<b>Applied Pressure (MPa)</b>	1 – 10	0.3 – 1.5	0.01-0.3	0.005 – 0.2
<b>Material</b>	1. Aromatic polyamide 2. Cellulose acetate	1. Aromatic polyamide 2. Polyvinyl alcohol	1. Polysulfone 2. Polyimide 3. Polyacrylonitrile Ceramics	1. Polyethylene 2. Polypropylene 3. Polyvinylidene fluoride 4. Ceramics
<b>Main Function</b>	1. Desalination of brackish and seawater. 2. Production of ultra-pure water.	1. Removal of micropollutants. 2. Desalination of brackish water. 3. Concentration on chemicals.	1. Drinking water production. 2. Clarification of fruit juice. 3. Membrane bioreactor. 4. Home water purifiers.	1. Removal of fine particles and bacteria. 2. Pre-treatment for RO and UF. 3. Membrane bioreactor.

Besides pressure-driven membrane processes, there is another type of membrane process which is forward osmosis (FO) that operates by utilizing the osmotic pressure caused by concentration gradient. This will be discussed in the next topic.

## 2.4 Forward osmosis

### 2.4.1 Osmosis and osmotic pressure

According to Helfer et al. (2014), osmosis occurs when two solutions of different concentrations (for example, different salinities) are separated by a membrane which will selectively allow some substances through it but not others. If these two solutions are fresh water and seawater, for example, and they are kept separated by a semipermeable membrane that is only permeable to water, then water from the less concentrated solution side (freshwater) will flow to the more concentrated solution side (seawater). According to McCutcheon et al. (2005) theoretically, the water flux in an osmosis process can be described as shown in equation (2.1) below:

$$J_w = A \Delta\pi \quad (2.1)$$

where  $J_w$  is the water flux,  $A$  is the pure water permeability coefficient while  $\Delta\pi$  is the difference in osmotic pressures across the membrane between the draw and feed solution sides. This flow will continue until the concentrations on both sides of the membrane are equalized or the pressure on the concentrated solution side is high enough to stop further flow. Under no flow conditions, this pressure will be equal to the osmotic pressure of the solution. Osmotic pressure is a pressure applied to the solution (but not the solvent) from outside in order to just prevent osmotic flow. Osmotic pressure is a colligative property which indicates the chemical potential of the solvent in the solution, or alternatively it includes vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure (Rudin, 1999). The osmotic pressure ( $\pi$ ) of an ideal dilute solution is given by Van't Hoff's equation as shown as equation (2.2) below:

$$\pi = nMRT \quad (2.2)$$

Where  $n$  is the Van't Hoff factor (accounts for the number of individual particles of compounds dissolved in the solution, for example  $n=2$  for NaCl,  $n=1$  for glucose),  $M$  is the molar concentration (molarity) of the solution,  $R$  is the gas constant ( $R=0.0821$  L atm mol<sup>-1</sup> K<sup>-1</sup>) and  $T$  is the absolute temperature (K) of the solution.

### 2.4.2 Fundamental principle of forward osmosis

Forward osmosis (FO) (also known as manipulated osmosis or engineered osmosis) is one of the emerging membrane technologies as it has the ability to desalinate seawater or brackish water at low-cost energy compared to traditional processes. The novelty of this process lies in utilizing the natural osmotic process for desalination rather than the hydraulic pressure as in Reverse Osmosis (RO). Figure 2-2 explains the fundamental of forward osmosis process. Forward osmosis is the transport of water through a semipermeable membrane from a relatively low concentration solution (feed) to a relatively high concentration solution (draw), that is, from a high to low water chemical potential (Wong et al., 2012). A synthetic membrane separates a feed stream and a concentrated draw solution, and the osmotic pressure difference ( $\Delta \pi$ ) across the membrane facilitates diffusion of water through the membrane while rejecting almost all dissolved and suspended constituents. Commonly, the FO process is completed in two separate steps: 1) recovery of water from a feed stream and dilution of the draw solution, and 2) production of high quality product water using RO or distillation while reconcentrating the draw solution. The reconcentrated draw solution is then reused in the FO process (Coday et al., 2014).

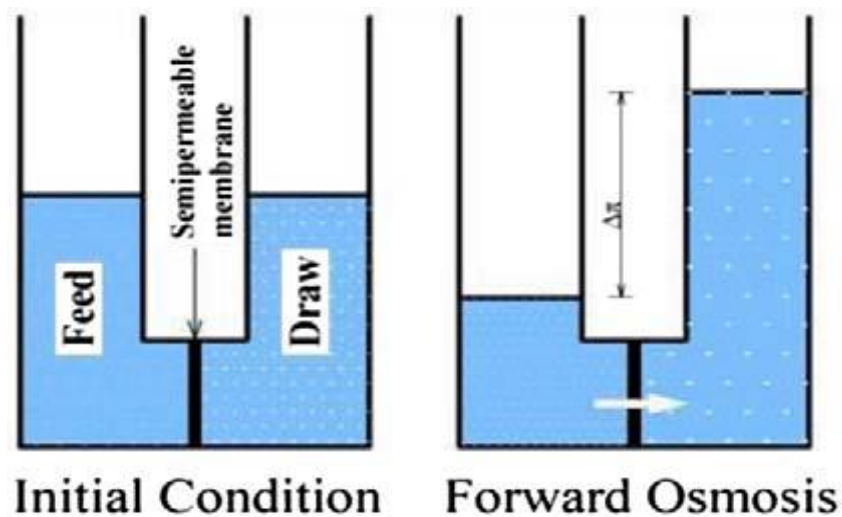


Figure 2-3: The principle of forward osmosis (FO) (Chekli et al., 2012).

### **2.4.3 Advantages of forward osmosis**

FO has many advantages over other membrane technologies. High rejection of almost all solutes and suspended solids while operating at very low or no hydraulic pressures and ambient temperature is the greatest benefits of FO (Coday et al., 2014). Besides, the advantages of using FO are that it can achieve high rejection of a wide range of contaminants, and it may have lower irreversible fouling than pressure-driven membrane processes such as the current most popular membrane process, Reverse Osmosis (RO) because of the lack of applied hydraulic pressure. Table 2-1 is the comparisons of RO with FO. It shows that FO has many advantages over RO in terms of driven pressure, water recovery, environment effect, membrane fouling, modules, application, energy consumption and equipments. These advantages significantly reduce energy consumption and capital costs associated with pumping and system design and construction. They also allow for the development of highly modular systems that can be operated in harsh conditions with minimal access to electric power and supplies (Mi & Elimelech, 2010).

According to Achilli et al. (2009), recent studies have demonstrated that membrane fouling in forward osmosis is relatively low and this is supported by which state that the absent of hydraulic pressure in forward osmosis which depends on osmotic gradient reduces the chance of foul material to remain on the surface of membrane, more reversible and can be minimized by optimizing the hydrodynamics (Lee et al., 2010). Forward osmosis also has the potential to help achieve high water flux and high water recovery due to the high osmotic pressure gradient across the membrane. High water recoveries could help reduce the volume of desalination brine, which is a major environmental concern forward for current desalination plants, particularly for inland desalination (McCutcheon et al., 2005).

Table 2-2: The comparisons between RO and FO (Liu et al., 2009).

Sort	Reverse Osmosis	Forward Osmosis
<b>Driven Pressure</b>	High hydraulic pressure	Osmosis pressure difference
<b>Water recovery</b>	30 %~50 %	At least 75 %
<b>Environment Effect</b>	Harmfully	Friendly
<b>Membrane Fouling</b>	Seriously	Hardly
<b>Modules</b>	Compression resistance	Without particular desire
<b>Application</b>	Normal separation system	Temperature-sensitive system; Pressure-sensitive system; Renew energy; Controlled Release of drug
<b>Energy Consumption</b>	High energy expenditure	Low energy demand
<b>Equipments</b>	High-pressure pumps; Energy recovery unit; Resistant high-pressure pipelines; High investment in equipments	Low investment in equipments

#### 2.4.4 Applications of forward osmosis

FO has been investigated in a wide range of applications, including power generation, seawater/brackish water desalination, wastewater treatment and food processing. All of these applications can be summarized under three general areas: water, energy and life science as illustrated Figure 2-3. Among these applications, desalination is the main concern of researchers nowadays. Studies on forward osmosis for seawater/brackish water desalination have been revitalized since commercial forward osmosis membrane is becoming more and more available.

Generally, forward osmosis desalination processes involve two steps which are osmotic dilution of the draw solution and fresh water generation from the diluted draw solution. All forward osmosis desalination processes can be classified into two types according to the differences of final water generation methods. One method of forward osmosis desalination employs thermolytic draw solutions which can be decomposed into volatile

gases (e.g. CO<sub>2</sub> or SO<sub>2</sub>) by heating after osmotic dilution. This method is however least employed in commercial desalination as compared to other methods (Zhao et al., 2012). The other method of forward osmosis desalination uses water-soluble salts or particles as the draw solutes, and fresh water is generated from the diluted draw solution by the reconcentration of draw solution by other membrane process.

