CHARACTERIZATION OF DRAW SOLUTION IN FORWARD OSMOSIS PROCESS FOR THE TREATMENT OF SYNTHETIC RIVER WATER

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CHARACTERIZATION OF DRAW SOLUTION IN FORWARD OSMOSIS PROCESS FOR THE TREATMENT OF SYNTHETIC RIVER WATER

RYAN YEO WHYE SEONG

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

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SUPERVISOR'S DECLARATION

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 families and my research supervisor, Dr. Mazrul Nizam as their words of encouragement and push had exponentially improved my tenacity in regards to completing this undergraduate research. Besides that, I would also like to dedicate this work to my friends, especially Alice Chong who had supported and accompanied me during ups and downs throughout this journey of completing the undergraduate research study. Lastly, I dedicate this work to University Malaysia Pahang for their given opportunity in performing a research study as an undergraduate chemical engineering student.

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ABSTRACT

Forward osmosis is a process that depends on the concentration gradient and also osmotic potential to treat water which is currently, applicable in many industries. The main factor which affects the entire process of forward osmosis is the draw solution as draw solution acts as the driving force which drives water to past through semi-permeable membrane by means of concentration gradient. This research focuses on the characterization of draw solution in order to provide the optimum effect in treating river water in Malaysia. Apart from that, this research used synthesized river water which consists of 15mg/L of humic acid to replace river water as feed solution. This research was done so as to fill the inadequate amount of research done on forward osmosis where river water was used as feed solution. This research was conducted based on two parameters which will impact the water flux and performance of draw solution namely, concentration of draw solution and also osmotic pressure of draw solution. Thus, 4 different draw solutions made up of inorganic salt, fertilizers and organic salts were tested based on 5 different concentrations. This research also measures the humic acid rejection for each draw solution by using UV-vis spectrometer. Besides, reverse salt diffusion caused by different draw solution was also tested in terms of conductivity to determine the best performing draw solution. This research was conducted by using polyamide coated ultrafiltration membrane to separate the feed and draw solution and the permeation module was constructed as the preliminary laboratory work. Based on the results obtained, increase in molarity of draw solution is proportional to the increase in flux of water. The water flux obtained by using related formula showed the highest figure with calcium nitrate at 2.7 x 10^-4 m^3/m^2.s at 1mol/L, whereas the lowest flux obtained was by fructose with the reading of 2.529 x 10^-05 m^3/m^2.s. Besides that, calculation shows that the increase in draw solution concentration causes a decrease in humic acid rejection. However, the data recorded showed that every draw solutions at concentrations of 0.1mol/L to 1mol/L have good humic acid rejection at approximately 100%. On the other hand, sodium chloride showed higher reverse salt diffusion than calcium nitrate and the value of reverse salt diffusion increases as the molarity increases. Based on the discussions, it is found that this research showed calcium nitrate at 1mol/L as the best performing draw solution in treating river water. This research can further assist future research on forward osmosis of treating river water by narrowing down the type of draw solution that can provide best efficiency in treating river water and also show the category of draw solution which provides best efficiency.

ABSTRAK

Osmosis hadapan adalah satu proses yang bergantung kepada kecerunan kepekatan untuk merawat air yang digunapakai dalam banyak industri. Faktor utama yang memberi kesan kepada keseluruhan proses osmosis hadapan adalah larutan penarik yang bertindak sebagai daya penggerak yang mendorong air melalui membran separa telap. Kajian ini memberi tumpuan kepada pencirian larutan penarik untuk memberikan kesan yang optimum dalam merawat air sungai. Selain itu, kajian ini menggunakan air sungai disintesis yang terdiri daripada 15mg/ L asid humik untuk menggantikan air sungai sebagai larutan suapan. Kajian ini dilakukan bagi mengisi jumlah penyelidikan berkaitan yang pada masa kini, tidak mencukupi. Kajian ini telah dijalankan berdasarkan kepada dua parameter yang akan memberi kesan fluks air dan prestasi larutan penarik iaitu kepekatan larutan penarik dan juga tekanan osmosis larutan penarik. Oleh itu, 4 larutan penarik terdiri daripada garam bukan organik, baja dan garam organik telah diuji berdasarkan 5 kepekatan yang berbeza. Kajian ini juga mengukur asid humik penolakan bagi setiap larutan penarik dengan menggunakan Uv-vis spektrometer. Penyebaran garam terbalik yang disebabkan oleh larutan penarik berbeza juga diuji dari segi kekonduksian untuk menentukan larutan penarik berprestasi terbaik. Kajian ini dijalankan dengan menggunakan poliamida bersalut membran ultrafiltration untuk memisahkan larutan suapan dan larutan penarik dan modul penyerapan itu dibina ketika kerja makmal preliminari. Fluks air diperolehi dengan menggunakan formula yang berkaitan menunjukkan angka tertinggi dengan kalsium nitrat pada 2.7 x 10^-4 m^3/m^2.s di 1mol/L, manakala fluks yang paling rendah diperolehi adalah dengan fruktosa dengan bacaan 2.529 x 10^-05 m^3/m^2.s. Selain itu, pengiraan menunjukkan bahawa peningkatan dalam kepekatan larutan penarik menyebabkan kurangnya penolakan asid humik. Tetapi, data yang direkodkan menunjukkan bahawa setiap larutan penarik pada kepekatan 0.1mol/L untuk 1mol/L mempunyai penolakan asid humik yang baik pada kira-kira 100%. Sebaliknya, natrium klorida menunjukkan penyebaran garam lebih tinggi terbalik daripada kalsium nitrat dan nilai terbalik penyebaran garam bertambah apabila kenaikan kemolaran. Berdasarkan perbincangan, didapati bahawa kalsium nitrat di 1mol/L adalah larutan penarik berprestasi terbaik dalam merawat air sungai. Kajian ini boleh terus membantu kajian akan datang yang berkaitan dengan mengurangkan jenis larutan penarik yang boleh memberikan kecekapan yang terbaik dalam merawat air sungai dan juga menunjukkan kategori larutan penarik yang menyediakan kecekapan yang terbaik .

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LIST OF ABBREVIATIONS

J_w	water flux
A	water permeability
ΔP	hydrostatic pressure
W	energy consumption
C_D	concentration of the solute in the draw solution
J_s	reverse flux of the solute
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
MW	molecular weight of solute
n	the number of moles of species
R	gas constant
c	solute concentration
K	solute resistance
t	thickness
τ	tortuosity
D_s	diffusion coefficient
ΔV	volume of water which permeates through the membrane
A	effective area of the membrane
Δt	time taken in minutes
M	Molarity
J	Van’t Hoff factor

Greek

$\Delta\pi$	Change in osmotic pressure
$\Delta\pi_m$	Osmotic pressure difference across the membrane
$\Delta\pi_{eff}$	Effective osmotic pressure driving force
δ	external boundary layer of thickness
ε	porosity

Subscripts

eff	effective
max	maximum

LIST OF ABBREVIATIONS

DS	Draw solution
FO	Forward osmosis
HTI	Hydration Technology Inc.
MD	Membrane distillation
MPD	Metaphenylenediamin
NF	Nanofiltration
RO	Reverse osmosis
TMC	Trimesoly Chloride
UF	Ultrafiltration

CHAPTER 1

INTRODUCTION

1.1 Background

In this current era, water treatment is one of the most vital fields which provides human with clean water to be consumed daily. In conjunction to that, many viable methods of water treatment in producing clean consumable water has been developed over the years to drastically decrease the cost and energy needed in addition of reducing any negative impacts it may cause to the environment. Among other researched water treatment methods, the method at which osmosis acts as the fundamental concept fits the current objectives of reducing cost, energy and environmental issues during the production of clean consumable water. Osmosis is a physical phenomenon that has been extensively studied by scientists in various disciplines of science and engineering. Early researchers studied the mechanism of osmosis through natural materials, and from the 1960s, special attention has been given to osmosis through synthetic materials.

Osmosis is a physical phenomenon that has been exploited by human beings since the early days of mankind. Early cultures realized that salt could be used to desiccate foods for long term preservation (Cath et al., 2006). In saline environments, most bacteria, fungi, and other potentially pathogenic organisms become dehydrated and die or become temporarily inactivated because of osmosis. Conventionally, osmosis is defined as the net movement of water across a selectively permeable membrane driven by a difference in osmotic pressure across the membrane (Cath et al., 2006). A selectively permeable membrane allows passage of water, but rejects solute molecules or ions. Present day applications of the osmosis phenomenon extend from water treatment and food processing to power generation and novel methods for controlled drug release (Cath et al., 2006).

Following the progress in membrane science in the last few decades, especially for reverse osmosis applications, the interests in engineered applications of osmosis has been spurred (Cath et al., 2006). The further development in this field of osmosis has brought to a newer form of water treatment process also known as forward osmosis. Osmosis, or as it is currently referred to as forward osmosis, has new applications in separation processes for water treatment, food processing, and seawater/brackish water desalination. Other unique areas of forward osmosis research include pressure retarded osmosis for generation of electricity from saline and fresh water and implantable osmotic pumps for controlled drug release (Cath et al., 2006). Unlike reverse osmosis where hydraulic pressure is required, forward osmosis process simply uses the intrinsic osmotic pressure differential between the two solutions of different osmotic potential (highly concentrated draw solution and saline feed water) separated by a semi-permeable membrane to desalinate water.

Although literatures on forward osmosis membrane fouling are still scarce, recent studies indicate that, membrane fouling may not be a significant issue for forward osmosis process, which is another significant advantage for forward osmosis over reverse osmosis process. In the absence of hydraulic pressure, membrane fouling during forward osmosis process is reported to be physically reversible indicating that chemical cleaning may not be essential for forward osmosis process like in reverse osmosis 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. The current asymmetrical membranes used for pressure based filtration result in concentration polarization effects that severely decrease the net osmotic pressure between the two solutions and hence lower the water flux across the membrane (Tang et al., 2010).While external concentration polarization that occurs on the membrane surface can be mitigated using crossflow, similar to pressure based membrane filtration system such as reverse osmosis, internal concentration polarization occurs within the porous support layer of the asymmetrical membranes and therefore cannot be mitigated (Cath et al., 2006).Internal concentration polarization is exclusive to forward osmosis process and is said to be mainly responsible for much lower water flux achieved in forward osmosis process than the expected or theoretical water flux (Gray et al., 2006). Several significant research breakthroughs have been however reported recently in the forward osmosis membrane fabrication particularly with thin film composites and also carbon nanotube membranes that may provide lower concentration polarization effects (Yip et al., 2010).

Since the forward osmosis process works based osmotic pressure, one of the most important components which needs to be present to enable the process of forward osmosis to occur efficiently is known as draw solution. Draw solution, also known as osmotic agent, osmotic media, brine or driving solution is the concentrated solution present in the permeable side of the membrane which acts as the source of driving force in forward osmosis process (Cath et al., 2006). There are many criterions such as osmotic pressure, water solubility and molecular weight which need to be considered in the selection of draw solution to enable the process of forward osmosis to run at optimum performance (Cath et al., 2006). Various chemicals including fertilizers had been suggested and tested as solutes of draw solution. Consequently, the results from the test done show that the selection of draw solution ranges from any organic to any inorganic materials depending on the type of feed for which water needs to be drawn.

1.2 Motivation

The world population is growing rapidly while the problems associated with a lack of fresh water is becoming a known fact affecting drinking water supplies, energy, food production, industrial output, and the quality of our environment ultimately undermining the economies of the world at large (Whetton et al., 1993). Water is also essential for improving the productivity of agricultural land to meet the world’s increasing food demand; however, fresh water scarcity is a serious issue in many parts of the world. Water shortages are further exacerbated by the impact of climate change resulting in frequent drought and unpredictable rainfall events (Whetton et al., 1993).

In Malaysia, river water plays an important role in providing water to citizens and also to the environment. However, despite holding such important position in providing clean consumable water to Malaysia citizens, the majority of the river water present in Malaysia is researched and found to contain low pH value which indicates that the river water in Malaysia is acidic (Katimon et al., 2010). As a result to that, the river water in Malaysia needs to be treated correctly at low cost and energy before distributing it to 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% (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).

Besides that, forward osmosis is an emerging technology that consists of an osmotically driven membrane technology where the treatment process occurs as accordance to the difference in osmotic pressure between the draw solution and feed solution which is separated by a semi permeable membrane (McGinnis & Elimelech, 2008). This further brings forward osmosis to another advantage where the absence of hydraulic pressure could potentially reduce membrane fouling and toxicity effects of product water (Suh & Lee, 2013). In spite of that, studies done on suitable draw solution for the process of forward osmosis thus far has only be revolving around seawater or brackish water as the feed solution and the research of suitable draw solution used to treat river water has been scarce and lesser still when it comes to river water in Malaysia.

Apart from that, it has been over forty years where the study of suitable inorganic draw solution has been done to for the desalination of seawater but the study of organic draw solution such as glucose has been in scarcity and fewer still the study of organic draw solution with river water as the feed solution. In addition, challenges now are also mostly related to separation and recovery of the draw solution from desalinated water. The success of forward osmosis desalination in the future especially for drinking purposes, will rely mainly on how easily and efficiently the draw solution can be separated and recovered from the desalinated water. Under all these. circumstances, the selection of suitable draw solution of either inorganic or organic for the process of forward osmosis where Malaysia river water acts as the feed solution remains skeptical to the industries, researches and students until today.

1.3 Problem statement

The following are the problem statements of this research:

1) Conventional treatment failed to treat water up to drinking water level.
2) Reverse osmosis is promising technology but too expensive.

3) Alternatively, new technology namely forward process could be used. However no studies reported on specific draw solution for treatment of Malaysia river water.

1.4 Objective

To determine the water flux of each draw solutions of different osmotic pressure at different concentration where humic acid was used as synthesized river water as feed solution, to determine the final concentration of humic acid in the product acquired, to determine the reverse salt diffusion of each draw solution and also to determine the most suitable draw solution which can be used to treat river water.

1.5 Scope

This research was done based on 4 solutes which were used to form the desired draw solutions. The solutes used can be categorized into 3 groups which are inorganic, organic and fertilizers. For inorganic solutes, sodium chloride was used. On the other hand, for organic, fructose this was used. Whereas, calcium nitrate was categorized under fertilizer. For feed solution, synthesized river water made of only humic acid was used due to the fact that it is the main and most abundant acidic component present in Malaysia’s river water.

This research discussed on the preparation of polyamide coated ultrafiltration membrane and characteristics each draw solutions which will affect the efficiency of forward osmosis process. The characteristics include molecular weight, osmotic pressure, concentration, diffusivity, recovery process and also cost. In addition, comparison between other different treatment method including pressure retarded osmosis and reversed osmosis were discussed in the literature review part. Apart from that, the effect of internal concentration polarization and also external concentration polarization were discussed in the literature review part.

Besides that, this research was also completed by performing experiments which provided the water flux of water across the membrane for each draw solutions to determine the most efficient draw solution for synthesized river feed solution. The parameter which were experimented and calculated is the concentration and osmotic pressure of draw solution.

Water flux of desired solution across the membrane from feed solution to the draw solution will determine the efficiency and also the performance of the draw solution used and will ultimately help in determining the better draw solution to be used in forward osmosis process for river water.

The content of the product was tested with UV-vis spectrometer to determine how acceptable the product is to be drinkable to human being.

1.6 Organisation of this thesis

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

Chapter 2 provides a description on the different method of osmosis currently used this era. Besides that, this chapter also discusses on the differences between all these 3 osmosis method and the advantages of using forward osmosis method. This chapter also discusses on the problem faced by forward osmosis known as concentration polarization and reverse salt flux diffusion. In addition, this chapter also discusses on the common membrane used for forward osmosis process known as cellulose triacetate membrane and also the discussion on the humic acid is also done as it is the feed solution for this research. The most important part which is the characteristics of draw solution which affects the forward osmosis process is also discussed on this chapter. Moreover, past research on different performance of draw solution used for desalination is also reviewed under this chapter. Lastly, the common applications of forward osmosis is also discussed in this chapter.

Chapter 3 provides description on the chemicals which was used to form the draw solution. Besides that, this chapter also discussed on the preparation of membrane which was used to perform the experiment in addition to the description on the specification of materials needed to construct the permeation module. This chapter also gives description on the tabulation of data obtained to enable the performance of forward osmosis with different draw solution under the parameter of osmotic pressure and concentration to be evaluated in the result. Besides that, this chapter also discussed on the method of evaluating the performance of forward osmosis for synthesized river water formed by humic acid.

Chapter 4 discusses on the experimental data which was obtained. This chapter discussed on the performance of draw solution by means of water flux from feed to permeate side, humic acid rejection and also reverse salt diffusion. Besides, this chapter also discussed on the best performing draw solution in treating river water.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter discusses and compares on the type of water treatment methods which is relatively close to the concept of forward osmosis, namely, pressure retarded osmosis and reverse osmosis. Besides that, this chapter also discusses on the advantages of using forward osmosis in water treatment over the other two methods. Moreover, this chapter also discusses on the two main problems faced by forward osmosis membrane known as concentration polarization and reverse flux diffusion which can gravely affect the efficiency of the process. Apart from that, this chapter also reviews on the properties of cellulose triacetate 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. In addition, this chapter also discusses on all of the main characteristics such as osmotic pressure, concentration, diffusion coefficient, molecular weight and temperature of draw solution inclusive of the recovery of draw solution which will effectively affect the performance and efficiency of the forward osmosis process. This chapter also reviews on the draw solutions used by past researches and their respective performance. Lastly, this chapter reviews on the recent application of forward osmosis in the field of desalination, wastewater treatment and also food concentration.

2.2 Theory of treatment methods

2.2.1 Forward osmosis

According to Cath et al. (2006), osmosis is the transport of water across a selectively permeable membrane from a region of higher water chemical potential to a region of lower water chemical potential. It is driven by a difference in solute concentrations across the membrane that allows passage of water, but rejects most solute molecules or ions. Osmotic pressure (π) is the pressure which, if applied to the more concentrated solution, would prevent transport of water across the membrane. Moreover also according to Cath and Childress (2006), forward osmosis uses osmotic pressure differential (π) across the membrane, rather than hydraulic pressure differential which is the concept used in reversed osmosis, as the driving force for transport of water through the membrane. The forward osmosis process results in concentration of a feed stream and dilution of a highly concentrated stream also known as draw solution. The process of forward osmosis occurs in a compartment where two solutions known as feed solution and draw solution are separated by a semi-permeable membrane. Besides that, in forward osmosis, the impaired water also known as the feed solution is in contact with the dense side of a semi-permeable membrane and a highly concentrated draw solution is in contact with the support side of the membrane. The illustration of forward osmosis process is in the figure 2-1 (Achilli et al., 2010).

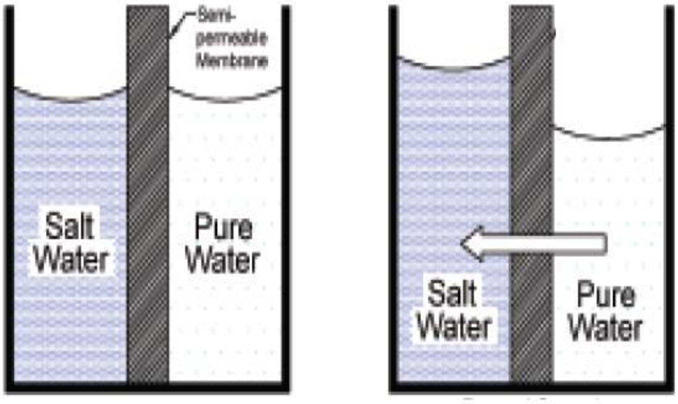

Figure 2-1: Process Model of forward osmosis (Duranceau, 2012).

2.2.2 Pressure retarded osmosis

Pressure retarded osmosis can be viewed as an intermediate process between forward osmosis and reverse osmosis, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient which is similar to reverse osmosis. However, the net water flux is still in the direction of the concentrated draw solution which is rather similar to forward osmosis. This is further supported by She et al. (2013), who also stated that pressure retarded osmosis is an osmotically driven membrane process due to the water which flows from a low osmotic pressure feed solution to a high osmotic pressure draw solution against a hydraulic pressure. This process converts the osmotic power into a mechanical energy, whose power is equal to the product of water permeation rate and applied hydraulic pressure (Loeb, 1976). The mechanical energy can be subsequently converted to other forms of useful energy (e.g., electricity by running the pressurized draw solution through a hydro turbine) (Loeb, 1976). In pressure retarded osmosis, the porous support layer faces the feed solution and the active layer of the membrane faces the draw solution. The chemical potential which is determined by the osmotic pressure difference across membrane is the effective force making energy and fresh water (She et al., 2013). The process of pressure retarded osmosis can be seen as in the figure 2-2.

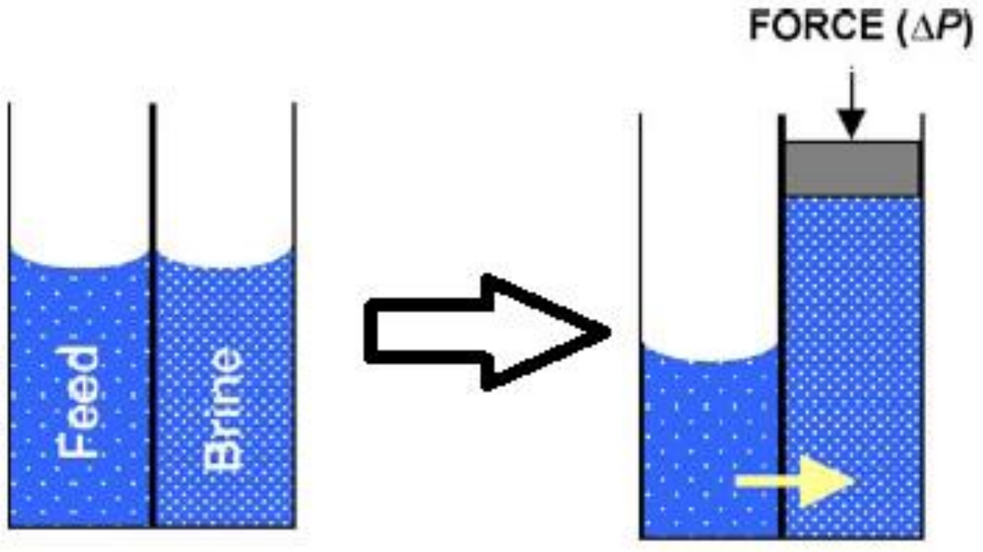

Figure 2-2: Process Model of pressure retarded osmosis (Cath et al., 2006).

2.2.3 Reverse Osmosis

According to Peñate (2011), reverse osmosis is the separation of dissolved solids from water by applying a pressure differential across a membrane that is permeable to water but not to the dissolved solids. As it is so aptly named, this process is the exact opposite of the natural phenomena of osmosis. In osmosis, water molecules flow through a semi-permeable membrane from the less concentrated solution to the more concentrated one, without external influence. This flow continues until the internal pressure of both concentrations is equal, creating a zero pressure differential and halting flow. In reverse osmosis, hydraulic pressure is applied to the more concentrated solution (containing dissolved solids) which causes water molecules to flow through a semi-permeable membrane to the dilute solution (without dissolved solids). Besides, as stated by Paul (2004), the membrane, made of either cellulose acetate or polyamide, rejects most of the solids creating two streams, one of pure water, product or permeate, and one with dissolved solids, concentrate or reject. Figure 2-3 shows the process of reverse osmosis.

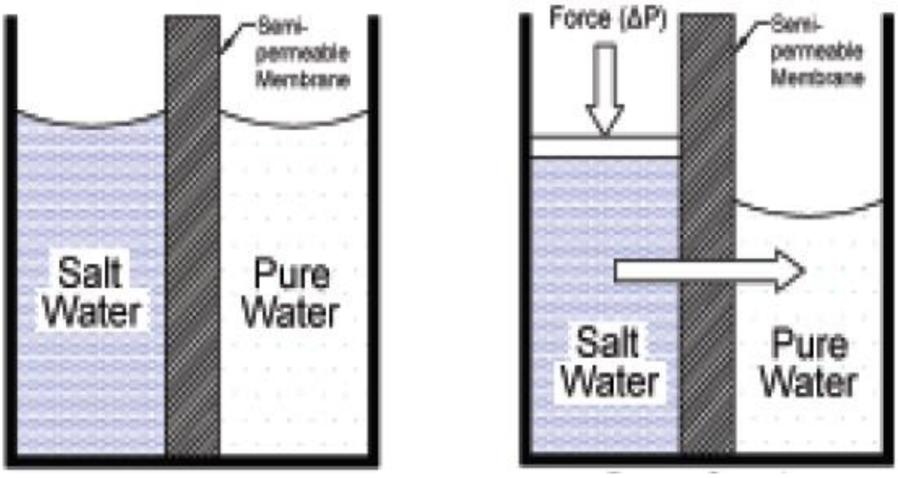

Figure 2-3: Process Model of reverse osmosis (Duranceau, 2012).

2.2.4 Differences between forward osmosis, reverse osmosis and pressure retarded osmosis

The differences between the processes of forward osmosis, pressure retarded osmosis and reversed osmosis can be seen by the water flux and energy consumption of these processes. According to Chou et al. (2012), theoretically, the water flux in an osmosis process can be described as shown in equation (1).

$$J_w = A \text{ x } (\Delta\pi - \Delta P) \text{ (1)}$$

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

$$W = A \text{ x } (\Delta\pi - \Delta P) \text{ x } \Delta P \text{ (2)}$$

where W is the energy consumption or power density, A is the water permeability while $\Delta\pi$ and ΔP is the osmotic and hydrostatic pressure respectively across the semi-permeable membrane. The figure below graphically shows the difference between these 3 processes in terms of water flux.

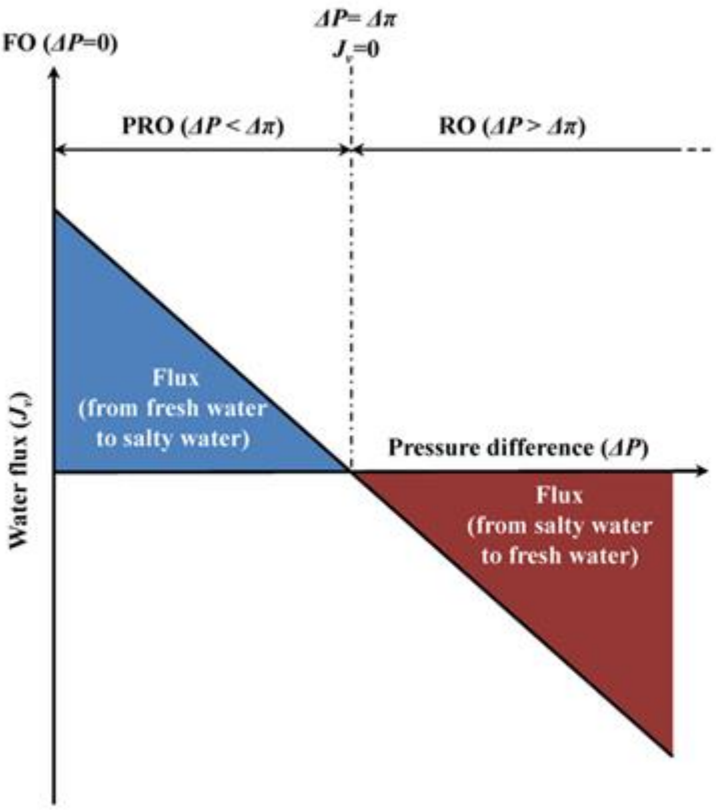

Figure 2-4: Water flux direction of forward osmosis, pressure retarded osmosis and reverse osmosis (Chou et al., 2012).

Based on figure 2-4, it is shown that the process of forward osmosis does not require hydrostatic pressure differential, where ΔP=0, to achieve high water flux value. However, as for pressure retarded osmosis, hydrostatic pressure difference across the semi-permeable membrane is needed for the process to occur. Moreover, this graph shows that the hydrostatic pressure in pressure retarded osmosis has to be lower than the osmotic pressure, $\Delta P < \Delta\pi$, to provide high water flux which is supported by the concept of pressure retarded osmosis (Loeb & Norman, 1975). On the other hand, for reverse osmosis process, hydrostatic pressure is needed to be higher than osmotic pressure for the process to occur. In addition, based on the graph, the higher the hydrostatic pressure, the higher the water flux; which is supported by the concept of reverse osmosis (Afonso et al., 2004). Hence, it can be concluded that the process of forward osmosis does not require any hydrostatic pressure for the process to occur thus making it the process with the least hydrostatic pressure while the process of reverse osmosis requires the highest hydrostatic pressure to work effectively with high water flux. On the other hand, the figure 2-5 graphically shows the difference in between the 3 osmotic processes in terms of energy consumption.