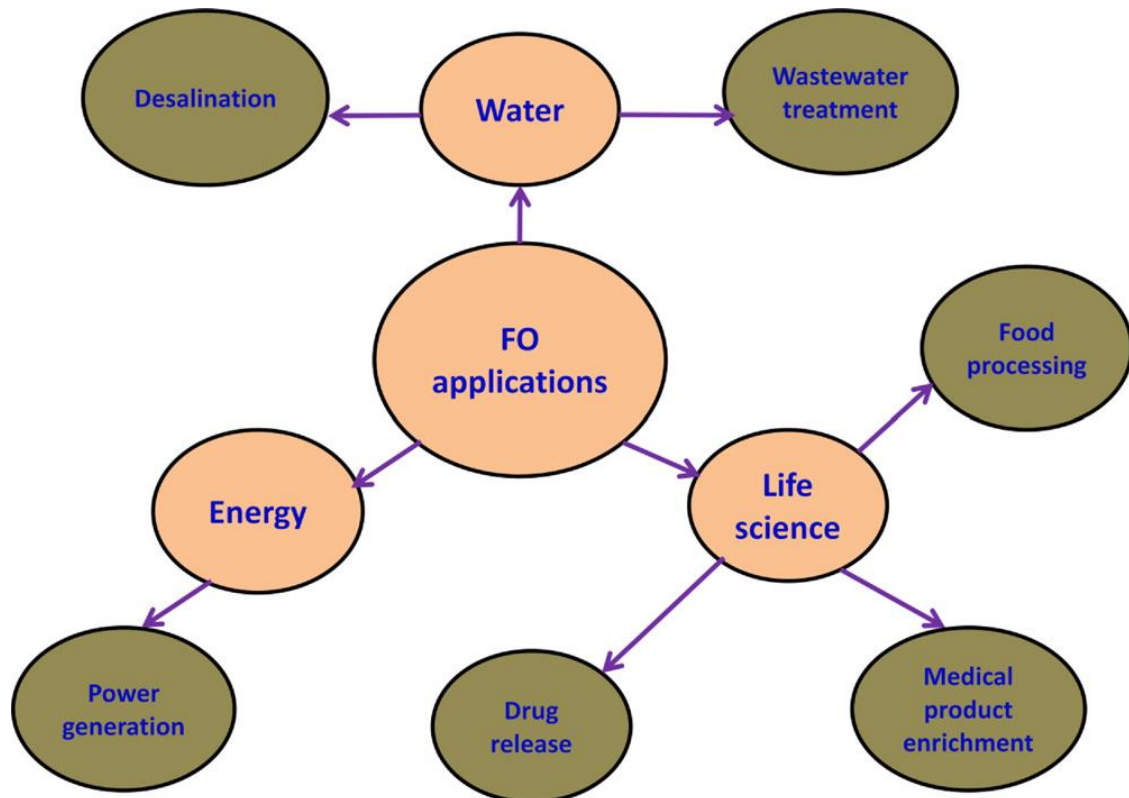


Figure 2-4: Applications of FO in the fields of water, energy and life science (Zhao et al., 2012).

## 2.5 Cellulose Triacetate (CTA) membrane for forward osmosis

Membranes are an integral part of the osmotic process because they allow only the solvent to pass through while retaining the solutes. The development of forward osmosis membranes remains in its primary stage, and the exploration of desirable membranes is an emerging field which has potentially wide applicability in water treatment. In the very early stages, various types of materials such as animal bladders, collodion (nitrocellulose), rubber and porcelain were tested for FO applications (Baker, 2004).



Since the 1960s when the Loeb–Sourirajan membrane was first developed, most of the studies on FO had used RO membranes (Cath et al., 2006). However, before the 2000s, there were few open studies on the membrane development specifically for FO applications. According to their fabrication methods, these recently developed membranes can be classified into three categories: phase inversion-formed cellulosic membranes, thin film composite (TFC) membranes and chemically modified membranes (Zhao et al., 2012).

In the 1990s, Osmotek Inc. and Hydration Technologies Inc. (now known as HTI, of Albany, Oregon), developed the first and the current only available commercial FO membrane which has since been used in a wide variety of applications by different research groups and in commercial applications, such as water purification for the military, emergency relief, and recreational purposes (Cath et al., 2006; Herron, 2008; Zhao et al., 2012). This is a proprietary membrane which is made of cellulose triacetate (CTA) embedded on the neatly woven polyester fabric with a total thickness of less than 50  $\mu\text{m}$  (Cath et al., 2006; McCutcheon et al., 2006; Zhao et al., 2012).

Normally, membrane material is manufactured from a synthetic polymer, although other forms, including ceramic and metallic membranes may be available. Almost all membranes manufactured for drinking water are made of polymeric material, since they are significantly less expensive than membranes constructed of other materials. CTA and polyamide-based thin-film composite (TFC) membranes are widely used for commercial RO processes due to their high hydrophilicity which favours the water transport. However, polyamide-based TFC RO membranes usually have a higher flux and rejection than the CTA membranes (Wei et al., 2011), whereas CTA membranes have superior resistance toward chlorine comparing to the polyamide-based TFC membranes which are weak against chlorine attack. Comparing CTA with cellulose acetate (CA), CTA is not as prone to biodegradation and hydrolysis as CA. These unique advantages make CTA a good candidate as a FO membrane material (Ong & Chung, 2012).

## ***2.6 Humic acid***

Humic acid is known as the natural organic matter (NOM) which can impart a dark brown colour in fresh water, ponds, lakes, and streams. It consists of a long chain polymer of high molecular weight that is soluble in alkaline solution. Many rivers are rich in dark

brown organic matter from natural sources, because the interactions between metal ions like  $\text{Fe}^{3+}$  and the organic fulvic and humic acids makes water treatment difficult (Weber & Wilson, 1975). In general, humic acid was found to be more active than fulvic acid. Humic acid is a principal component of humic substances, which are the major organic constituents of soil (humus), peat, coal, many upland streams and ocean water. Humic substances are not believed to be harmful to human health. At higher concentrations, humic substances can impart a characteristic yellowish to brownish colour in water, and can cause drinking water to have a bitter taste or unpleasant odour. The odour is not from the humic substances themselves. Humic acid may stimulate the growth of aquatic micro-organisms, some of which may produce an odour. The presence of humic substances in drinking water may be due to natural organic sources, but may also indicate contamination from surface water sources. The presence of pathogens or other contaminants present in surface water may cause adverse health effects. Humic substances can adsorb a variety of organic substances. Many metals present in drinking water can also react with humic substances in water, which can increase the concentration of metals in the water (Eggins et al., 1996).

## ***2.7 pH effect of sodium hydroxide addition to humic acid solution***

Humic acid is defined as the constituent that is insoluble in acidic condition and soluble at higher pH which is in alkaline solution. In order to keep the humic acid in soluble form, sodium hydroxide (NaOH) is added to adjust the pH value to be higher (Nguyen et al., 2004; Tang et al., 2007; Zhang et al., 2012). However, for macromolecules like humic acid, solution chemistry such as pH can affect the conformation of molecules which will give an impact in solute diffusivity thus affecting the solute rejection, water flux and reverse salt flux of forward osmosis process.

For the effect of feed solution pH on solute rejection, research done by Wang et al. (2001) shows that the diffusivity of humic acid molecules through the forward osmosis membrane is inversely proportional to the pH of humic acid feed solution, causes an increase in the solute rejection. This phenomenon is explained by Jiahui et al. (2011) who stated that at neutral to high pH, humic acids are more negatively charged due to the ionization of  $-\text{COOH}$  and phenolic  $-\text{OH}$  groups thus inducing higher intermolecular electrostatic repulsion which repulses the humic acids away from the membrane and result in a reduction in diffusivity. The decrease in diffusivity implies that the

hydrophobicity of humic acid towards the membrane decreases which ultimately reduces flux of humic acid across membrane also known as solute rejection. On the contrary, the diffusivity of humic acid is high at low pH values because, at this condition, the functional groups -COOH and -OH are mostly protonated, causing the negatively charged dependent electrostatic repulsion to decrease. At this condition, the increase in diffusivity due to the reduction in intermolecular electrostatic repulsion results in a greater flux of humic acid across the membrane and hence, a decrease in solute rejection. In addition, Jucker (1994) further supports the relation between solute rejection and pH of humic acid by stating that the intermolecular electrostatic repulsion of the membrane reduces as pH of humic acid decreases which consequently, allows more humic acid to permeate across the membrane due to less repulsion, hence, decreasing the solute rejection count.

For the impact of pH on water flux, Ming et al. (2012) stated that water flux is a function of feed solution pH whereby the increase in pH of feed solution causes an increase in water flux across the membrane. This behaviour can be attributed to the changes of the cross-linked membrane polymer structure and the changes in membrane hydrophilicity as a function of solution pH. The membrane polymer structure is influenced by the electrostatic repulsion between ionisable functional groups of membrane polymeric matrix that increases along with solution pH. This increase in electrostatic repulsion between the functional groups causes an increase in average pore size which will ultimately allow more water to permeate through the membrane, increasing the water flux. Besides that, the membrane becomes more hydrophilic through the dissociation of carboxyl functional groups of the active layer as the solution pH increases. The increase in hydrophilicity of the membrane further favours the transport of water across the membrane which will result in an increase in water flux (McCutcheon & Elimech, 2008). In addition, the relation of water flux as a function of feed solution pH is further supported by Ming et al. (2013), who stated that the increase in pH of feed solution causes the surface of the membrane to be more negatively charge and can improve the transport of water from the feed side to the draw side while reducing the transport of ions by repulsion from feed side to the draw side.

As for the impact of pH on reverse salt flux, Hancock & Cath (2009) stated that while the increase in pH increases the water flux, the reverse salt flux is suppressed. This condition occurs because the increase in pH of the feed solution increases also the negative charge

of the membrane which prevents the ions by repulsion from the draw side to permeate to the feed side.

## ***2.8 Selection of NaCl draw solution***

A draw solution (DS) is any aqueous solution which exhibits high osmotic pressure. In the FO process, the DS should provide sufficient driving force to cause a net flow of water through the membrane and therefore form an integral part of the FO process. As the osmotic pressure of the DS is the driving force in the FO process, it is crucial to select an appropriate concentrated solution prior to any application (Achilli et al., 2010). The draw solute must be highly soluble and must generate osmotic pressure that is much higher than the feed solution.

Many types of DS have been studied in the past and they can be generally classified as inorganic-based DS, organic-based DS and other compounds such as magnetic nanoparticles. The sub-classification includes electrolyte (ionic) solutions and non-electrolyte (non-ionic) solutions depending on whether the solution is made up of charged ions or neutral/non-charged solutes respectively (Chekli et al., 2012). Based on past research done by Achilli et al., (2010), for inorganic salt, both sodium chloride (NaCl) and calcium chloride ( $\text{CaCl}_2$ ) had recorded the highest water flux in forward osmosis where seawater is used as feed solution at  $3.38 \times 10^{-6}$  m/s and  $3.22 \times 10^{-6}$  m/s respectively. However, these two inorganic salts also recorded a very high reading of reverse salt diffusion flux which is  $9.1 \text{ g/m}^2\text{h}$  for NaCl and  $9.59 \text{ g/m}^2\text{h}$  for  $\text{CaCl}_2$ . On the other hand, the total cost for forward osmosis of NaCl as draw solution and sea water as feed solution is  $0.011 \text{ \$/L}$  while for  $\text{CaCl}_2$ , total of  $0.029 \text{ \$/L}$  is recorded (Achilli et al., 2010). Based on these figures, it is shown that NaCl has high performance and high reverse salt diffusion flux setback at the same time but is compensated with the low process cost.