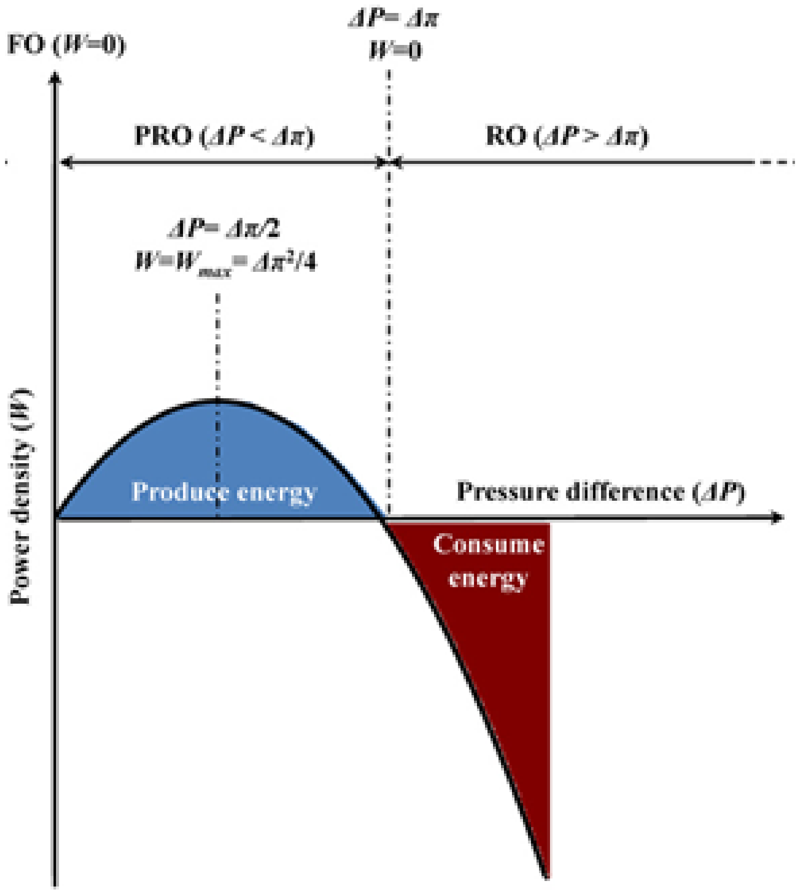

Figure 2-5: Energy consumption/production of forward osmosis, pressure retarded osmosis and reverse osmosis (Chou et al., 2012).

2.2.5 Advantages of forward osmosis

Forward osmosis has a range of potential benefits, mainly due to the low hydraulic pressure required by this osmotically driven process. The potential benefits of forward osmosis as used in various water treatment applications are illustrated in figure 2-6. First, forward osmosis holds the promise of helping achieve low energy consumption due not having to supply external forward osmosis or pressure forward osmosis the process to occur, thereby lowing costs, if suitable draw solutes and their regeneration methods can be economically and technically developed (Elimelech & Philip, 2011). This could be one of the most attractive points of forward osmosis, especially under the stress of energy crises. Furthermore, energy can be harvested from the mixing of freshwater and saline water by pressure retarded osmosis (Lee et al., 1981).

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). Additionally, a variety of contaminants can be effectively rejected via the forward osmosis process (Cartinella et al., 2006). 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).

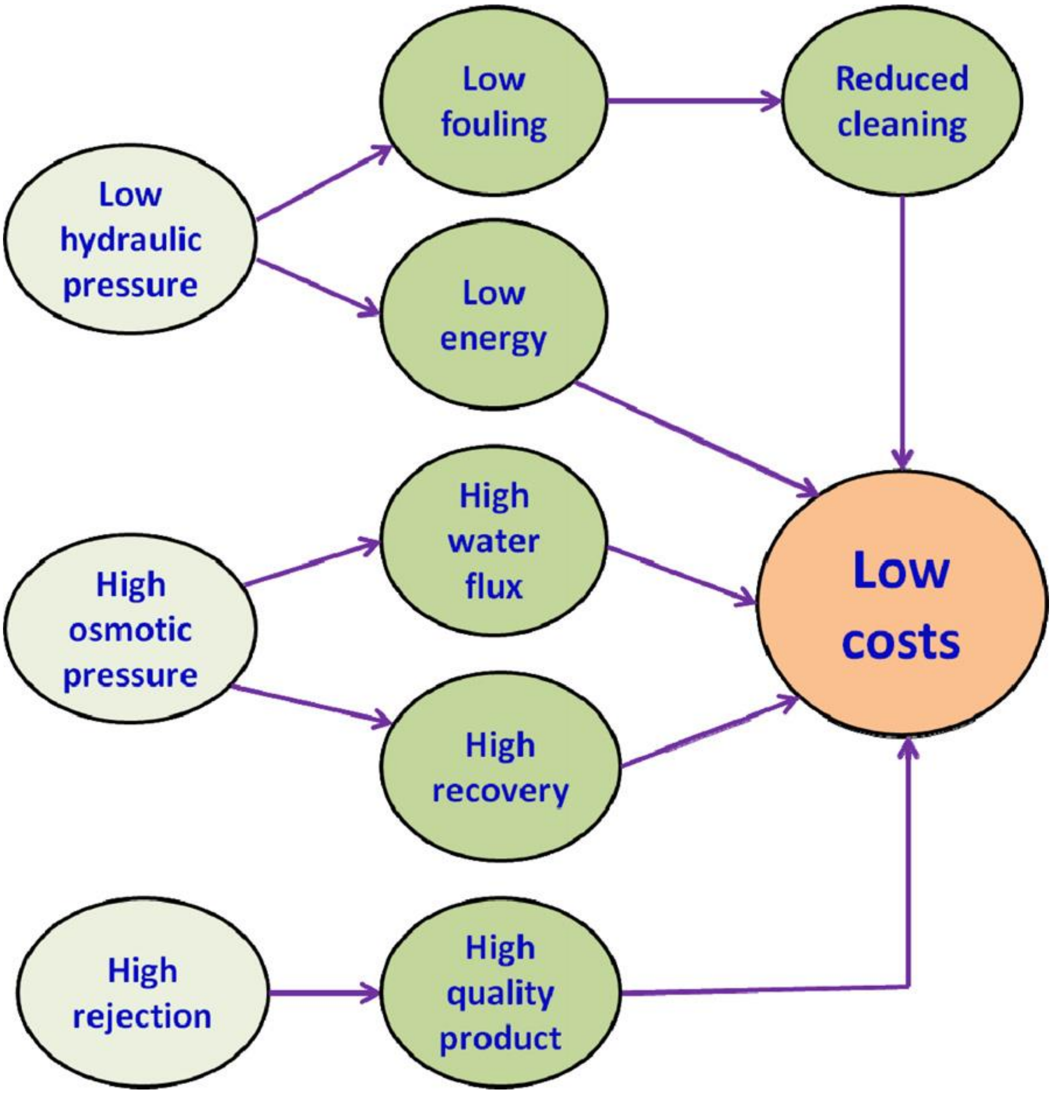

Figure 2-6: Potential benefits of forward osmosis in water treatment (Zhao et al., 2012).

2.3 Concentration polarization of forward osmosis

The water flux in osmotic driven membrane processes is described by equation (1). In this equation, $\Delta\pi$ represents the osmotic pressure difference across the active layer of the membrane. In such processes, the osmotic pressure difference across the active layer is much lower than the bulk osmotic pressure difference, which results in much lower water flux than expected (Mehta & Loeb, 1978). The lower than expected water flux is often attributed to several membranes associated transport phenomena. Specifically, two types of concentration polarization phenomena external concentration polarization and internal concentration polarization can take place in osmotic driven membrane processes. In pressure driven membrane processes, convective permeate flow causes a buildup of solute at the membrane active layer surface and this is referred to as concentration polarization, this phenomenon reduces permeate water flux due to increased osmotic pressure that must be overcome with hydraulic pressure (Song & Elimelech, 1995). Concentration polarization due to water permeation is not limited to pressure driven membrane processes and also occurs during osmotic driven membrane processes, on both the feed and permeate sides of the membrane (Cath et al., 2006).

2.3.1 External concentration polarization

When the feed solution flows on the active layer of the membrane like in reverse osmosis, solutes build up at the active layer which causes a phenomenon that may be called concentrative external concentration polarization and this phenomenon is similar to concentration polarization in pressure driven membrane processes (Cath et al., 2006). Simultaneously, the draw solution in contact with the permeate side of the membrane is being diluted at the permeate membrane interface by the permeating water. This is called dilutive external concentration polarization. Both concentrative and dilutive external concentration polarization phenomena reduce the effective osmotic driving force (Cath et al., 2006). The adverse effect of external concentration polarization on osmotic driven membrane processes can be minimized by increasing flow velocity and turbulence at the membrane surface or by manipulating the water flux (Mulder, 1997). However, because water flux in forward osmosis is already low, the ability to diminish external concentration polarization by reducing flux is limited.

For modeling external concentration polarization phenomena in forward osmosis, equations similar to those developed for concentration polarization of pressure driven membranes can be used (Sablani et al., 2001). Due to the low hydraulic pressure used in forward osmosis, membrane fouling induced by external concentration polarization has milder effects on water flux compared to the effects in pressure driven membrane processes. However, it has been shown that external concentration polarization plays a minor role in osmotic driven membrane processes and is not the main cause for the lower than expected water flux in such processes (McCutcheon et al., 2006).

2.3.2 Internal concentration polarization

When an osmotic pressure gradient is established across a completely rejecting dense symmetric membrane, as depicted in figure 2-7(a), the driving force is the difference in osmotic pressures of the bulk solutions in the absence of external concentration polarization. However, forward osmosis membranes are asymmetric, adding more complexity to the concentration polarization phenomena. When a composite or asymmetric membrane consisting of a dense separating layer and a porous support layer is used in forward osmosis, two phenomena can occur depending on the membrane orientation (Cath et al., 2006). If the porous support layer of an asymmetric membrane faces the feed solution, as in pressure retarded osmosis, a polarized layer is established along the inside of the dense active layer as water and solute propagate the porous layer as shown in figure 2-7(b) (Cath et al., 2006). McCutcheon et al. (2006) referred this condition as concentrative internal concentration polarization, this phenomenon is similar to concentrative external concentration polarization, except that it takes place within the porous layer, and therefore, cannot be minimized by cross flow. In forward osmosis applications for desalination and water treatment, the active layer of the membrane faces the feed solution and the porous support layer faces the draw solution. As water permeates the active layer, the draw solution within the porous substructure becomes diluted. This is referred to as dilutive internal concentration polarization as shown in figure 2-7(c).

Besides that, it can be clearly seen in figure 2-8 that the osmotic pressure difference between the bulk feed and bulk draw solution, $\Delta\pi$ bulk, is higher than the osmotic pressure difference across the membrane, $\Delta\pi_m$, due to external concentration polarization and that the effective osmotic pressure driving force, $\Delta\pi_{eff}$, is even lower due to internal concentration polarization. Furthermore, similar to the operation of heat exchangers, operation of forward osmosis in a counter current flow configuration (feed and draw solution flowing tangential to the membrane but in opposite directions) provides constant $\Delta\pi$ along the membrane module and makes the process more efficient (Loeb & Bloch, 1973).

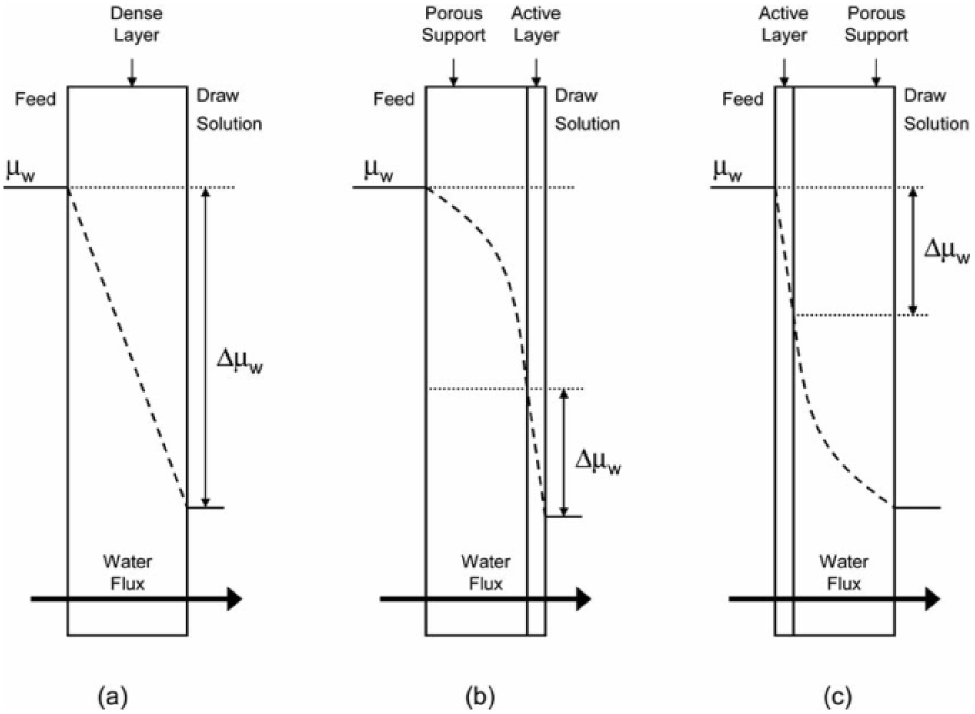

Figure 2-7: Illustration of driving force profiles, expressed as water chemical potential for osmosis through several membrane types and orientations. (a) Asymmetric dense membrane. (b) An asymmetric membrane with the porous support layer facing the feed solution which illustrates concentrative internal polarization. (c) An asymmetric membrane with the dense active layer facing the feed solution which illustrates dilutive internal polarization (McCutcheon et al., 2006).

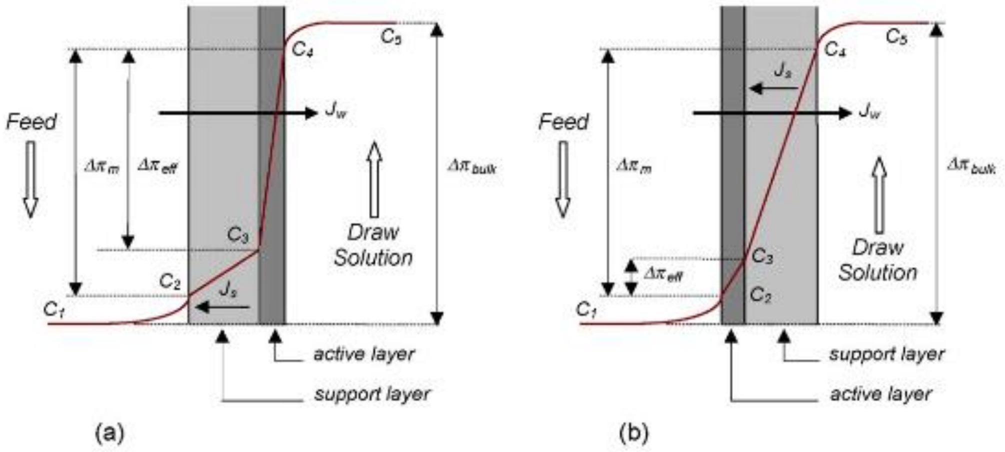

Figure 2-8: (a) Concentrative internal concentration polarization (b) Dilutive concentration polarization (McCutcheon et al., 2006).

2.3.3 Influence of internal concentration polarization

Mehta and Loeb (1978), studied the effect of the porous support layer on internal concentration polarization and the effect of high draw solution concentrations on the overall permeability coefficient of the membrane and the results show that upon swapping the working fluids on the two sides of the membrane, flux sharply declines due to internal concentration polarization. Experimenting with flat sheet and hollow fibre reverse osmosis membrane, Mehta and Loeb (1979), pointed out that membrane permeability is not constant in forward osmosis and pressure retarded osmosis; it declines with increasing osmotic pressure (i.e., increasing concentration) of the draw solution. The decline of membrane permeability was explained by partial drying or osmotic dehydration of the membrane at high osmotic pressures. Such partial drying can be accompanied by pore contraction, known as “osmotic deswelling”, and hence increased resistance to water transport. This is supported by the results from recent studies by Gray et al. (2006), who confirmed that internal concentration polarization is actually the cause of the substantial flux decline.

2.4 Reverse salt diffusion in forward osmosis

Reverse permeation also known as reverse salt diffusion of draw solutes in osmotically driven membrane processes is a direct result of the solute concentration difference across the membrane, which is necessary to generate the driving force for water permeation. This reverse flux of solute reduces the effective osmotic pressure difference across the membrane, and thus the efficiency of forward osmosis systems (Ge et al., 2011). 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 or also known as water. 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 2-9, a schematic of an asymmetric membrane operating with reverse salt flux in forward osmosis mode.

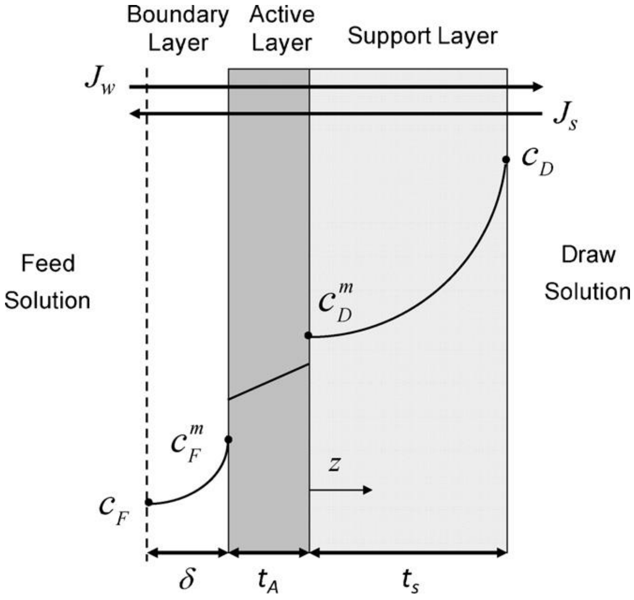

Figure 2-9: Schematic diagram for the process of reverse salt diffusion in forward osmosis (Yong et al., 2012).

The explanation of reverse salt diffusion route is done based on figure 2-9 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, δ. $C_D^m$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).

2.5 *Cellulose triacetate membrane for forward osmosis*

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 such water and water treatment (Nguyen et al., 2013). The early study of forward osmosis membranes employed reverse osmosis membranes of cellulose acetate polymers; which, when applied to forward osmosis, show low permeate water flux since their porous support layer lead to great internal concentration polarization (Nguyen et al., 2013). A forward osmosis membrane should, therefore, comprise a single thin and dense layer without any support layer (Su & Chung, 2011), though the ensuing mechanical weakness may restrict wide applicability. This is further supported by, who stated that a high performance forward osmosis process requires a membrane with high hydrophilic dense active layer for high rejection rate and high water flux, thin porous area and high porosity and also high mechanical strength (Li et al., 2013).

Various studies and research had been done to search for a membrane which suits the process of forward osmosis. Among others is the modification on cellulose acetate membrane such as flat sheet cellulose acetate based membranes that could eliminate internal concentration polarization have been made using double-skinned membranes (Wang et al., 2010); which, however, showed additional resistance to water transport and consequently low water flux. Besides that, other membranes had been used to test their performance in forward osmosis such as Wei et al., (2011), who prepared thin film composite forward osmosis membranes by interfacial polymerization without using nonwoven fabric substrates and Saren et al. (2011), who synthesized polyelectrolyte layer membranes using layer by layer assembly. However, all these attempts have led to higher reverse solute flux than shown by commercial forward membranes.

The current only available commercial forward osmosis membranes are developed by HTI (Hydration Technologies Inc.) using cellulose triacetate as the membrane material (Ong & Chung, 2012). Cellulose triacetate and polyamide based thin film composite membranes are widely used for commercial reverse osmosis processes due to their high hydrophilicity which favours the water transport. However, polyamide based thin film composite reverse membranes usually have a higher flux and rejection than the cellulose triacetate membranes, whereas cellulose triacetate membranes have superior resistance toward chlorine comparing to the polyamide based thin film composite membranes which are weak against chlorine attack (Sagle & Freeman, 2004). Comparing cellulose triacetate with cellulose acetate, cellulose triacetate is not as prone to biodegradation and hydrolysis as cellulose acetate (Ong & Chung, 2012). In addition to all these comparisons, cellulose triacetate possesses the characteristics needed as a forward osmosis membrane such as high hydrophilic dense active layer, thin porous area, high porosity and also high mechanical strength. These unique advantages make cellulose triacetate a good candidate as a forward osmosis membrane material (Ong & Chung, 2012).

2.6 *Humic acid*

Humic acids are very common naturally occurring molecules in terrestrial and aquatic ecosystems. They are extracted from the soil, river, lake sediments, coal, fresh water, waste waters, plants and coral skeletons (Al-Faiyz & Yasair, 2012). Humic acids are complex molecules made up of various structural units of different sizes and lengths link together in a random. Therefore, their structure and physicochemical characteristics are affected by their origins, geographic location, and climate zones (Al-Faiyz & Yasair, 2012).

One particular group of contaminants that is present in water supplies and which has brought about concern in the water industry are humic substances (Lowe & Hossain, 2008). There are three substances which make up humic substances and they are; humin which is completely insoluble, humic acid which is insoluble at a pH of 1 and fulvic acid which is soluble at any pH. Humic acids are suspected to be a result of condensation polymerisation reactions, amino acid sugar interactions, lignin biodegradation, animal and plant decays (Schafer, 2001). However there have also been humic acid concentrations in surface waters that are heavily affected by changes in the weather. High temperatures will induce the decomposition of microorganisms and organic material while heavy rainfall will increase water runoff into rivers and lakes, giving rise to significant seasonal variation in non-temperate environments (Lowe & Hossain, 2008).

Humic acids are categorised under dissolved organic carbon and at concentrations above 5 mg/L have an impact on water colour (Schafer et al., 2000). In addition to that, Malaysia's river water is known to have high concentration of river acid due to various sources of its components (Sim et al., 2006). Though water colour is an important aesthetic property, the necessity for its removal has recently become more significant. Trihalomethane and haloacetic acids are by products of humic acid from conventional water treatment processes, such as chlorination and are known to be carcinogenic and hazardous to human health (Domany et al., 2002). Hence, as a result of that, the removal of humic acid from aqueous solutions is by far very important and has been investigated by a number of researchers (Jones & O'melia, 2001). The application of ultrafiltration and other membrane based techniques such as forward osmosis despite its lack in reliable reference, have shown great potential in treating of humic acid (Lowe & Hossain, 2008).

2.7 *Properties of draw solution in forward osmosis process*

The performance of forward osmosis gravely depends on the characterization and selection of the right and suitable draw solution as it is the main driving force which enables this process to occur (Chekli et al., 2013).

2.7.1 Osmotic pressure

Osmotic pressure is the primary characteristic which is needed for a draw solute and it is required to be higher than that of feed solution for forward osmosis to occur. This is essential due to the fact that the fundamental of this process lies in utilizing the natural osmotic process which depends on osmotic pressure for desalination rather than hydraulic pressure in reverse osmosis (Chekli et al., 2013). Based on the studies done by Phuntsho et al., (2011), high osmotic pressure in the draw solution pratically means the concentration of draw solution is high which thus creates a higher osmotic potential where water from feed solution will be drawn to the draw solution by forward osmosis.

According to Hoff et al. (1887), osmotic pressure can be defined based on the formula derived in equation (3).

$$\pi = n\left(\frac{c}{MW}\right)RT \text{ (3)}$$

Where n is the number of moles of species formed by the dissociation of solutes in the solution, c is the solute concentration in g/L of solution, MW is molecular weight of solute while R is the gas constant which is 0.0821 and T is the absolute temperature of the solution. However, according to Yokozek (2006), this equation is limited to dilute solutions and is usually used for the determination of large MW. For general solutions, the osmotic pressure can also be derived in the concentration dependence osmotic equation (Stigter & Hill, 1959). The virial equation is shown as below.

$$\frac{\pi}{cRT} = 1 + Bc + Cc^2 + Dc^2 \text{ .... (4)}$$

Where B, C and D are the osmotic virial coefficients that can be determined empirically by fitting experimental osmotic pressure data, and generally by determination of B and C is sufficient to reproduce observed data. Based on the above equation, it is clearly shown that the osmotic pressure of any solutions is dependent the solute concentration where it can be concluded that higher concentration of solute brings to higher osmotic pressure (Stigter & Hill, 1959).

2.7.2 Diffusion coefficient

Apart from osmotic pressure, the performance of forward osmosis is also affected by other properties of the draw solution such as diffusion coefficient where the formula is shown below (Hoff et al., 1887).

$$K = t\tau/\varepsilon D_s \ (5)$$

Where K represents the solute resistance to diffusion within the membrane support layer, t,τ, and ε represent the thickness, tortuosity and porosity of the membrane porous support layer respectively while D_s represents the diffusion coefficient of the solute. The value of K is inversely proportional to the function of diffusion coefficient, D_s which shows that the higher the diffusion coefficient of the solute the lower the resistance of solute to the diffusion within the membrane support layer. This also indirectly shows that the solutes will be more readily diffuse through the membrane support layer to lower internal concentration polarization effect (Chekli et al., 2013). Internal concentration polarization is a phenomenon where there is difference in concentration of solute at the transverse boundaries of that layer thus resulting in a reduction of osmosis pressure gradient across the active layer of membrane and a corresponding reduction of water flux (Gray et al., 2006). This is a critical phenomenon as studies done by indentified that internal concentration polarization occurrence is capable of reducing water flux of a forward osmosis process by 80%. (Mehta & Loeb, 1979).

2.7.3 Molecular weight

Molecular weight is another property which needs to be considered during the characterization and selection of draw solution. Small molecular weight solutes produce higher osmotic pressure than larger molecular weight solute for equal mass of draw solution but at the same time, it induces higher reverse draw solute flux than larger molecular weight draw solution (Chekli et al., 2013). This can be explained by the studies done by Ng and Tang (2006) which show that solutes with lower molecular weight usually have higher diffusion coefficient compared to those with larger molecular weight. However, despite so, draw solution with small molecular weight also showed to have higher reverse salt diffusion which could potentially have an adverse impact on the forward osmosis performance especially when high quality product water is required (Wang et al., 2010). On the other hand, solutes with high moleuclar weight have lower diffusion coefficient than those with small molecular weight and is prone to cause more severe internal concentration polarization effects (Achilli et al., 2010). Besides that, a solute with small molecular weight can generate higher osmotic pressure if it has high solubility and therefore can lead to higher water fluxes (Hoff et al., 1887).

2.7.4 Concentration

The draw solution concentration also 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, 2010). However, past research shows that the high increasing of draw solution concentration could also potentially cause internal concentration polarization in the porous support layer which is greater at higher permeate flux resulting in less effective water flux improvement (Tan & Ng, 2010).

2.7.5 Temperature

The efficiency of forward osmosis is also affected by draw solution temperature as osmotic pressure, viscosity and diffusivity are imporoved 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. Similarly, the diffusion coefficient of the draw solution is usually higher at higher temperature which ultimately decreases the value of K which is the solute resistance as shown in the equation (5) and as a result, increases the water flux (Petrotos et al., 1998). 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 Zhou (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.

2.7.6 Recovery of draw solution

One of the biggest challenges faced by forward osmosis process is the recovery, regeneration and recyclingof draw solution after the process of seperation, especially for drinking water production when high quality water is required (Chekli et al., 2013). In order for the process of forward osmosis to compete with other membrane processes, the draw solution reconcentration and recovery should operate at low cost energy. It should also provide high recovery of draw solution while producing high quality product. Thus, right recovery processes need to be selected for specific draw solution to reduce cost and energy (Chekli et al., 2013).