In FO, the draw solution used is typically an aqueous solution of a low molecular weight salt (Cath et al., 2006). Numerous studies have used sodium chloride as DS in a wide range of applications. Generally, it has been applied in food production and water and wastewater treatment. The fact that NaCl is used as DS for many FO studies is mainly because saline water is abundant on earth making seawater a natural and cheap source of DS (Chekli et al., 2012). NaCl is also often utilised because it is highly soluble, non-toxic at low concentrations, exhibits high osmotic pressure and relatively straightforward to

reconcentrate with RO process without the risk of scaling (Holloway et al., 2007). Moreover, Chekli et al. (2012) stated that the thermodynamic properties of NaCl have been widely investigated making it easier for the study. Other chemicals have also been suggested and tested as draw solutes. Petrotos et al. (1999) investigated the concentration of tomato juice with FO using  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$ , and NaCl; McCutcheon et al. (2005) reported a method for seawater desalination using a thermolytic draw solution based on ammonia and carbon dioxide.

## ***2.9 Properties of draw solution influencing forward osmosis performance***

### **2.9.1 Concentration**

The draw solution concentration influences the performance of forward osmosis process significantly. This can be further elaborated as previous studies done show that higher water fluxes can be achieved by increasing draw solution concentration as increase in concentration will also increase the osmotic pressure thus promoting the process of forward osmosis (Xu et al., 2010). According to the research done by McCutcheon et al. (2005), an increase in the driving force should lead to an increase in water flux, as demonstrated in Figure 2-5. In the research, for a feed concentration of 0.5 M NaCl, increasing the concentration and thus osmotic pressure of the draw solution leads to an increase in permeate water flux where feed concentration is held constant (0.5 M NaCl) while draw solution concentration is varied. The x-axis in the graph,  $\pi_D - \pi_F$  represents the osmotic pressure difference,  $\Delta\pi$ , where  $\pi_D$  is the bulk osmotic pressure of the draw solution and  $\pi_F$  is the bulk osmotic pressure of the feed solution. The experimental conditions are cross-flow rate (feed and draw solution) of 30 cm/s and temperature of both feed and draw solutions of 50 °C.

Based on equation (2.1), the increase in flux should be linear with the osmotic pressure difference,  $\Delta\pi$ . Figure 2-5 however, shows a non-linear phenomenon, especially at higher driving forces. This phenomenon is attributed to internal concentration polarization, most likely due to microporosity at the membrane permeate side. The draw solution will begin to diffuse into the porous backing layer immediately upon exposure to the membrane. Once the osmotic pressure driving force is established across the dense

active layer, water begins to permeate the membrane. The draw solution that resides within the membrane microporous substructure is diluted by the permeating water, reducing the overall driving force that is established across the dense active layer (McCutcheon et al., 2005). Past research of Tan and Ng (2008) also shows that the high increasing of draw solution concentration could potentially cause internal concentration polarization in the porous support layer which is greater at higher permeate flux resulting in less effective water flux improvement.

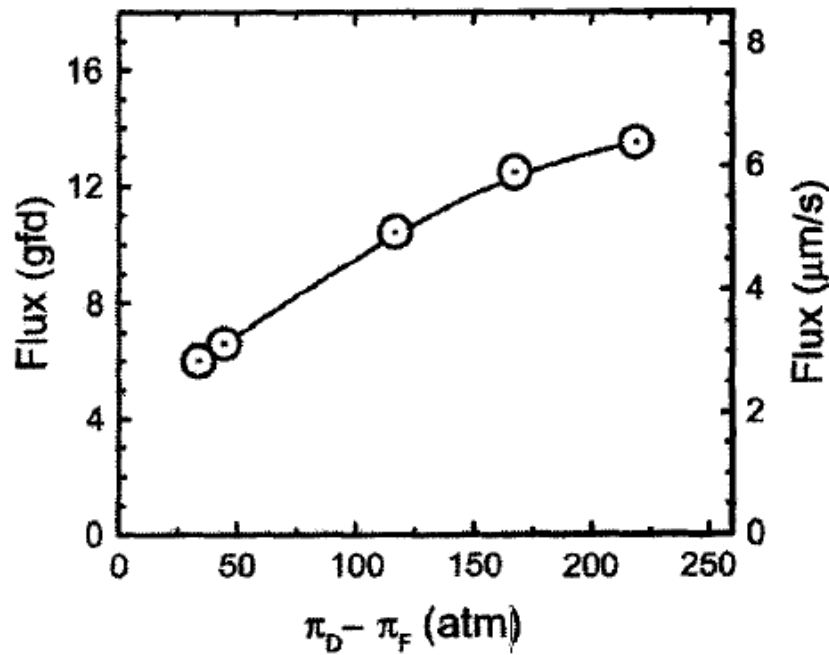


Figure 2-5: FO (CTA) membrane water flux over a range of osmotic pressure differences (i.e., draw solution osmotic pressure minus feed osmotic pressure) (McCutcheon et al., 2005).

## 2.9.2 Temperature

The efficiency of forward osmosis is also affected by draw solution temperature as osmotic pressure, viscosity and diffusivity are improved significantly at higher draw solution temperature as shown in past research (McCutcheon et al., 2006). These studies attributed this enhanced water flux due to reduced water viscosity and thus enhancing mass transfer. In spite of that, the relationship between temperature and water flux is more complex as some recent studies have demonstrated that higher temperature will also induce more negative impacts on the membrane scaling in the presence of certain scaling species which may at the very end result reduce the water flux of the forward osmosis

process. According to Garcia-Castello et al. (2009) and Zhao and Zou (2011), it is observed that at higher temperature, more compact crystals are deposited onto the membrane surface which reduces the efficiency of water cleaning. Hence temperature can enhance water flux to a certain critical point when membrane scaling starts to affect the process performance by causing decrease in flux.

## ***2.10 Challenges of Forward Osmosis***

### **2.10.1 Concentration polarization phenomenon in forward osmosis**

Many studies have demonstrated that, although a high driving force which is osmotic pressure ( $\Delta\pi$ ) in the FO process can be obtained using highly concentrated draw solutions, the actual water flux is observed to be very low compared to the traditional RO process. The lower than expected water flux is attributed to the modification of the solute concentrations at the boundary layer with the membrane surface, known as concentration polarisation (CP) effects (McCutcheon & Elimelech, 2006; Hancock & Cath, 2009). Concentration polarization refers to the build-up of solute species at the membrane surface that adversely affects the membrane performance (Wu et al., 2004). It increases the osmotic pressure at the membrane surface, which causes a reduction in water flux and increase in salt transport across the membrane (Peeva et al., 2004). If the concentration of sparingly soluble salts in the boundary layer exceeds their solubility limits, precipitation or scaling will occur on the membrane surface. At such higher concentration, colloidal materials become less stable and may agglomerate and cause fouling on the membrane surface (Lee et al., 2010).

According to Zhao et al. (2012), all of the membranes used in FO applications are asymmetric. In osmotically driven membrane processes, concentration polarization is caused by the concentration difference between the two independent solutions on each side of the membrane which are feed solution and draw solution through an asymmetric FO membrane. The phenomenon of concentration polarization is associated with the membrane characteristics and it is mainly due to the salt concentration at the membrane surface relative to bulk solution (McCutcheon & Elimelech, 2006). Depending on the flow mode of the draw and feed solutions, concentration polarization is classified into internal and external effects. Both external concentration polarization (ECP) and internal

concentration polarization (ICP) can take place in FO processes. Generally, ECP occurs at the surface of the dense active layer of the membrane and ICP occurs within the porous support layer of the membrane.

#### **i. External concentrative polarization (ECP)**

ECP is formed at the surface of the active layer of the membrane. During the separation process, the concentration of the solution near the membrane surface increases gradually, which results in the reduction of the osmosis driving force and the water flux. The effects of this phenomenon can be largely mitigated by increasing the shear rate and turbulence of flow across the membrane. This is explained by the research done by Liu et al. (2009), who stated that external CP plays a minor role in osmosis driven processes and is not the main cause for the lower than expected water flux in such processes.

According to Gray et al. (2006), both RO and FO are accompanied by ECP. The difference is that only concentrative ECP can take place in a pressure-driven membrane process, while both concentrative ECP and dilutive ECP may occur in an osmotically driven membrane process depending on the membrane orientation. Concentrative ECP occurs when the membrane support layer is facing the draw solution, while dilutive ECP occurs when the membrane support layer is facing the feed solution. Concentrative concentration polarization usually refers to the change in the concentration of feed solution and it is due to the increase in the concentration of feed solution at the membrane surface leading to a decrease in the osmotic pressure gradients across the membrane. As a result, fresh water flow across the membrane declines with time.

On contrast, the dilutive concentration polarization is associated with the draw solution which results in a reduction in the concentration of draw solution. In response to this effect the osmotic pressure gradient is decreased as well as water flux across the membrane (Altaee, 2012). The advance in the membrane manufacturing technology successfully minimized the internal concentration polarization problem. This was achieved by reducing the thickness of the membrane support layer (Loeb et al., 1997). However, the effect of external concentration polarization is an inherent nature of the FO membrane process and can't be avoided. ECP reduces the net driving force due to increased osmotic pressure at the membrane active layer interface on the feed side of the membrane, or decreased osmotic pressure at the membrane active layer surface on the draw solution side (Zhao et al., 2012).



## **ii. Internal Concentration Polarization**

ICP is one of the most important phenomena in osmotically driven membrane processes and is exclusive to FO. ICP occurs when the solute concentration in the support layer was significantly lower than the bulk concentration in the draw solution, which led to a drastic reduction of the available driving force. The effect of internal concentration polarization was found to be more serious than the external concentration polarization (Altaee, 2012). It has been recognized that the water flux decline in FO is predominantly caused by ICP (McCutcheon & Elimelech, 2006). The earliest FO studies found that ICP could reduce the water flux by more than 80% (Mehta & Loeb, 1978). When FO membrane is asymmetric, ICP occurs within the support layer of the membrane, and is characterized more complexly than the ECP phenomena. The result is a reduction in the osmotic pressure gradient across the active layer of the membrane and a corresponding reduction in water flux (Gray et al., 2006).

Two types of ICP, namely dilutive ICP and concentrative ICP can occur within the membrane support layer depending on the membrane orientation as illustrated in Figure 2-6. When the draw solution is placed against the membrane support layer, dilutive ICP will occur within the membrane support layer as water permeates across the membrane from the feed solution to the draw solution. In the alternative membrane orientation (i.e. the feed solution facing the membrane support layer), concentrative ICP occurs as the solute in the feed solution accumulates within the membrane support layer. More critically, because ICP occurs within the support layer, it cannot be mitigated by altering hydrodynamic conditions such as increasing the flow rate or turbulence (Zhao et al., 2012).