Table 2-1 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 solutios 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^{o}c (McCutcheon et al., 2006). However, the proximity of low grede 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, 2011). Such applications include emergency water supply, diultion of input stream to reverse osmosis desalination plant, dilution of riverse osmosis brine before discharging into the environment, osmotic cleaning of fouled reverse osmosis, production of biofuel from algae and direct irrigation (Chekli et al., 2013).

Table 2-1: Summary of draw solution and the recovery and reconcentration methods (Chekli et al., 2013).

Draw Solution	Reconcentration and Regeneration Methods
Volatile solutes (SO_2)	Heating or air stripping
Alcohol	Distillation
Al_2SO_4	Doped $Ca(OH)_2$
Glucose	Direct application
Glucose and fructose	Direct application
Fructose	Direct application
Glucose/fructose	RO
$MgCl_2$	Direct application NF process
KNO_3 and SO_2	SO_2 is removed through standard means
NH_4HCO_3	Heating-decomposition into NH_3 and CO_2
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
$MgSO_4$ and Na_2SO_4	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

2.8 Past research on performance of draw solution in forward osmosis process

Based on past research done by Achilli et al., (2010), for inorganic salt, both sodium chloride (NaCl) and calcium chloride ($CaCl_2$) recorded the highest water flux in forward osmosis where seawater is used as feed solution at 3.38 and 3.22 x 10^{-6} m/s respectively. However, these two inorganic salts also recorded a very high reading of reverse salt diffusion flux which is 9.1g/m^2h for NaCl and 9.59g/m^2h for $CaCl_2$. On the other hand, the total cost for forward osmosis of NaCl as draw solution and sea water as feed solution is 0.011$/L while for $CaCl_2$, total of 0.029$/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. Same goes to $CaCl_2$ which also has high forward osmosis performance for sea water feed solution with relatively low process cost.

As for fertilizers, based on the research done by Achilli et al. (2010), potassium chloride (KCl) and calcium nitrate ($Ca(NO_3)_2$) recorded the highest water flux reading for seawater feed solution at 3.74 and 2.97 x 10^{-6}m/s respectively. On the other hand, as for reverse salt diffusion flux, KCl recorded a high reading of 15.6g/m^2h whereas $Ca(NO_3)_2$ recorded a low reading of 6.6g/m^2h. Whereas for process cost, the result of the research where seawater is used as feed solution shows that KCl exhibits the figure of 0.042$/L while $Ca(NO_3)_2$ exhibits the figure of 0.029$/L (Achilli et al., 2010). Based on the data, it is shown that KCl has very high performance based on water flux figure which compensates with it's high process cost and also relatively high reverse salt diffusion flux. However, $Ca(NO_3)_2$ shows good performance of water flux with low process cost and also low reverse salt diffusion flux which makes it a very good solute to be used in draw solution for forward osmosis process.

Over the decades, past research shows that organic compounds particularly fructose and glucose solutions have been tested as draw solution in food production applications and also seawater desalination (Petrotos et al., 2010). The past research also shows that glucose and fructose provide high water flux performance for forward osmosis process in seawater desalination and this is due to the fact that they have high osmotic pressure as they are highly soluble (Beaudry & Lampi, 1990). This is also supported by the fact that glucose and fructose are currently the most widely used draw solutions in forward osmosis processes due to their good characteristics (Chekli et al., 2013).

2.9 Recent application of forward osmosis process

2.9.1 Desalination

Along with the development of reverse osmosis, forward osmosis has also been proposed for removing salts from saline water since the 1970s (Kravath & Davis, 1975). However, in early years, most of the studies reported in the form of patents were based on the investigators' ideas, and few matured into operational systems. Recently, 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_2 or SO_2) 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 other methods. Utilizing solar power to produce fresh water from the diluted draw solution after osmotic dilution is among other methods which was proposed by Khaydarov and Khaydarov (2007). Besides that method, Choi et al. (2009) also proposed a method using a pressure assisted forward osmosis process (i.e. using low hydraulic pressure on the feed side) for seawater desalination, yet no final water generation method was suggested. Tan and Ng (2010), investigated seven draw solutes namely, NaCl, KCl, $CaCl_2$, $MgCl_2$, $MgSO_4$, Na_2SO_4 and $C_6H_{12}O_6$ for seawater desalination using a hybrid forward osmosis and nano filtration system. Ling and Chung (2011), used hydrophilic nanoparticles as the draw solutes for desalination and the nano particles could be regenerated by ultra filtration. In addition to those Zhao et al. (2012), also proposed a new method using divalent salts (e.g. Na_2SO_4) as the draw solutes for brackish water desalination because the diluted draw solution could be recovered via nano filtration. Cath et al. (2010), employed forward osmosis as an osmotic dilution process using seawater as the draw solution for impaired water purification in a hybrid forward and reverse osmosis process. Similar forward and reverse osmosis desalination systems were proposed to generate both potable water and the osmotic power of reverse osmosis brine (Bamaga et al., 2011). In these sort of combinations, forward osmosis provides several major benefits, including high quality of drinking water due to the multi barrier protection, reduced reverse osmosis fouling because of the pre treatment by forward osmosis, recovery of osmotic energy of reverse osmosis brine, low energy input and no need for chemical pretreatment. As the matter of fact, the forward osmosis process acts as a pretreatment process or also known as osmotic treatment in the second type of forward osmosis desalination. In order to obtain fresh water, further water recovery methods must be used to desalinate the diluted draw solution (Zhao et al., 2012).

Furthermore, forward osmosis has also been proposed for brine concentration (Votta et al., 1974). Desalination brine has become a critical environmental concern in desalination plants, especially for inland communities, where brine discharge sources are not always available. Tang and Ng (2008), investigated the effects of membrane structure on forward osmosis performance during brine concentration. Besides that, Martinetti et al., (2009), found that high recoveries up to 90% from concentrated reverse osmosis brines could be achieved by forward osmosis.

2.9.2 Wastewater treatment

Compared to seawater, general wastewater has lower osmotic pressure but much higher fouling propensity. Low fouling tendency is one of the most pronounced advantages of forward osmosis. Hence, forward osmosis holds great promise in wastewater treatment. As early as the 1980s, the feasibility of using forward osmosis for industrial wastewater treatment was investigated and from there seawater was suggested as the draw solution because of its low cost and high availability in coastal areas (Votta et al., 1974). Recently, Cath et al. (2009), created a similar idea to produce drinking water using impaired water and saline water sources as the feed and draw solutions in forward osmosis respectively, which brought to some benefits, including multi barrier protection leading to high quality drinking water, low membrane fouling and low costs.

In addition, Cath et al. (2005) investigated forward osmosis in membrane contactors for long term space missions and it is found that forward osmosis has several benefits for space missions, including high wastewater recovery, low energy cost and minimized resupply can be achieved in. Moreover, forward osmosis membrane contactors can also be used to remove natural steroid hormones from wastewater (Cartinella et al., 2006). According to the supplier of the commercial forward osmosis membrane, Hydration Technology Innovations, forward osmosis can be used with many kinds of wastewater such as oil and gas wastewater, industrial and municipal wastewater, nuclear wastewater and landfill leachate (Zhao et al., 2012).

2.9.3 Liquid and food concentration

In the food industry, it is often necessary to remove water from liquid food to increase the stability, improve the shelf life and reduce storage and transportation costs (Petrotos & Lazarides, 2001). Compared with the conventional evaporative concentration techniques, forward osmosis can provide advantages in maintaining the physical properties (e.g. color, taste,aroma and nutrition) of the liquid food without deteriorating its quality (Petrotos & Lazarides, 2001). Therefore, forward osmosis has been widely used to concentrate various water containing foods, including tomato juice, mushrooms, fruit juice, pears, carrots, papayas, potatoes, apricots, strawberries, pineapples and peppers (Ozdemir et al., 2008). In these applications, forward osmosis acts as the osmotic dehydration process to remove water from the liquid food (Zhao et al., 2012).

2.10 Summary

This chapter shows the differences and also 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 characteristic of draw solution which affects and improves the performance of forward osmosis is also discussed alongside with the potential application of forward osmosis in industries in this chapter. In a nutshell, this chapter generally describes the general theory, applications and also parameters of forward osmosis process.

CHAPTER 3

MATERIALS AND METHODS

3.1 Overview

This chapter discusses on how the experiment is being carried out. It includes the chemicals which are needed for the draw solutions and also for the feed solution. Apart from that, this chapter also includes the membrane which is needed by the experiment, known as polyamide coated ultrafiltration membrane. The construction of module for the forward osmosis process is also discussed in this chapter. Lastly, the method for which the data is tabulated and also the way of discussion of results are discussed in this chapter.

3.2 Chemicals

The solutes used to form draw solutions are purchased from various sources namely Fisherci (solid calcium chloride 95% purity, solid sodium chloride 95% purity, solid calcium nitrate 95% purity and liquid fructose 96% purity). These draw solutions will be categorized under inorganic, organic and fertilizers draw solutions. All these chemicals are chosen as the draw solution for the treatment of synthesized river water because according to the data obtained by Achilli et al. (2010), these chemicals show the highest performance in forward osmosis for the treatment of seawater and also blackish water. Besides that, the treatment of seawater and blackish water are the nearest possible connection to be related to the treatment of synthesised river water by forward osmosis.

3.3 Preparation of Membrane

The membrane which was be used in this study is known as polyamide membrane which was coated over ultrafiltration membrane. In order to coat the membrane, two types of polymer solutions were prepared. The first solution prepared was metaphenylenediamin (MPD), where 2% by weight of solid MPD was dissolved into

100ml of distilled water. Following that, trimesoly chloride (TMC) solution was prepared. This solution was prepared by mixing 0.15% by weight of solid TMC into 100ml of hexane solution. After the preparation of these two solutions, ultrafiltration membrane with the width and length of 3.5 inches was cut and soaked into distilled water for 1 day in order to remove the glycerine protective layer blocking the pores of membrane. Following that, the membrane was sandwiched by two frames with smooth side of membrane facing top. MPD solution was then poured adequately to completely cover the top side of the ultrafiltration membrane and left for 30minutes for the solution to diffuse into the pores of membrane. After that, the rough surface of the membrane was dried by using tissue in order to prevent any reactions from occurring at the rough surface and then the membrane was left drying for 2 minutes before immersing it into TMC solution for 30 seconds. The membrane was then dried for 1 day and immersed into distilled water for 2 hours. These steps were repeated for 4 times with each membrane catered for each type of draw solutions. The size of the membrane which was covered by feed and draw solution is 3inches (Low, 2010).

3.4 Preparation of draw solution

Each solute was dissolved in water into 5 same draw solutions with different concentrations of 0.1M, 0.3M, 0.5M, 0.7M and 1.0M (Choong et al., 2012). The volume of draw solution at each concentration was 2L.

3.5 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. The volume of the humic acid solution was 2L.

3.6 Permeation module

The permeation module was constructed by using 3 inch polyvinyl chloride pipes, aluminum supports, 8mm transparent tube with 7mm inner diameter, 16mm transparent tube with 15mm inner diameter, 16 M12 hex bolt, 16 M12 washer, 3mm thick gasket, 2

3 inch polyvinyl chloride flange, 2 perspex transparent sheet and 1 10mm inlet hole with cap. The construction of the module is as shown in figure 3-2. Based on the figure 3-2, the polyvinyl chloride pipes act as the compartment to fill the feed and draw solution at which the one attached with the 16mm transparent pipe is for the draw solution and the one attached with 8mm transparent tube is for the feed solution. The function of the transparent tube is to read the increase of water in the draw solution and the decrease in water in the feed solution. The function of the gasket is to hold the membrane in the middle of the module to enable the process of forward osmosis between the feed solution and the draw solution to take place.

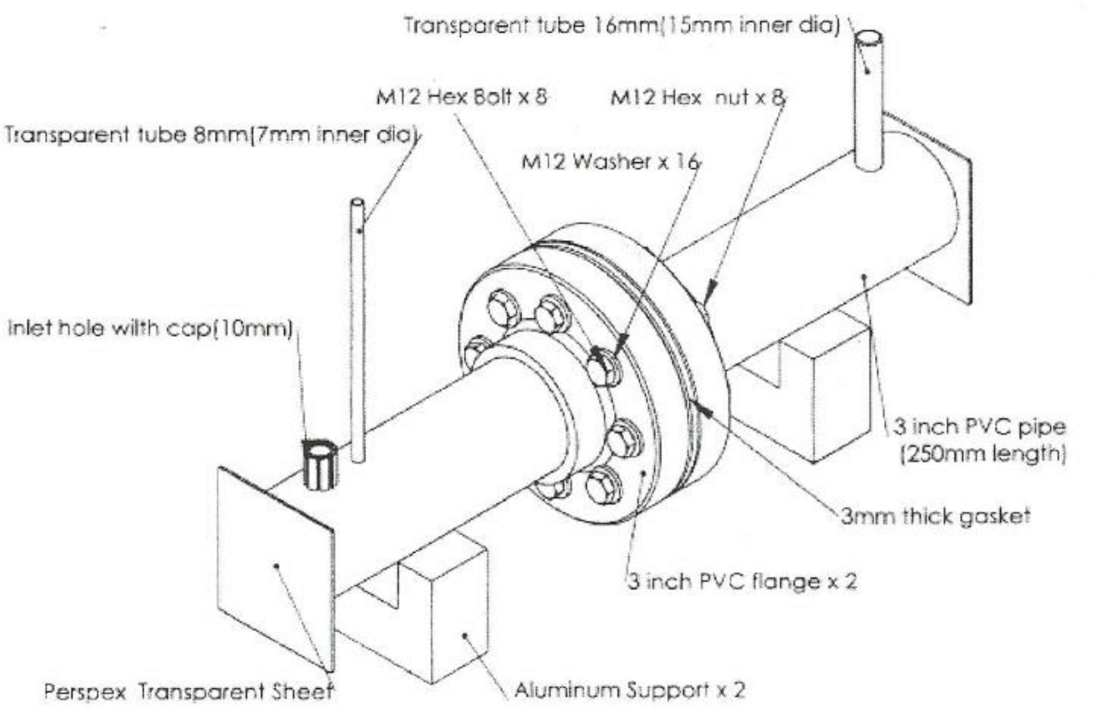

Figure 3-1: Permeation module for forward osmosis (Low, 2010).

3.7 *Methodology*

This forward osmosis experiment was conducted on a lab scale unit. The polyamide membrane was positioned vertically between the 2 compartments, one containing the draw solution and the other containing the feed solution as shown in figure 3-2. The membrane was orientated such that its active layer was facing the draw solution compartment to reduce the internal concentration polarization and thus obtaining the higher flux flow. This experiment was conducted by measuring and recording the conductivity of feed solution before filling 2L of each draw and feed solution into respective compartments and was left untouched until the measuring tube shows an increase of 10mm of solution at the draw solution compartment. The time taken for that to occur was taken down. The time taken was repeated for 5 times, where a total of 50mm and interval of 10 mm of water was diffused into draw solution in order to attain the average time required to process 10mm of water from feed side to draw solution side. Temperature was maintained at room temperature and also pressure is maintained at 1atm. After the increase in 10mm was achieved, the draw solution was taken to UV-vis spectrometer to check to concentration of humic acid which was present in the used draw solution while the final conductivity of feed solution was measured and recorded again to know the amount of reverse salt diffusion. UV-vis spectrometer test was done by taking a pure draw solution as the base and any increase in concentration of humic acid of the used draw solution was recorded whereas conductivity of feed solution was measured by using conductivity meter. Following that, the apparatus was cleaned by using ionized water and the experiment was repeated by using new polyamide coated ultrafiltration membrane for each concentration for each draw solutions. The volume of water permeated was calculated by using equation (6)

$$V = \pi r^2 L \quad (6)$$

Where V is the volume of water permeated, r is the radius of membrane and L is the increase in water level as shown in the tubes of feed solution compartment. After that, the water flux of each draw solution at different concentration was calculated by equation (7).

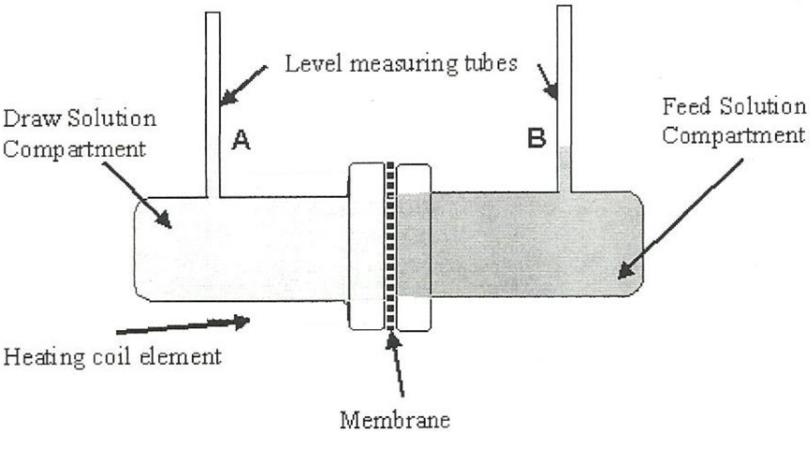

Figure 3-2: Schematic diagram of the laboratory scale forward osmosis setup (Low, 2010)

$$J_w = \frac{\Delta V}{A \Delta t} \text{ (7)}$$

Where ΔV is volume of water which permeates through the membrane, Δt is time taken in minutes and A= effective area of the membrane. The osmotic pressure of each draw solution was also calculated by using Van't Hoff equation as in equation (8).

$$\pi = JMRT \text{ (8)}$$

Where J is Van't Hoff factor, M is molarity, R is gas constant and T is temperature. A graph was constructed to illustrate the water flux of each draw solutions with their respective concentration. Following that, graph of osmotic pressure against molarity was plotted to illustrate the performance of each draw solution in the forward osmosis process where synthesized river water is used as feed solution with respect to osmotic pressure. Then, a graph which shows the concentration of humic acid present in each of the draw solution of different concentration after the process of forward osmosis was tabulated to show the efficiency of forward osmosis process in treating river water. Following that, the regression coefficient and equation of line were constructed to show the validity of the experimental value. Besides that, a table which shows the amount of reverse salt diffusion which was caused by the different type of draw solution at different concentration was tabulated to show the efficiency of draw solution by the discussing on the relation between the concentration of draw solution and type of draw solution. Lastly, the best performing draw solution was chosen based on the results obtained to treat river water by forward osmosis process.

3.8 Summary

This chapter shows the overall chemicals needed, equipment for process and also the method of performing this research to achieve the stated objectives. Thus it is important to follow this chapter strictly during the performance of experiment to obtain the best possible result to enhance the research's reliability in the future.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

This chapter discusses on the results obtained by performing forward osmosis with four different types of draw solutions. In conjunction to that, this chapter compares and discusses on the factors which influences the flux of each draw solution. Besides that, this chapter also discusses and compares on the humic acid rejection for each of the draw solutions. In addition to that, reverse salt diffusion was also discussed for each of the draw solution to determine which salt has the highest reverse salt diffusion which can gravely affect the efficiency of forward osmosis. Based on these discussions, best performing draw solution made up of inorganic, organic and fertilizers was selected as the draw solution for the treatment of synthetic river water.

4.2 Average time taken to reach desired volume

4.2.1 Sodium Chloride

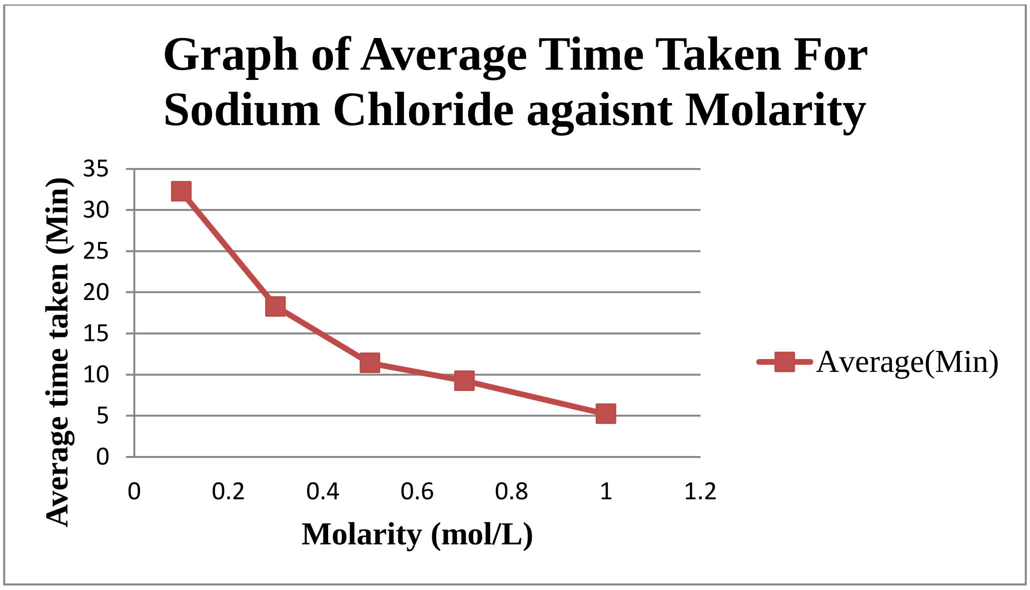

Figure 4-1: Graph of average time taken (Min) for sodium chloride draw solution against molarity

Table 4-1: Table of average time taken for sodium chloride

	Sodium Chloride				
Molarity(mol/L) Interval(min)	0.10	0.30	0.50	0.70	1.00
1st	30.05	19.30	12.20	8.50	5.00
2nd	33.50	18.37	11.14	9.20	5.14
3rd	37.08	18.06	10.19	8.10	5.33
4th	28.28	17.22	11.31	9.30	5.32
5th	30.20	18.30	12.16	9.10	5.31
Average(Min)	32.22	18.25	11.40	9.24	5.22

Based on the results obtained as shown in the figure 4-1 and table 4-1 for sodium chloride, it is found that the time taken for the draw solution to draw 10mm of water from humic acid solution decreases as the molarity of draw solution increases from 0.1mol/L to 1mol/L. This implies that the increase in draw solution concentration quickens the time needed for the water at the feed solution to be drawn to the sodium chloride draw solution. This phenomenon is explained by Ge et al. (2013), who stated that higher concentration of draw solution enable water at feed solution to be pulled at higher rate as compared to lower concentration of draw solution as higher concentration of solute in draw solution increases the solvent concentration gradient between the permeate side and the feed side, thus causing an increase in water potential from feed side to permeate side.

4.2.2 Calcium Nitrate

Table 4-2: Table of average time taken for calcium nitrate

	Calcium Nitrate				
Molarity(mol/L) Interval(min)	0.1	0.3	0.5	0.7	1
1st	26.55	15.2	10.07	8.3	3.1
2nd	27.31	15.33	10.29	7.35	3.34
3rd	25.17	13.32	9.14	8.15	3.07
4th	27.36	16.34	10.12	8.19	3.33
5th	26.39	5.73	11.36	8.14	3.03
Average(min)	26.556	13.184	10.196	8.026	3.174

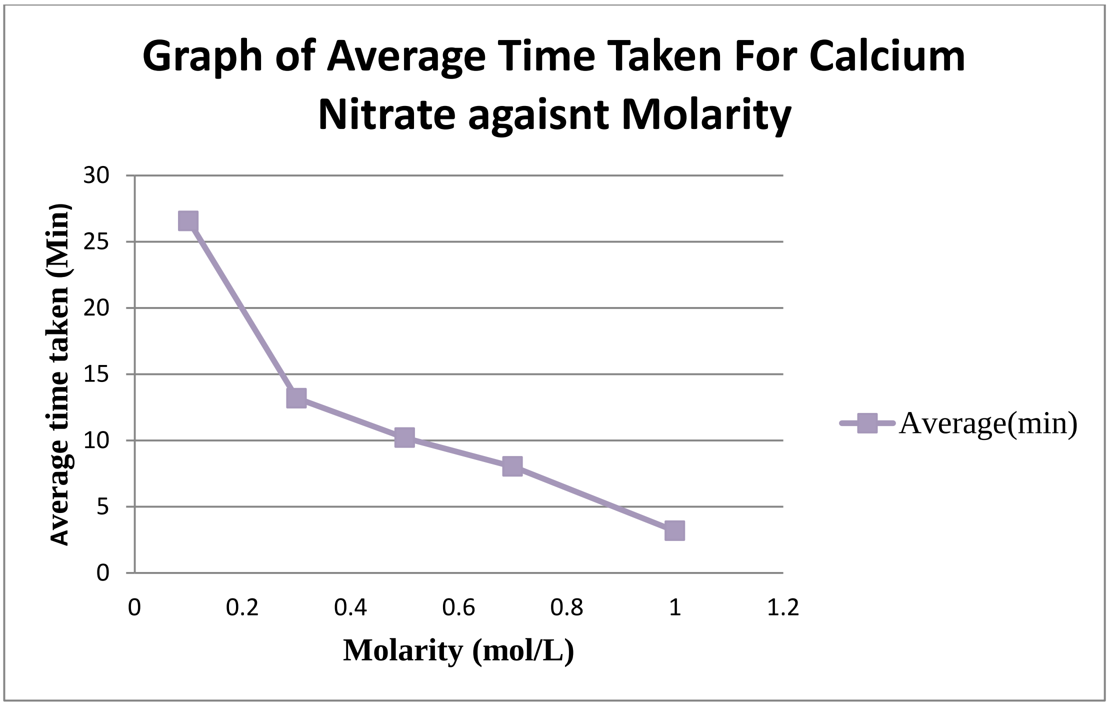

Figure 4-2: Graph of average time taken (Min) for calcium nitrate draw solution against molarity

Similar to sodium chloride draw solution, the graph and table obtained from the experiment with the use of calcium nitrate as draw solution shows that the increase in molarity is directly proportional to the decrease in time needed for water in feed solution to permeate through the membrane in a forward osmosis process into the draw solution. The results obtained show that the fastest time taken to drive water from feed side to permeate side for calcium nitrate draw solution is at the concentration of 1.0mol/L with the time of 3.174 minutes whereas the slowest time is at 0.1mol/L with the time of 26.55 minutes. This phenomenon, is very similar to the trend acquired by using draw solution, thus can be explained by Ge et al. (2013), which states that higher concentration of draw solution will bring to faster permeation of water from feed side to permeate side in forward osmosis process due to higher water potential.

4.2.3 Calcium Chloride

Table 4-3: Table of average time taken for calcium chloride

	Calcium Chloride				
Molarity(mol/L) Interaval(min)	0.1	0.3	0.5	0.7	1
1st	33.08	18.55	12.12	10.12	5.43
2nd	33.08	18.54	12.03	10.23	5.3
3rd	34.28	18.3	12.4	9.27	5.17
4th	32.54	18.01	12.19	12.21	5.39
5th	31.46	19.15	12.24	10.11	6.07
Average	33.288	18.51	12.196	10.388	5.472

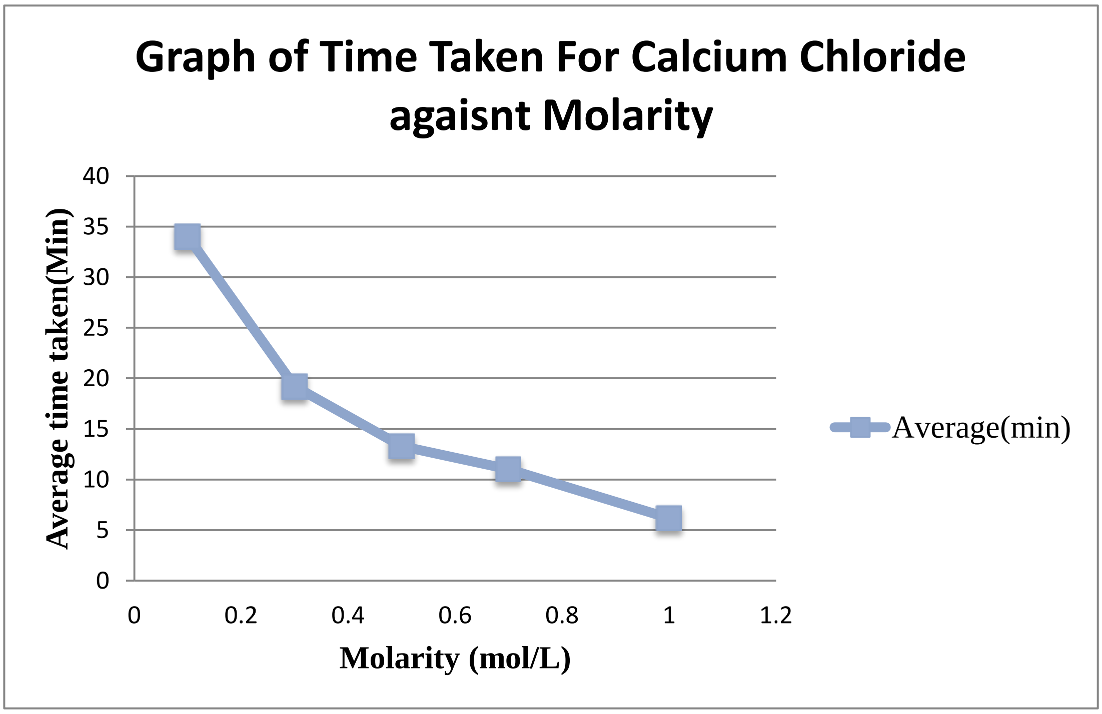

Figure 4-3: Graph of average time taken (Min) for calcium chloride draw solution against molarity

Based on the results obtained where calcium chloride is used as the draw solution, the fastest time acquired for the water in humic acid to be drawn into the draw solution at desired volume is 5.47 minutes at 1.0mol/L. Whereas, the slowest time taken for the water to be drawn to permeate side is 33.28 minutes at 0.1mol/L. This trend of data achieved is similar to with the other draw solutions used and the phenomenon can be explained by the same author, where higher concentration causes higher water potential thus fasten the process of forward osmosis.