Recent investigations have established that internal concentration polarization is a major factor in limiting water flux in osmotically driven membrane processes (McCutcheon & Elimelech, 2006). There is agreement that internal concentration polarization is influenced by the structure (thickness, tortuosity, and porosity) of the membrane support layer (Tan & Ng, 2008). However, there is not unanimous agreement as to whether internal concentration polarization is influenced by the diffusion coefficient of the draw solution. McCutcheon and Elimelech (2006) improved a model that was initially developed by Lee et al. (1981) in which the solution diffusion coefficient and the membrane support layer characteristics contribute to internal concentration polarization,

while Tan and Ng (2008) suggest that only the membrane characteristics influence water flux.

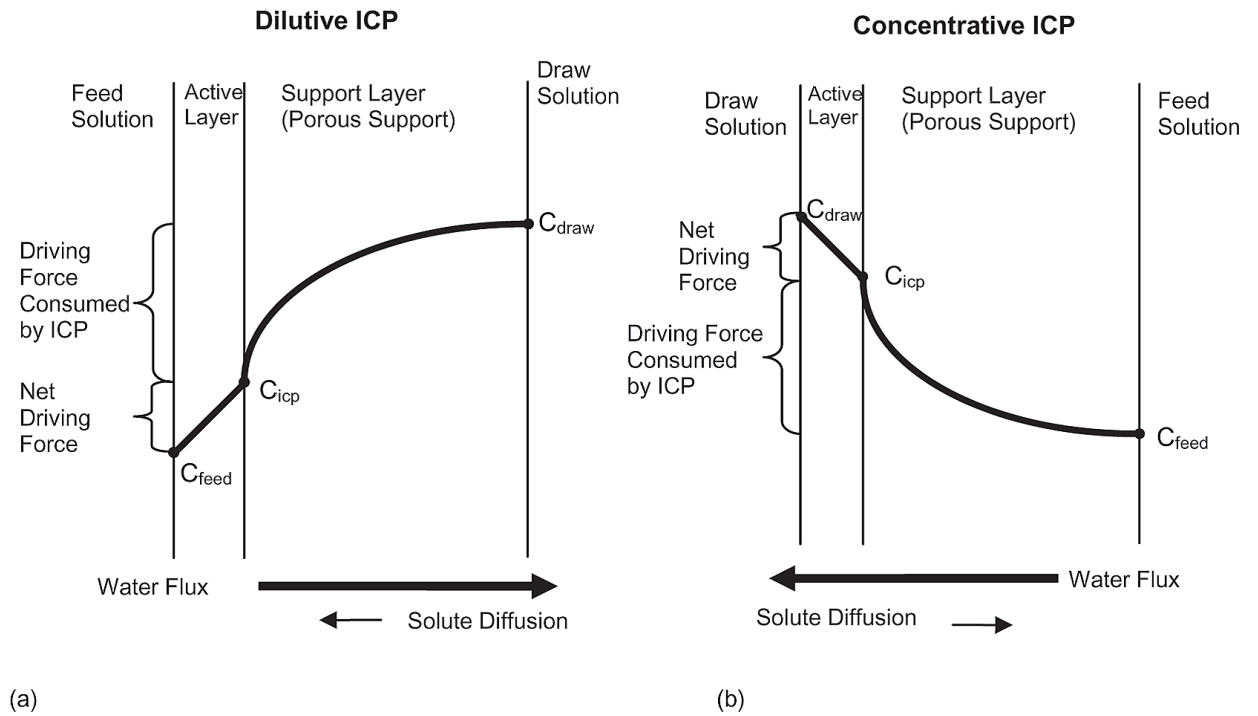


Figure 2-6: The schematic representation of (a) dilutive internal concentration polarization (ICP) and (b) concentrative internal concentration polarization (ICP) (Gray et al., 2006).

## 2.10.2 Reverse salt diffusion of draw solution

Reverse draw salt flux is also an important parameter that has to be assessed when evaluating the performance of FO process. Similar to RO, trace quantities of salts diffuse through the membrane from the feed solution into the draw solution. However, in osmotically driven membrane processes, salts also diffuse from the draw solution into the feed solution (Hancock & Cath, 2009). In the FO process, reverse diffusion of the draw solutes from the DS through the membrane towards the FS is inevitable due to large difference in solute concentration between the draw solution and the feed solution. The diffusion of solutes ( $J_s$ ) through a semi-permeable membrane is described by Fick's Law as shown in equation (2.3) below (Mulder, 1991):

$$J_s = B \Delta C \quad (2.3)$$

where  $B$  is the solute permeability coefficient and  $\Delta C$  is the solute concentration difference across the membrane.

According to Yong et al. (2012), for the draw solution to leak into the feed solution, a draw solute first diffuses through the support layer in the opposite direction of the convective flow of solvent. At the interface between the support layer and the active layer, the solute partitions into the active layer before diffusing across it. The rapid transport of highly permeable solutes across the active layer results in a boundary layer forming adjacent to the membrane active layer on the feed solution side as shown in Figure 2-7, a schematic of an asymmetric membrane operating with reverse salt flux in forward osmosis mode. The explanation of reverse salt diffusion route is done based on Figure 2-7 where the high concentration of the solute in the draw solution,  $C_D$ , creates a chemical potential gradient which drives both the water flux,  $J_w$ , and the reverse flux of the solute,  $J_s$ . For the draw solute to permeate across the asymmetric membrane into the bulk feed solution where its concentration,  $C_F$ , is negligible, it first must be transported across the support layer of thickness,  $t_s$ , followed by the active layer of thickness,  $t_A$ , and finally through an external boundary layer of thickness,  $\delta$ .  $C_D^m$  and  $C_F^m$  represent the draw solute concentration in solution at the active layer solution interface on the support layer side and the boundary layer side, respectively (Yong et al., 2012).

In fact, several studies from Hancock and Cath (2009) and Lee et al. (2010) have demonstrated that this phenomenon can jeopardise the process. Reverse salt diffusion can decrease the net osmotic pressure across the membrane which results in flux decline. Moreover, reverse salt transport is not only an economical loss, but can also complicate concentrate management. The accumulation of DS solutes in the feed solution may induce toxicological challenges for sensitive receiving environment or affect adjacent treatment processes if contaminants such as nitrate, phosphate or heavy metals present in the feed concentrate (Hancock & Cath, 2009). For example, if FO is used in food concentration, reverse salt diffusion can degrade the quality of the concentrated product, and if FO is used in desalination, reverse salt diffusion could have an impact on the disposal of the concentrate stream. In the Osmotic Membrane Bioreactor (OMBR) process, reverse salt diffusion could inhibit or have toxic effects on the microbial community in the bioreactor, although preliminary results have shown that this is not likely (Achilli et al., 2009). While numerous FO investigations have focused on attainable water fluxes as a function of the draw solution composition and concentration, only few studies have reported data on

reverse salt diffusion into the feed solution and its dependence on membrane characteristics and draw solution composition (Cornelissen et al., 2008).

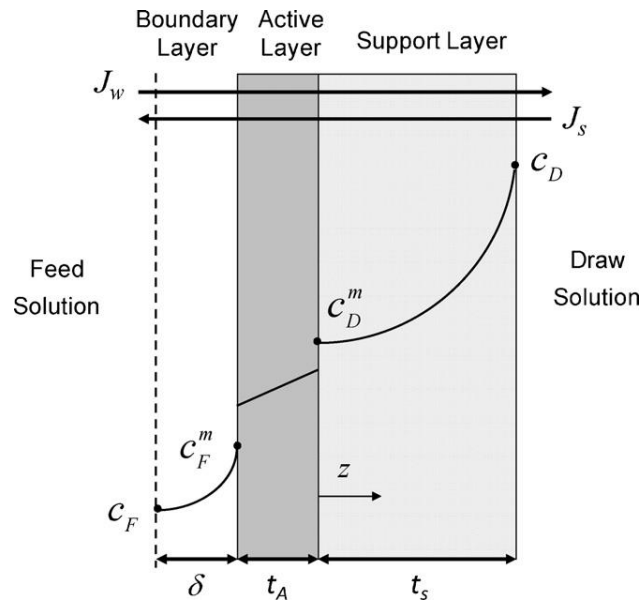


Figure 2-7: Schematic diagram for the process of reverse salt diffusion in forward osmosis (Yong et al., 2012).

### 2.10.3 Recovery of draw solution

Another important criterion in some FO applications is the availability of a suitable process for effective recovery, reconcentration and recycling of the draw solution after it has been diluted. The reconcentration process should achieve high recovery of the draw solution to minimize losses, be affordable, and be able to produce high-quality product water. For example, when considering FO for production of potable water, it is important that draw solutes are not present in the final product water, and if trace concentrations are present, they must be below the drinking water maximum contaminant level (Achilli et al., 2010). Thus, right recovery processes need to be selected for specific draw solution to reduce cost and energy (Chekli et al., 2012).

Table 2-3 summarizes some of the most famous draw solution reconcentration and recovery methods. Since the mid-1960s, attempts have been made to find a draw solution that can be easily separated, recovered and regenerated. For instance, Batchelder (1965), was the first to test volatile solutes as draw solution and recovery was made by heating and air stripping process. Later, thermolytic solutions such as carbonates of ammonia were

found to be readily recovered through distillation process using low heat energy as this draw solution can decompose into ammonia and carbon dioxide by heating up to only 60°C (McCutcheon et al., 2006). However, the proximity of low grade heat from thermal power plants for instance is required to ensure that the recovery process is economically viable.

For some specific applications, however, the diluted draw solution can be used directly without the need for separation processes which considerably reduce the cost of the process (Hoover et al., 2011). Such applications include emergency water supply, dilution of input stream to reverse osmosis desalination plant, dilution of reverse osmosis brine before discharging into the environment, osmotic cleaning of fouled reverse osmosis, production of biofuel from algae and direct irrigation (Chekli et al., 2012).

Table 2-3: Summary of draw solution and the recovery and reconcentration methods  
(Chekli et al., 2012).

<b>Draw Solution</b>	<b>Reconcentration and Regeneration Methods</b>
Volatile solutes (SO <sub>2</sub> )	Heating or air stripping
Alcohol	Distillation
Al <sub>2</sub> SO <sub>4</sub>	Doped Ca(OH) <sub>2</sub>
Glucose	Direct application
Glucose and fructose	Direct application
Fructose	Direct application
Glucose/fructose	RO
MgCl <sub>2</sub>	Direct application
	NF process
KNO <sub>3</sub> and SO <sub>2</sub>	SO <sub>2</sub> is removed through standard means
NH <sub>4</sub> HCO <sub>3</sub>	Heating-decomposition into NH <sub>3</sub> and CO <sub>2</sub>
MNPs	Magnetic field separators
	FO process using RO brines as DS
	UF process
Albumin	Denatured and solidified upon heating
Dendrimers	Wide range of pH values and UF
2-methylimidazole-based compounds	FO-MD
NaCl	RO process
	Distillation/RO process
	Direct application
MgSO <sub>4</sub> and Na <sub>2</sub> SO <sub>4</sub>	NF process
Micelles close to the draft point	Temperature swing with low-grade heat and crystallization
RO brine	RO process
Ionic polymer hydrogel particles	Direct application
	Heating or pressure stimuli
Fertilisers	Direct application

## ***2.11 Summary***

This chapter shows the advantages of using forward osmosis process. Based on this chapter, it can be seen that forward osmosis process faces many problems which includes concentration polarization and reverse salt diffusion despite having numerous advantages. In addition to that, the characteristics of feed and draw solutions which affect the performance of forward osmosis are also discussed. In a nutshell, this chapter describes the general theory, applications and also parameters of forward osmosis process.

## **3 MATERIALS AND METHODS**

### ***3.1 Overview***

This chapter discusses on how the experiment was carried out. It includes the chemicals needed for the draw solution and feed solution. Besides that, this chapter includes the membrane used in the experiment, known as cellulose triacetate (CTA) membrane. The methodology are divided into two parts which are the characterization of CTA membrane in terms of physical and chemical properties. In addition, the permeation module for the forward osmosis process is demonstrated in this chapter. Lastly, the method for which the data was tabulated and also the way of discussion of results are discussed in this chapter.

### ***3.2 Chemicals***

The chemicals used in this experiment were solid sodium chloride,  $\geq 99.5\%$  purity (Sigma-Aldrich), humic acid powder (Aldrich Chemical) and solid sodium hydroxide (R & M Chemical); while the membrane used was cellulose triacetate (CTA) membrane (HTI water). Sodium chloride was used to form draw solution while humic acid was used to form the feed solution. Sodium hydroxide was added to the feed solution to keep humic acid in soluble form. CTA membrane was used to separate the humic acid feed solution from the draw solution and allowed forward osmosis to occur.

### ***3.3 Preparation of draw solutions***

Sodium chloride was dissolved in water into draw solutions with different concentrations of 0.5M, 1.0M, 1.5M, 2.0M and 2.5M. The volume of pure water at each concentration was 1L.

### ***3.4 Preparation of synthesized river water by using humic acid***

A 15mg/L humic acid solution was prepared as synthesized river water to be used as the feed solution for the forward osmosis experiment. 15mg/L of humic acid was used as it is the highest recorded humic acid concentration to be present in the river water in Malaysia and this allows the result of research if successful, to prove that any



concentration of humic acid below 15mg/L can be treated by forward osmosis process. Two different stock solutions of humic acid were prepared by addition of 1g and 10g of NaOH respectively to keep humic acid in soluble form. First of all, two stock solutions were prepared by dissolving 1g of humic acid powder in 1L of pure water. Then, 1g and 10g of sodium hydroxide were added to the different solutions and labelled. After that, the feed solution was prepared by taking out 15 mL of the stock solution by using pipette and diluted to 1L using pure water. 15 mg/L of humic acid solution was prepared.

### 3.5 Permeation module

The permeation module is shown in Figure 3-1.

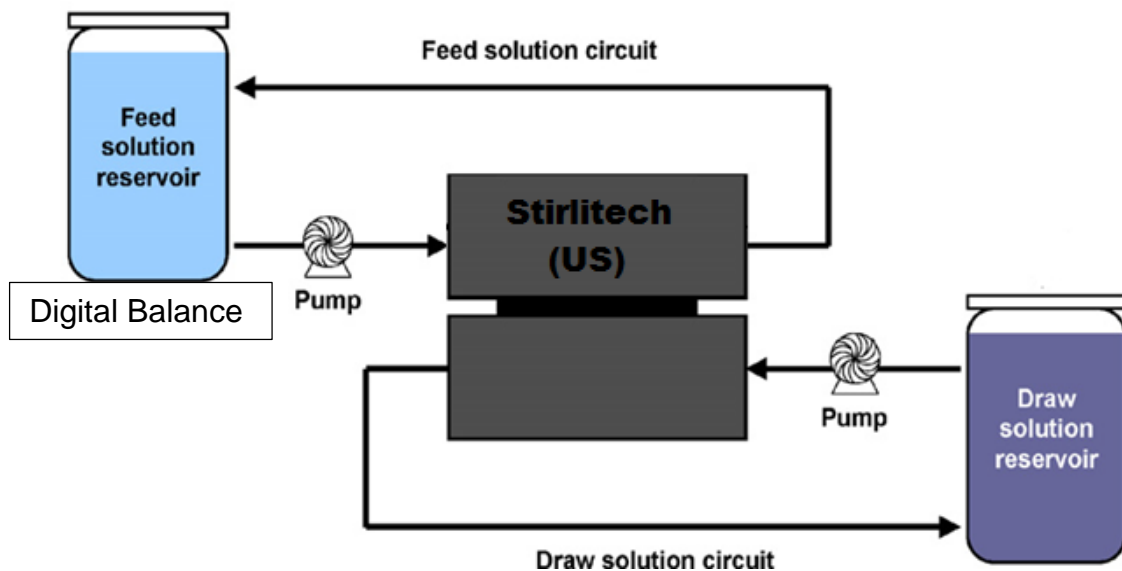


Figure 3-1: Schematic diagram of bench-scale forward osmosis system  
(Achilli et al., 2010)

### 3.6 Methodology

#### 3.6.1 Characterization of CTA membrane performance

The forward osmosis experiment was conducted on a lab scale unit. First, the Cellulose Tri Acetate (CTA) Membrane was inserted between two chambers to separate the feed solution from the draw solution. The membrane was orientated such that its active layer faced the draw solution compartment to reduce the internal concentration polarization and

thus obtaining the higher flux flow. Then, 1L of 0.5 M NaCl draw solution and 1L of humic acid feed solution with 1g of NaOH added were prepared in respective beakers. The feed solution was placed on a digital balance and weight changes were recorded for 1 hour in 10 minutes interval after the peristaltic pump was turned on to calculate the permeate flux. Peristaltic pump was used to circulate the feed and draw solutions in the process. Before the experiment starts, the pH of feed solution was determined by using pH meter. Besides, the conductivity of the two solutions were measured and recorded using conductivity meter before the experiment. The absorption values of the solutions were also determined before the experiment by using UV-vis spectrometer at a wavelength of 254nm (UV<sub>254</sub>) according to Tang et al. (2007). Temperature was maintained at room temperature and the pressure was 1 atm. After running the experiment for 1 hour, the absorption values were taken for both the feed and draw solutions by using UV-vis spectrophotometer in order to determine the concentration of humic acid in the solutions; while the final conductivities of feed and draw solutions were measured and recorded again to know the amount of reverse salt diffusion in the feed solution. UV-vis spectrometer test was done by taking pure water as the base and any increase in concentration of humic acid of the used solution was recorded whereas conductivity of solutions was measured by using conductivity meter. Following that, all the apparatus was cleaned by using deionized water and the experiment was repeated by using the same cellulose triacetate (CTA) membrane for the draw solution concentrations of 1.0M, 1.5M, 2.0M and 2.5M. The whole experiment was repeated by using another feed solution with 10g of NaOH added.

After the experiment, the volume of water permeated was calculated by using equation (3.1) as shown below:

$$\Delta V = \frac{\Delta Mass}{Density\ of\ water} \quad (3.1)$$

where  $\Delta V$  is the volume of water permeated,  $\Delta Mass$  is the changes in mass of feed solution and density of water is 1000 kg/m<sup>3</sup>. After that, the water flux of each draw solution at different concentration was calculated by using equation (3.2) (You et al., 2012):

$$J_w = \frac{\Delta V}{A \Delta t} \quad (3.2)$$

where  $J_w$  is the water flux,  $\Delta V$  is volume of water which permeates through the membrane,  $\Delta t$  is time taken in minutes and  $A$  is the effective area of the membrane which is  $0.042 \text{ m}^2$  in this experiment. Then, a graph of water flux against concentration of draw solution was constructed to illustrate the relationship between them for two types of feed solution used. In addition, according to Hwang et al. (2011), the humic acid rejection was calculated using equation (3.3) below:

$$R = \left(1 - \frac{C_p}{C_b}\right) \times 100\% \quad (3.3)$$

where  $R$  is the humic acid rejection in percentage (%),  $C_p$  is the humic acid concentration in permeate and  $C_b$  is the bulk concentration of humic acid. After that, a graph of humic acid rejection against concentration of draw solution was constructed for the different feed solutions used. Furthermore, tables showing the amount of reverse salt diffusion caused by the different concentrations of draw solution were tabulated to show the efficiency of draw solutions by using two different feed solution pH. The amount of reverse salt diffusion was determined by calculating the difference in conductivity of the feed solution before and after the experiment. The amount of reverse salt diffusion was determined by calculating the difference in conductivity of the feed solution before and after the experiment. Lastly, the characteristics and performance of cellulose triacetate (CTA) membrane to treat river water by forward osmosis process were discussed.

### **3.6.2 Characterization of CTA membrane morphology**

Cellulose Tri Acetate (CTA) membrane was characterized in terms of physical properties by using Field Emission Scanning Electron Microscopy (FESEM) located at the Central Lab. First, samples of CTA membrane before and after the experiment were prepared. Then, the samples were dried in oven to remove excess water in order to allow vacuum process in the equipment. After that, the samples were cut into small pieces with 5mm width and coated with platinum prior to observation under FESEM. The surface morphologies and properties of the membrane were examined.

### **3.7 Summary**

This chapter shows the overall chemicals needed, equipment for process and also the method of performing this research to achieve the stated objective. Thus it is important

to follow this chapter strictly during the performance of experiment to obtain the best possible result to enhance the reliability of this research in the future.

## 4 RESULTS AND DISCUSSION

### 4.1 Overview

This chapter discusses on the results obtained by performing FO using five different concentrations of NaCl draw solution with two different pH of feed solution due to different amount of NaOH added. In conjunction to that, this chapter compares and discusses on how the draw solution concentration and feed solution pH influence the performance of FO. Besides that, this chapter also discusses and compares on the humic acid rejection for each concentration of the draw solution at two different feed solution pH. In addition, reverse salt diffusion will be discussed to determine which concentration of NaCl draw solution has the highest reverse salt diffusion which can gravely affect the efficiency of forward osmosis. The effect of feed solution pH on reverse salt diffusion will be discussed too. Based on these discussions, the optimal draw solution concentration and feed solution pH due to different amount of NaOH added will be determined for the treatment of synthetic river water using FO.