4.2.4 Fructose

As for organic salt, fructose which is used as the draw solution, the fastest time acquired for water to be drawn from feed side to permeate side is 6.19 minutes at 1.0mol/L. On the other hand, the slowest time taken is at 0.1mol/L with the time of 34.04 minutes. The trend of time acquired shows that higher concentration leads to faster time needed for water to be drawn to draw solution at a desired volume. Similar to the previous salts trend, this phenomenon is explained by Ge et al. (2013), who states that higher concentration leads to higher water potential from feed side to permeate side in forward osmosis process that ultimately quickens the flow of water.

Table 4-4: Table of average time taken for fructose

	Fructose				
Molarity(mol/L)	0.1	0.3	0.5	0.7	1
Interaval(min)					
1st	34.44	19.34	13.39	11.29	6.29
2nd	34.07	19.11	13.27	12.04	7.26
3rd	33.42	19.07	13.19	12.15	5.25
4th	32.16	19.3	13.37	9.08	6.06
5th	36.15	19.2	13.2	10.54	6.09
Average(min)	34.048	19.204	13.284	11.02	6.19

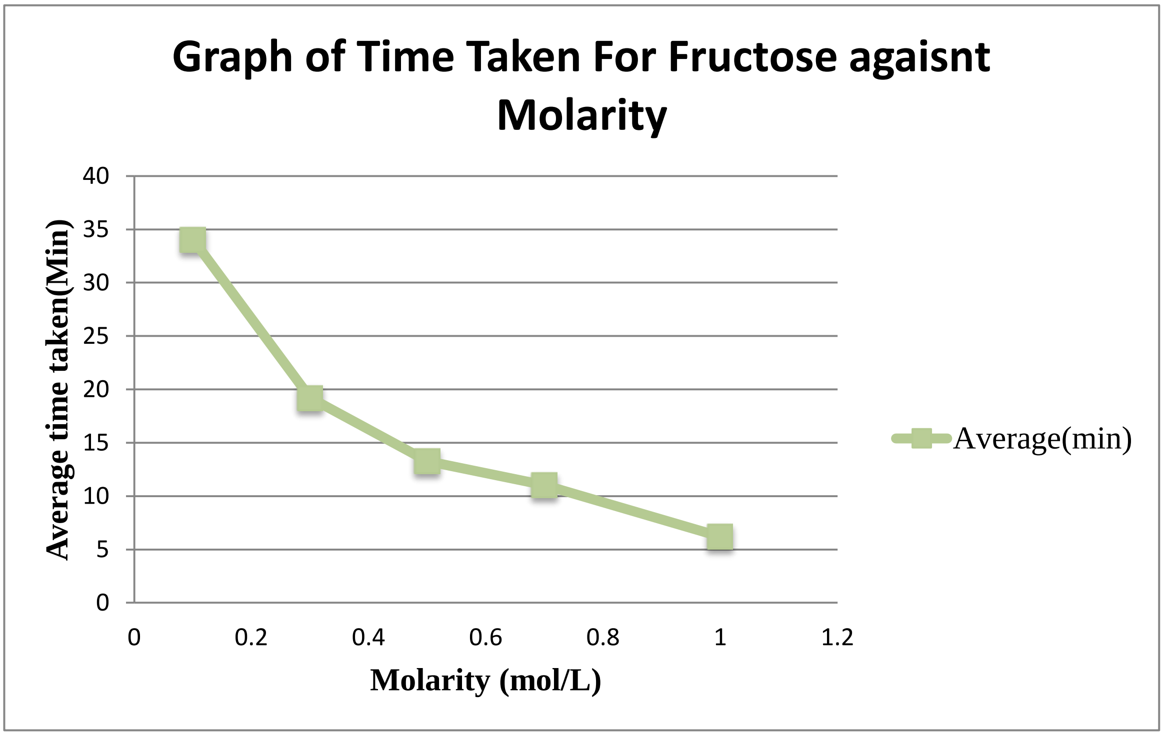

Figure 4-4: Graph of average time taken (Min) for fructose draw solution against molarity

4.3 Discussion and comparison of flux for each draw solutions

4.3.1 Discussion of flux for each draw solutions

By refering to Low (2010), the method of calculating flux is derived in the following formula.

$$J_w = \frac{\Delta V}{A\Delta t}(9)$$

Where ΔV is volume of water which permeates through the membrane, Δt is time taken in minutes and A= effective area of the membrane. This research is done where the only changing variable is Δt with the other two variables remain constant that are, volume of water which permeats through the membrane and also the effective are of the membrane. Thus, the 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 is calculated to determine the efficiency of the draw solutions. The flux value for each draw solution can be seen in. A graph of flux of water across the membrane against the molarity of draw solution is also shown in table 4-5 and figure 4-5.

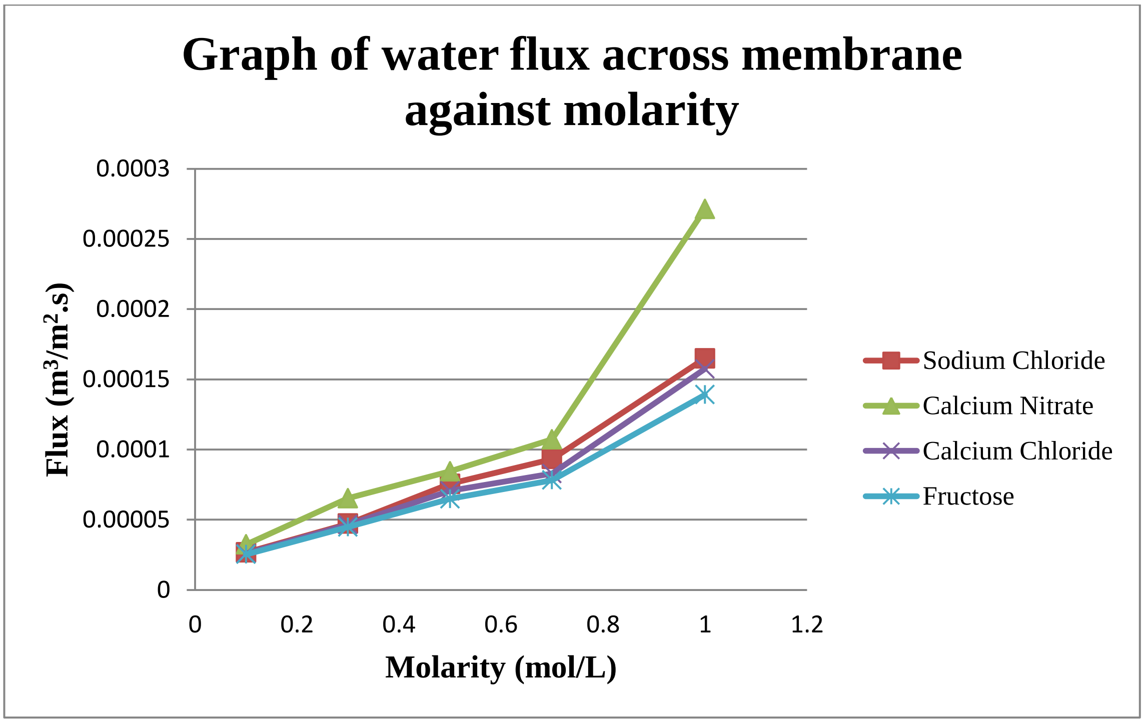

Figure 4-5: Graph of flux across membrane against molarity of draw solution

Table 4-5: Table of flux for each draw solutions

	Flux($m^3/m^2.s$)				
Molarity(mol/L) Draw solution	0.1	0.3	0.5	0.7	1
Sodium Chloride	2.672E-05	4.7E-05	7.6E-05	9.3E-05	0.00016
Calcium Nitrate	3.242E-05	6.5E-05	8.4E-05	0.00011	0.00027
Calcium Chloride	2.586E-05	4.7E-05	7.1E-05	8.3E-05	0.00016
Fructose	2.529E-05	4.5E-05	6.5E-05	7.8E-05	0.00014

Based on the graph as shown in figure 4-5. It can be seen that the trend of flux increases with the increase in molarity of draw solution. This phenomenon can be explained by equation (9) 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 for each draw solutions. Besides that, this phenomenon is further supported by previous studies done by Xu (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. In order to further support this statement, according to Checkli et al. (2013), for forward osmosis process, osmotic pressure is the primary characteristic and the fundamental need in order to utilize natural osmotic process. This is because as stated by Phuntsho et al. (2011), high osmotic pressure in draw solution implies that the concentration of draw solution is high and will ultimately form a high osmotic potential which will enhance the drawing of water from feed solution to draw solution. The osmotic pressure of each draw solution with varied concentration is calculated by using formula (10),

$$\pi = JMRT \quad (10)$$

Where J is the van hoff’s factor, M is the molarity in mol/L, R is the gas constant in L atm/mol K and T is the temperature in Kelvin. The van hoff’s factor is different for inorganic and also organic matter. Van hoff’s factor for each draw solution and also humic acid is shown in table 4-1.Whereas, the osmotic pressure for each draw solution is as shown in figure 4-6.

Table 4-6: Van Hoff's factor for each draw solution.

Draw solution	Dissociation	Van hoff factor
Sodium Chloride	$Na^+ + Cl^-$	2
Calcium Chloride	$Ca^{2+} + 2Cl^-$	3
Calcium Nitrate	$Ca^{2+} + 2NO_3^-$	3
Fructose	-	1
Humic Acid	-	1

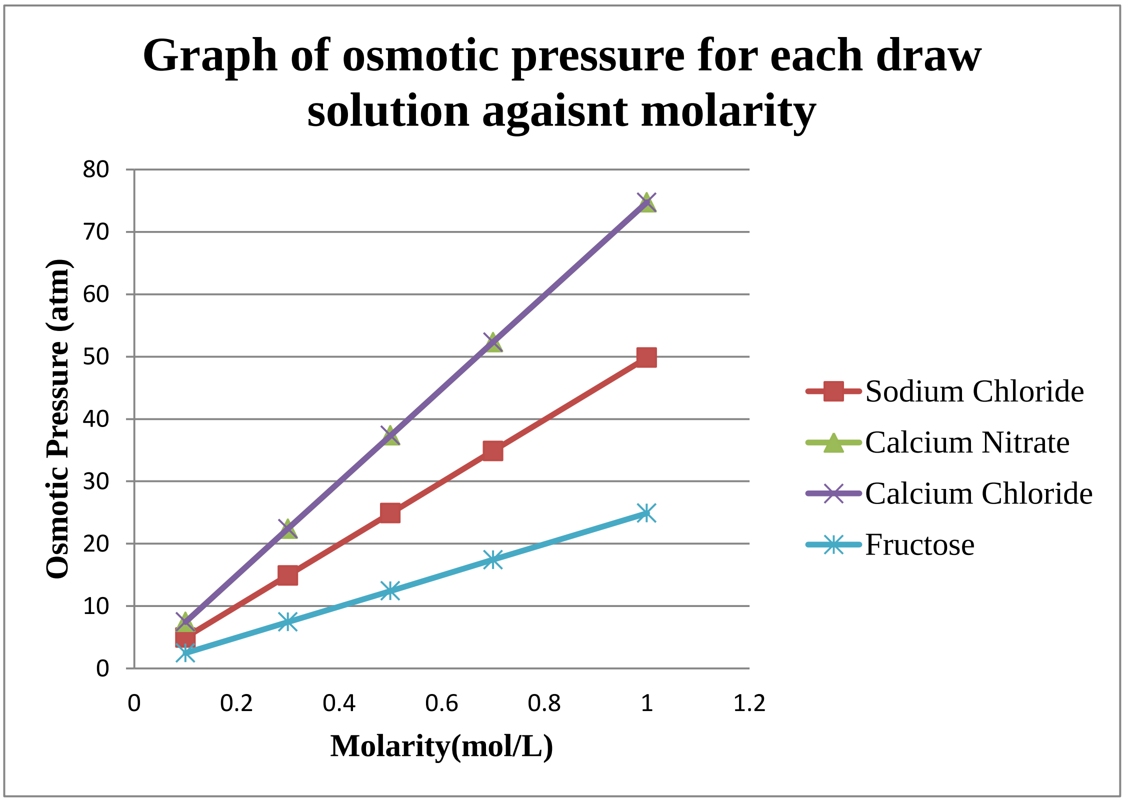

Figure 4-6: Graph of osmotic pressure for each draw solution against molarity

Based on the calculation of osmotic pressure done and the trend of data calculated as shown in figure 4-6, it can be said that the increase in molarity will increase the osmotic pressure of draw solution. Hence, based on all these calculations, it can be said 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.