### 4.2 Water flux for each concentration of draw solution at different pH

By referring to You et al. (2012), the method of calculating flux was derived in the following formula.

$$J_w = \frac{\Delta V}{A\Delta t} \quad (3.2)$$

where  $J_w$  is the water flux,  $\Delta V$  is volume of water which permeates through the membrane,  $\Delta t$  is time taken in minutes and  $A$ = effective area of the membrane which is  $0.042 \text{ m}^2$  in this experiment. Based on the formula, it is safe to declare that the flux of water which permeates through the membrane is inversely proportional to the time taken. By using the data obtained from the experiment, a series of flux was calculated to determine the efficiency of the different concentrations of NaCl draw solution with different feed solution pH.

### 4.2.1 Data collected

The pH of feed solution for 1g of NaOH added was determined to be 9.73 while for 10g of NaOH added was 11.65. The mass and volume change of the feed humic acid solution were recorded for 1 hour in 10 minutes interval for each concentration of draw solution at different feed solution pH. The data collected can be seen in Table 4-1 and Table 4-2.

Table 4-1: Table of changes in HA feed solution volume with pH 9.73 for different concentration of NaCl draw solutions.

DS Concentration (M)	FS Volume (m <sup>3</sup> )				
	0.5	1.0	1.5	2.0	2.5
Time (min)					
0	0	0	0	0	0
10	6.810E-06	1.536E-05	1.337E-05	1.582E-05	1.661E-05
20	8.924E-06	1.811E-05	1.649E-05	2.063E-05	2.487E-05
30	1.046E-05	2.096E-05	2.072E-05	2.613E-05	2.996E-05
40	1.424E-05	2.372E-05	2.583E-05	3.265E-05	3.787E-05
50	1.612E-05	2.634E-05	2.872E-05	3.709E-05	4.330E-05
60	1.763E-05	2.865E-05	3.122E-05	4.224E-05	4.979E-05

Table 4-2: Table of changes in HA feed solution volume with pH 11.65 for different concentration of NaCl draw solutions.

DS Concentration (M)	FS Volume (m <sup>3</sup> )				
	0.5	1.0	1.5	2.0	2.5
Time (min)					
0	0	0	0	0	0
10	5.341E-05	5.500E-05	5.439E-05	5.281E-05	5.554E-05
20	5.876E-05	5.954E-05	6.180E-05	5.849E-05	6.568E-05
30	6.064E-05	6.366E-05	6.673E-05	6.668E-05	7.320E-05
40	6.224E-05	6.504E-05	7.019E-05	7.307E-05	8.151E-05
50	6.412E-05	6.834E-05	7.322E-05	7.852E-05	8.993E-05
60	6.634E-05	7.165E-05	7.812E-05	8.311E-05	9.867E-05

### 4.2.2 Results

The results obtained are tabulated in Table 4-3 and a graph is plotted to compare the results trend in Figure 4-1.

Table 4-3: Table of flux for each concentration of NaCl draw solution at different HA feed solution pH.

DS Concentration (M)	Water flux, $J_w$ ( $\text{m}^3/\text{m}^2.\text{min}$ )	
	FS pH 9.73	FS pH 11.65
0.5	5.152E-06	6.157E-06
1.0	6.200E-06	7.925E-06
1.5	8.499E-06	1.130E-05
2.0	1.258E-06	1.443E-05
2.5	1.580E-06	2.054E-05

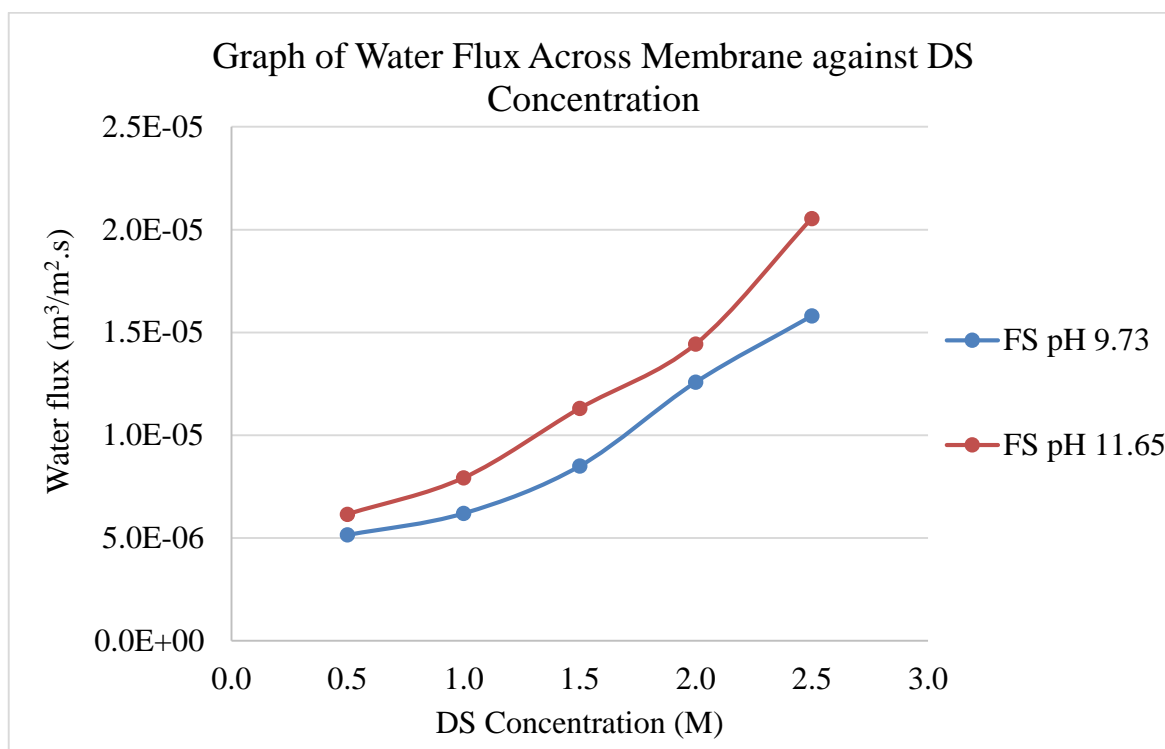


Figure 4-1: Graph of flux for each concentration of NaCl draw solution at different feed solution pH.

### 4.2.3 Discussions

Based on the results, it can be seen that the trend of flux increases with the increase in concentration of draw solution for both pH of feed solutions. The water flux obtained by using related formula showed the highest figure by 2.5M NaCl draw solution with the reading of  $1.580 \times 10^{-6} \text{ m}^3/\text{m}^2.\text{min}$  for feed solution pH of 9.73 and  $2.054 \times 10^{-5} \text{ m}^3/\text{m}^2.\text{min}$

for feed solution pH of 11.65; whereas the lowest flux obtained is by 0.5 M NaCl draw solution with the reading of  $5.152 \times 10^{-6} \text{ m}^3/\text{m}^2.\text{min}$  for feed solution pH of 9.73 and  $6.157 \times 10^{-6} \text{ m}^3/\text{m}^2.\text{min}$  for feed solution pH of 11.65. This phenomenon can be explained by equation (3.2) which shows that the flux is inversely proportional to the time taken for the water to permeate through the membrane. In conjunction to this, due to high water potential at high concentration, the time taken for the water to permeate through membrane is relatively shorter at higher concentration which ultimately causes an increase in flux. Besides that, greater permeate flow rate was observed at higher draw solution concentration was due to the increased driving force which is osmotic pressure difference across the membrane. This phenomenon is supported by previous studies done by Xu et al. (2010), who proved that higher water fluxes can be achieved by increasing draw solution concentration as increase in concentration will also increase the osmotic pressure thus promoting the process of forward osmosis. The osmotic pressure ( $\pi$ ) of an ideal dilute solution is given by Van't Hoff's equation as shown as equation (2.2) below:

$$\pi = nMRT \quad (2.2)$$

Where  $n$  is the Van't Hoff factor (accounts for the number of individual particles of compounds dissolved in the solution,  $n=2$  for NaCl),  $M$  is the molar concentration (molarity) of the solution,  $R$  is the gas constant ( $R=0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (K) of the solution. From the equation, osmotic pressure is directly proportional to molar concentration of the solution. When concentration increases, osmotic pressure also increase. Hence, it is proven that the increase in molarity of draw solution causes an increase in osmotic pressure of draw solution which ultimately increase the flux of water from feed side to permeate side.

However, although the water flux increased with the increase in the osmotic pressure of the draw solution, the increase was non-linear unlike the classical solution-diffusion model which predicts that the water flux in the absence of applied pressure shall be directly proportional to the osmotic pressure difference generated by different draw solution concentrations. This shows that increasing the draw solution concentration will not lead to proportionate increase in the water flux, as reported in other studies (Xu et al., 2010). When the draw solution concentration is increased, the net osmotic pressure increases, generating higher water fluxes temporarily but, the increased incoming water flux causes enhanced dilutive internal concentration polarization (ICP) within the membrane support layer, thereby keeping the overall gain in water lower. ICP occurred



when the solute concentration in the support layer was significantly lower than the bulk concentration in the draw solution, which led to a drastic reduction of the available driving force (Zhao et al., 2012). This indicates that no matter how high the osmotic pressure a DS can generate, it will not be able to produce proportionate water flux by the FO process.

Other than the effect of draw solution concentrations, feed solution pH has greatly affect the water flux across the membrane. Results showed that as pH increases, water flux also increases. This can be explained by the research done by Ming et al. (2012) who stated that water flux is a function of feed solution pH whereby the increase in pH of feed solution causes an increase in water flux across the membrane. This can be explained by the membrane polymer structure which is influenced by the electrostatic repulsion between ionisable functional groups of membrane polymeric matrix that increases along with solution pH causes an increase in average pore size which will ultimately allow more water to permeate through the membrane, thus increasing the water flux. Besides that, as the solution pH increases, the membrane becomes more hydrophilic through the dissociation of carboxyl functional groups of the active layer further favours the transport of water across the membrane (McCutcheon & Elimech, 2008). In addition, the relation of water flux as a function of feed solution pH is further supported by Ming et al. (2013), who stated that the increase in pH of feed solution causes the surface of the membrane to be more negatively charge and can improve the transport of water from the feed side to the draw side while reducing the transport of ions by repulsion from feed side to the draw side.

### ***4.3 Humic acid rejection***

In order to obtain the concentration of humic acid in the draw solution, a calibration curve is initially drawn in order to provide the relation between absorption and humic acid concentration. The absorption of humic acid solution at different concentrations was tested by using UV-vis spectrometer and the graph is shown in Figure A-1. This graph was used to determine the humic acid rejection by using equation (3.3):

$$R = \left(1 - \frac{C_p}{C_b}\right) \times 100\% \quad (3.3)$$

where R is the humic acid rejection in percentage (%),  $C_p$  is the humic acid concentration in permeate and  $C_b$  is the bulk concentration of humic acid.

### 4.3.1 Results

Table 4-4: Table of humic acid rejection for each concentration of NaCl draw solution at different feed solution pH.

DS Concentration (M)	Humic acid rejection (%)	
	FS pH 9.73	FS pH 11.65
0.5	98.7034	99.2958
1.0	97.6589	99.2966
1.5	97.1145	98.0392
2.0	96.3048	97.7805
2.5	96.2264	97.6879

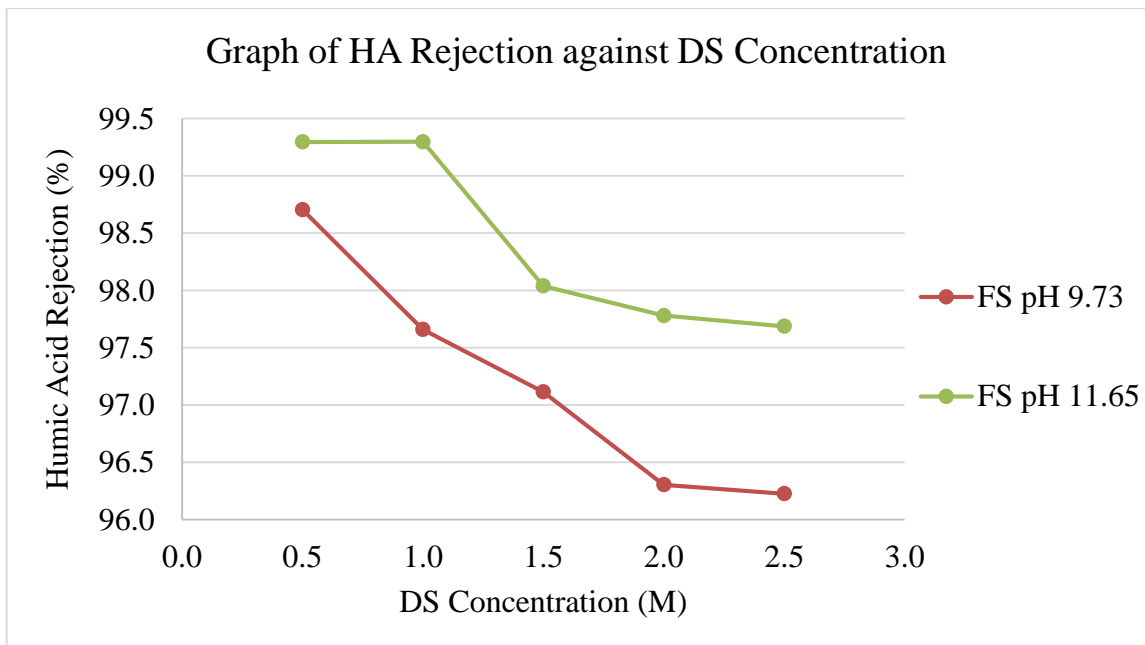


Figure 4-2: Graph of humic acid rejection for each concentration of NaCl draw solution at different feed solution pH.

### 4.3.2 Discussions

Based on the results obtained, it can be clearly seen that the increase in concentration of NaCl draw solution causes the decrease in humid acid rejection for both feed solution pH. At concentration of 0.5 M, the reading of humic acid rejection is the highest, which is 98.7034% for feed solution pH of 9.73 and 99.2958% for feed solution pH of 11.65; whereas the lowest humic acid rejection is shown by 2.5 M NaCl draw solution with the reading of 96.2264% for feed solution pH of 9.73 and 97.6879% for feed solution pH of

11.65. This phenomenon can be explained by Kong et al. (2014) who stated that the increase in draw solution concentration will increase the solute flux of feed solution and decrease the solute rejection, due to the increase of solute flux that causes the feed solute to penetrate through the membrane to the draw solution side. This is further explained by Xie et al. (2013) who stated that the increase in flux of water caused by increase of draw solution concentration will decrease salt rejection as the driving force of water flux pulls and moves along a small amount of feed solute towards the membrane and forces some to seep through the membrane. Thus, it is reasonable to have 0.5 M NaCl draw solution with the lowest flux to have the highest rejection for both feed solution pH as the driving force is not strong enough to pull along a large quantity of humic acid solute to penetrate across the CTA membrane into the draw solution side.

For the effect of feed solution pH on humic acid rejection, Wang et al. (2001) stated that the diffusivity of humic acid molecules through the forward osmosis membrane is inversely proportional to the pH of humic acid feed solution, causes an increase in the solute rejection when pH increases. This phenomenon is explained by Jiahui et al. (2011) who stated that at neutral to high pH, humic acids are more negatively charged due to the ionization of -COOH and phenolic -OH groups thus inducing higher intermolecular electrostatic repulsion which repulses the humic acids away from the membrane, thus resulting in a reduction of diffusivity and flux of humic acid across membrane. On the contrary, the diffusivity of humic acid is high at low pH values because, at this condition, the functional groups -COOH and -OH are mostly protonated, causing the negatively charged dependent electrostatic repulsion to decrease. At this condition, the diffusivity of humic acid across the membrane is increased results in a greater flux of humic acid across the membrane and hence, a decrease in solute rejection. In addition, Jucker (1994) further supports the relation between solute rejection and pH of humic acid by stating that the intermolecular electrostatic repulsion of the membrane reduces as pH of humic acid decreases which consequently, allows more humic acid to permeate across the membrane due to less repulsion, hence, decreasing the solute rejection count.

#### ***4.4 Reverse salt diffusion***

In order to determine the amount of reverse salt diffusion, it is necessary to identify the concentration of NaCl that will possibly exist in the feed solution. A calibration curve is initially drawn in order to provide the relation between conductivity and NaCl

concentration in Figure A-2. The amount of reverse salt diffusion was determined by calculating the difference in conductivity of the feed solution before and after the experiment.

#### 4.4.1 Results

Table 4-5: Table of conductivity reading of HA feed solution with pH 9.73 at different NaCl draw solution concentration.

DS Concentration (M)	Conductivity of FS ( $\mu\text{S/m}$ )		
	Before	After	Change
0.5	70.50	87.52	17.02
1.0	66.56	92.13	25.57
1.5	68.23	102.17	33.94
2.0	71.02	112.31	41.29
2.5	69.35	119.1	49.75

Table 4-6: Table of conductivity reading of HA feed solution with pH 11.65 at different NaCl draw solution concentration.

DS Concentration (M)	Conductivity of FS ( $\mu\text{S/m}$ )		
	Before	After	Change
0.5	723.7	725.1	1.4
1.0	738.5	742.8	4.3
1.5	736.4	744.8	8.4
2.0	684.8	697.9	13.1
2.5	695.5	714.3	18.8

#### 4.4.2 Discussions

Based on the results obtained in Table 4-5 and Table 4-6, it can be seen that the difference in conductivity before and after the experiment increases as concentration of draw solution increases for both feed solution pH. The largest difference of conductivity reading is shown by 2.5 M of NaCl draw solution, which is 49.75  $\mu\text{S/m}$  for feed solution

pH of 9.73 and 18.8  $\mu\text{S/m}$  for feed solution pH of 11.65; whereas 0.5 M NaCl draw solution shows the lowest value which is 17.02  $\mu\text{S/m}$  for feed solution pH of 9.73 and only 1.4  $\mu\text{S/m}$  for feed solution pH of 11.65. This phenomenon can be explained by Phillip et al. (2010) who stated that a high concentration of draw solute at membrane interface is necessary to generate a large osmotic gradient, which drives a high water flux; however, this higher concentration of draw solute also increases the concentration gradient across the active layer, which increases the reverse salt flux. This is further supported by Chekli et al. (2012), who stated that the increase in draw solution concentration increases the amount of solutes in draw solution side which indirectly increases the possibility of more solutes at the draw solution side to permeate through the membrane into the feed side of the system.

As for the impact of pH on reverse salt flux, Hancock & Cath (2009) stated that while the increase in pH increases the water flux, the reverse salt flux is suppressed. This condition occurs because the increase in pH of the feed solution increases also the negative charge of the membrane which prevents the ions by repulsion from the draw side to permeate to the feed side.

#### ***4.5 Morphology of CTA Membrane***

As shown in the micrographs in Figure 4-3, there were no obvious changes for CTA membranes at both active and support layer before and after the forward osmosis experiment. According to Alsvik & Hägg (2013), foulant deposition occurs on the relatively smooth active layer in FO mode. However, the result obtained can be supported by Mi and Elimelech (2010) who stated that CTA membranes showed almost no natural organic matter (NOM) fouling and were easier to clean. The low fouling tendency of the CTA membrane confirms prior literature reports that CTA based commercial FO membranes have low fouling tendency (Jin et al., 2012; She et al., 2012).

The uneven active layer surface of CTA membrane as shown in Figure 4-3(a) and Figure 4-3(b) is caused by the drying process of the membranes in oven which has caused the shrinking of membrane pores (Ji & Wei, 2009). CTA membranes were cast with an embedded polyester mesh for membrane support as shown in Figure 4-3(c) and Figure 4-3(d). Due to the presence of such woven meshes, the thickness of the membranes was highly non-uniform, and regions away from the mesh fibers were thinner than regions where fibers were located (Fane et al., 2012).

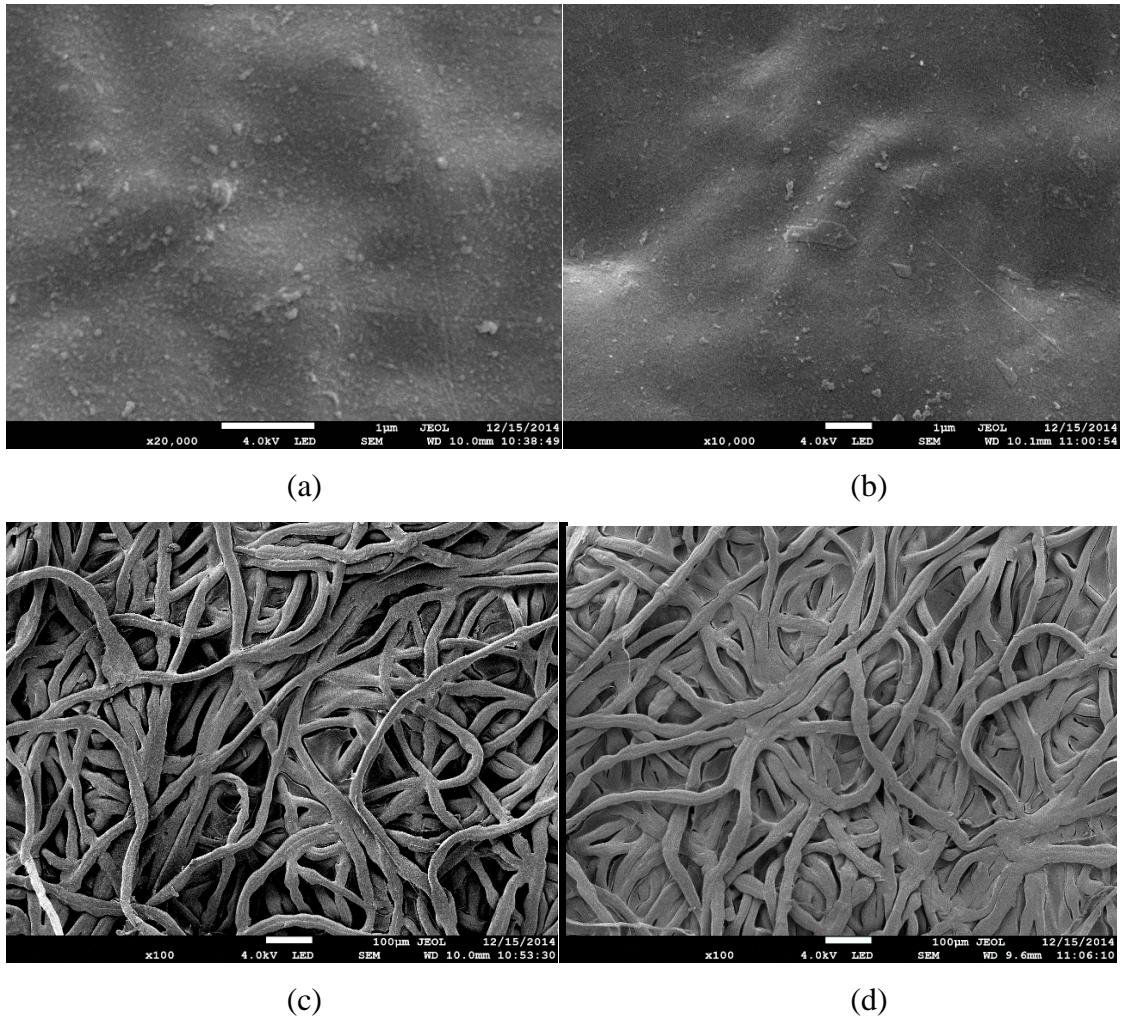


Figure 4-3: FESEM images of CTA membrane (a) at active layer before the FO process, (b) at active layer after the FO process, (c) at support layer before the FO process, (d) at support layer after the FO process.

## 5 CONCLUSION AND RECOMMENDATIONS

### 5.1 Conclusion

This research had characterized the performance of cellulose triacetate (CTA) forward osmosis membrane in humic acid removal by using NaCl as draw solution in different concentrations and humic acid as feed solution in different pH. The performance of CTA membrane was characterized in terms of water flux, humic acid rejection and reverse salt diffusion. Water flux was obtained by using five different concentrations of NaCl draw solutions to identify the optimum concentration for FO process to provide the highest water flux. Besides, the impact of humic acid feed solution pH on the water flux was discussed. It was found that increase in both draw solution concentration and feed solution pH increase the water flux. The highest water flux,  $2.054 \times 10^{-5} \text{ m}^3/\text{m}^2\cdot\text{min}$  was obtained by using 2.5M NaCl draw solution with feed solution pH of 11.65. Besides that, humic acid rejection was determined by using UV-Vis spectrophotometer and the results were discussed. It was found that the increase in draw solution concentration causes a decrease in humic acid rejection for both feed solutions with pH of 11.65 showed a higher solute rejection of more than 97%. Furthermore, reverse salt diffusion of the process was determined by using conductivity meter. Results showed that the increase in concentration and water flux causes an increase in reverse salt diffusion for both feed solutions with pH of 9.73 showed a higher reverse salt diffusion. Apart from that, the CTA membrane morphology before and after the experiment was identified and it was found that the changes on the membrane surfaces are negligible which showed that CTA has low fouling tendency.

As a conclusion, it was found that the optimum condition for treating river water by using CTA membrane can be achieved at high concentration of draw solution with high pH of feed solution. The objective of the research was achieved. From this research, it can be seen that CTA membrane exhibited a high potential of treating river water in Malaysia by forward osmosis process which is a good option of water treatment in order to overcome the problem of water depletion in Malaysia.

## ***5.2 Recommendations***

In order to improve the research, there are several aspects should be remarked. First, it is recommended to extend the time taken for the experiment to obtain a more accurate result in order to characterize the performance of CTA membrane more precisely. Besides that, it is also recommended that polyamide membrane is used together with CTA membrane in order to compare which membrane would be the better performing membrane in forward osmosis process. In addition, more feed solution with different pH values should be tested and compared to further investigate the effect of feed solution pH on the process. Furthermore, to maintain the temperature of the forward osmosis process at room temperature, insulation made by covering the beakers of feed and draw solution is recommended to reduce heat transfer. Moreover, it is recommended that other types of draw solution should be used together with NaCl draw solution to determine the most suitable draw solution for humic acid removal by using CTA membrane.



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## APPENDICES

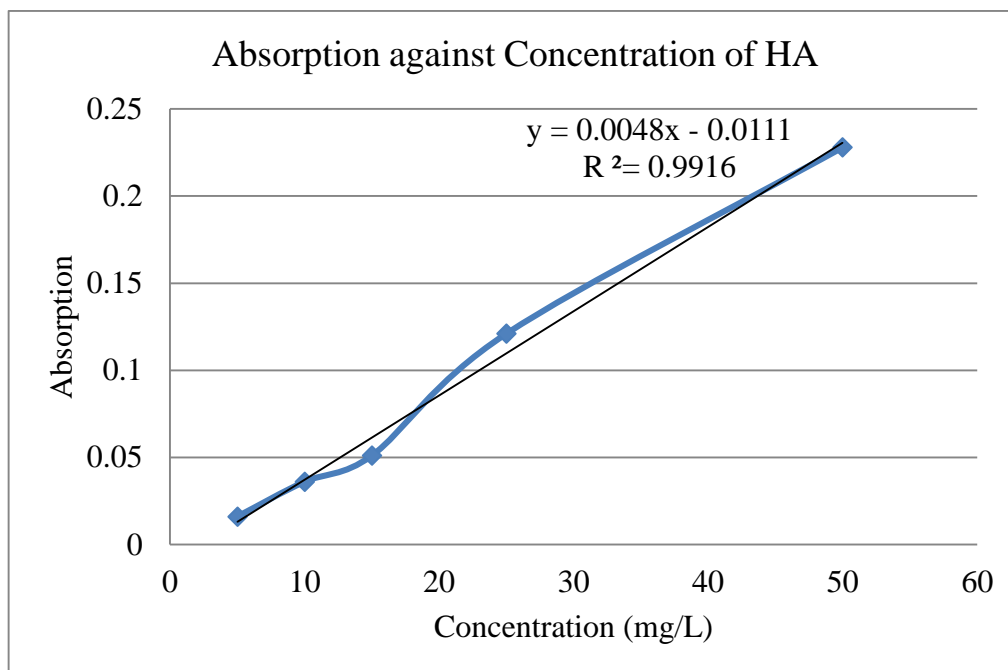


Figure A-1: Calibration curve of absorption against concentration of humic acid.

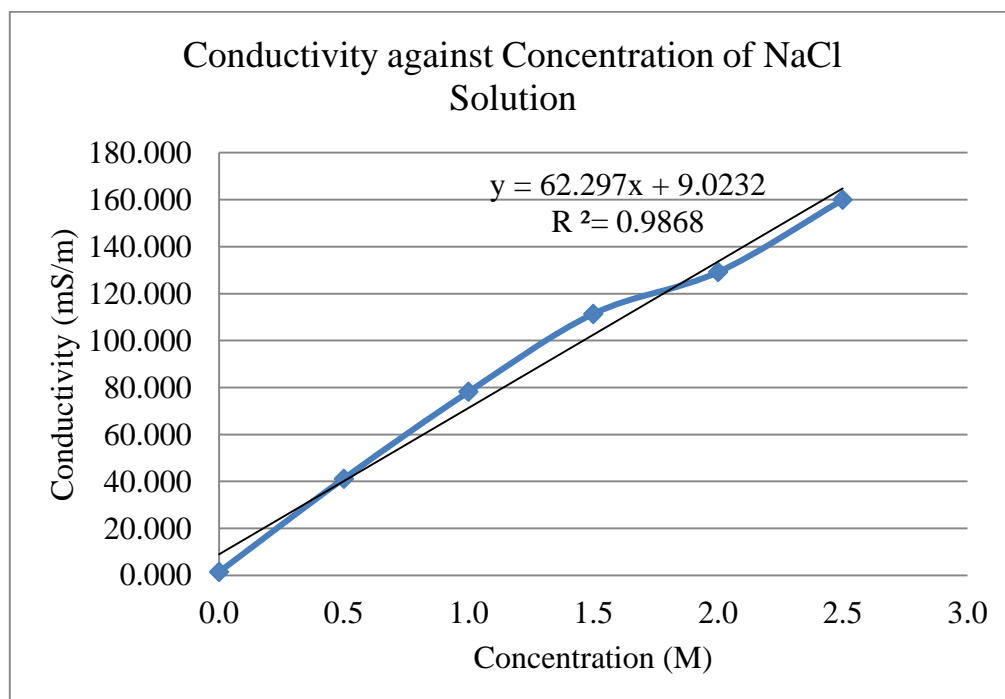


Figure A-2: Calibration curve of conductivity against concentration of NaCl solution.