4.3.2 Comparison of draw solutions' flux

Based on the experimental data tabulated in figure 4-5, it is shown that throughout the experiment, calcium nitrate shows the highest flux of water from feed side to permeate side at 2.7 x 10^-4 $m^3/m^2.s$ at 1mol/L, while the lowest flux is shown by fructose as draw solution at 1.4 x 10^-4 m^3/m^2.s at 1 mol/L. On the other hand, calcium chloride and sodium chloride shows relatively close flux of water from feed side to permeate side, showing 1.57 x 10^-4 m^3/m^2.s and 1.65 x 10 ^-4 m^3/m^2.s respectively at 1mol/L. Fructose recorded the lowest flux achieved because at 1 mol/L it has the lowest osmotic pressure of 24.9atm compared to the other draw solution which causes it to have the lowest driving force to draw water from feed side to the permeate side.

Whereas, calcium nitrate recorded the highest possible flux of water from feed side to permeate because it has the highest osmotic pressure of 74.74atm at 1mol/L that causes it to have the highest driving force to draw water from feed side to permeate side. These two phenomenons can also be explained by Su et al. (2013), who states that forward osmosis depends very much on osmotic gradient where higher osmotic pressure of draw solution will increase the water potential of water flow from feed side to permeate side and this statement is clearly shown in the difference of flux between calcium nitrate and fructose.

However, the flux of calcium chloride is experimented to be lower than calcium nitrate despite having similar osmotic pressure at 1mol/L. This phenomenon is explained by Chekli et al. (2012), who states that high solubility of draw solution induces higher osmotic pressure and therefore can achieve higher water flux. Besides that, according to Wilson and Steward (2013), high solubility is essential in selecting draw solution because high solubility enables the draw solution to dissociate into its respective ions more easily and at a faster rate which will ultimately increase the osmotic pressure of that particular draw solution and lastly induces higher water flux of water from feed side to permeate side in forward osmosis process. The solubility of calcium chloride is of 7.4M which is lower than the solubility of calcium nitrate of 7.9M thus causing calcium chloride to have lower osmotic pressure than calcium nitrate (Chekli et al., 2013). The calculated osmotic pressure of calcium chloride and calcium nitrate shows the similar result as the formula used is theoretical where solubility of solution is ignored and if considered, will provide a different value of osmotic pressure.

For the case of sodium chloride and calcium chloride, even though calcium chloride has higher osmotic pressure than sodium chloride of 74.74atm and 49.83atm respectively, it shows lower flux than sodium chloride. This is condition can be explained by McCutcheon et al. (2006), who state that solutes with heavier molecular weight tend to produce less flux in the presence of internal concentration polarization which can reduce the flux of forward osmosis progressively compared to solutes with lighter molecular weight. The presence of internal concentration polarization as mentioned by Gray et al. (2006) which occurs within the support layer of the membrane and is characterized by differing solute concentrations at the transverse boundaries of that layer result in a decrement osmotic pressure gradient across the active layer of the membrane and a corresponding reduction in water flux across the membrane. Thus, due to calcium chloride having the molecular weight of 111g/mol and sodium chloride having a much lower molecular weight of 58g/mol, the internal concentration polarization occurs until the extend where flux of calcium chloride to be lower than the flux of sodium chloride. This explanation can also be used on the flux of fructose which is the lowest among all the draw solutions as it has a very high molecular weight of 180g/mol which can cause high internal concentration polarization which will reduce the flux of water from feed side to permeate side.

4.3.3 Validity of data obtained

The validity of experimental data can be seen by comparing the flux of each draw solutions as shown in figure 4-5 with the data obtained by previous research. By referring to the research done by Chekli et al. (2012), at draw solution with the highest flux obtained is calcium nitrate with flux of 5.022 x 10^-6 m^3/m^2.s followed by sodium chloride with flux of 2.68 m^3/m^2.s then calcium chloride of 2.64 m^3/m^2.s and lastly fructose at 2.09 m^3/m^2.s at 2mol/L. The trend of flux obtained is similar to the trend of data obtained by Checkli et al. (2012), where the draw solution which provides the highest flux is calcium nitrate followed by sodium chloride and calcium nitrate and the lowest is fructose as draw solution. However, despite having the same trend of flux, the value obtained through experiment at 1mol/L is much higher than the value obtained at 2mol/L by past researches. The reason for this occurrence is explained by the research done by Wei et al. (2011), who stated that polyamide membrane has bigger pores and is usually more porous than cellulose triacetate membrane, thus causing the water particles to be able to pass through polyamide membrane more easily compared to cellulose membrane. Besides that, according to Alsvik and Hag (2013), polyamide membrane has higher water permeability compared to cellulose triacetate membrane, which implies that it is more hydrophilic than cellulose triacetate membrane thus allowing more water to pass through the membrane from feed side to the permeate side hence increasing the flux of the water.

In order to further prove the validity of the data obtained, regression coefficients of every line in the graph of flux against molarity for each draw solutions are calculated. The value of regression coefficients and equations of each line obtained are as shown in table 4-2 and from figure 4-7 to figure 4-10.

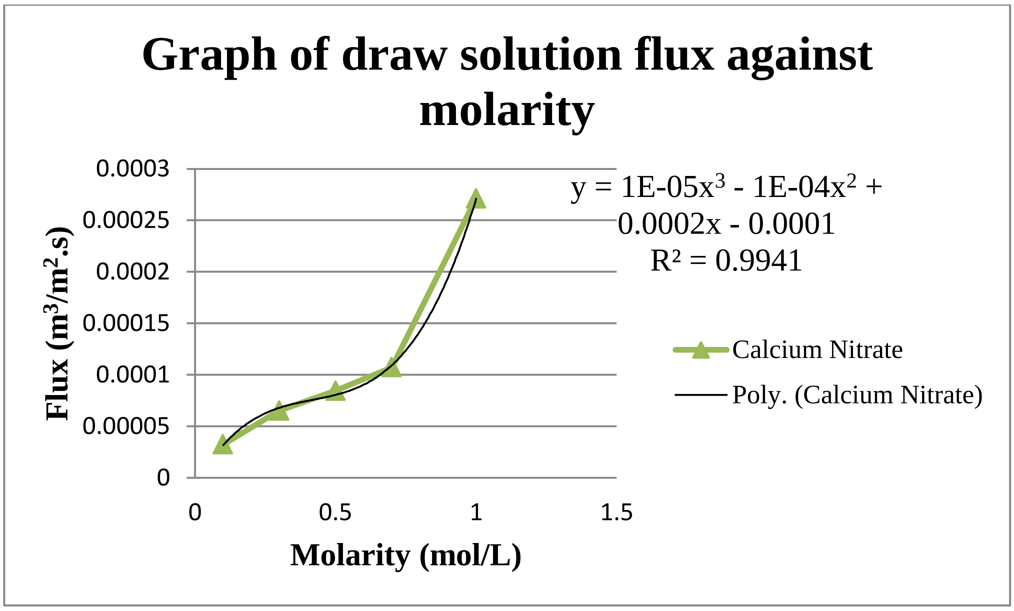

Figure 4-7: Trend line and regression coefficient for calcium nitrate flux

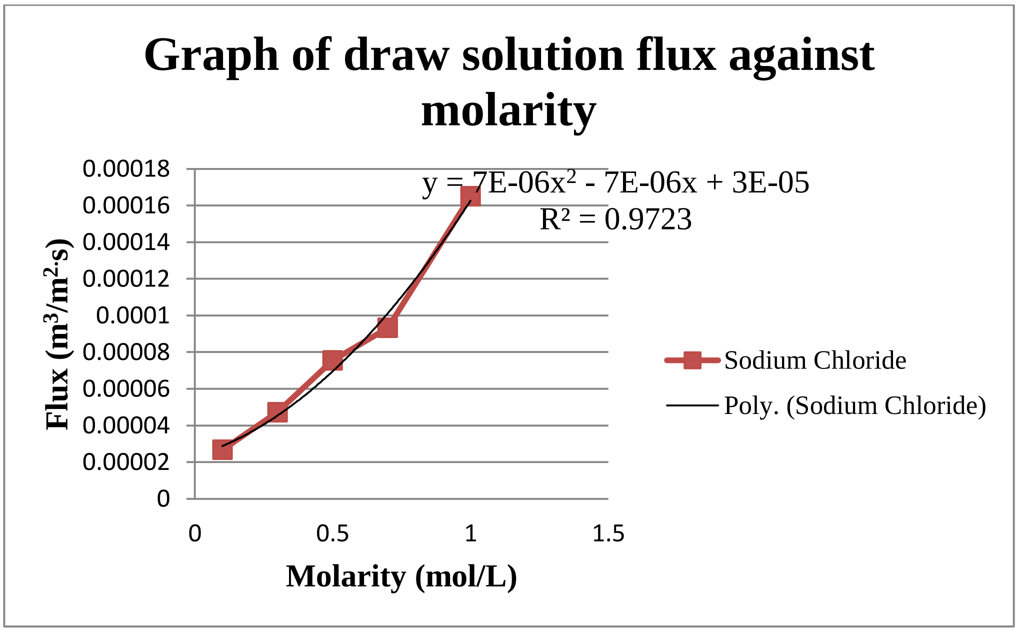

Figure 4-8: Trend line and regression coefficient for sodium chloride flux

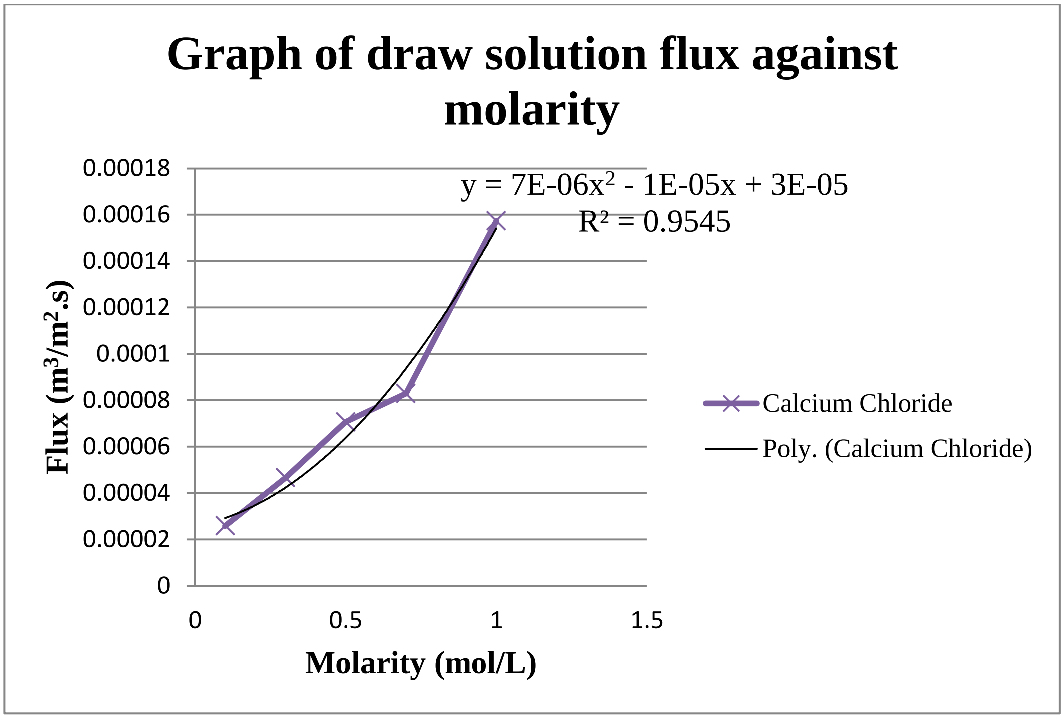

Figure 4-9: Trend line and regression coefficient for calcium chloride flux

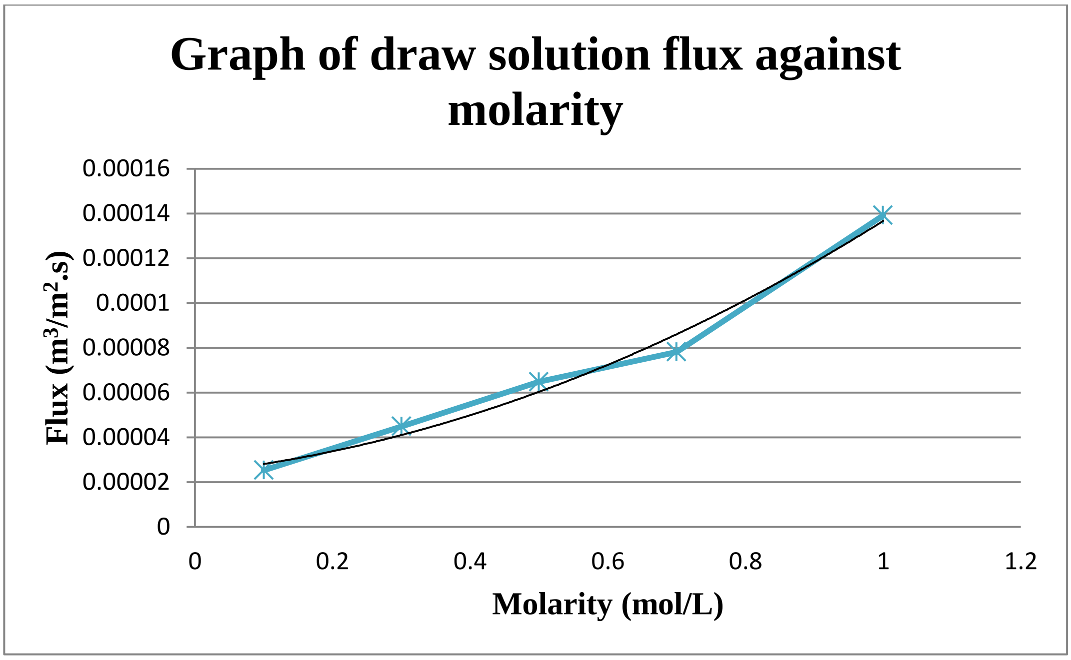

Figure 4-10: Trend line and regression coefficient for fructose flux

Table 4-7: Line equation and regression coefficient for each draw solutions

Draw solution	Line Equation	Regression Coefficient
Calcium Nitrate	$y = 1E\text{-}05x^3 - 1E\text{-}04x^2 + 0.0002x - 0.0001$	0.9941
Sodium Chloride	$y = 7E\text{-}06x^2 – 7E\text{-}06x + 3E\text{-}05$	0.9723
Calcium Chloride	$y = 7E\text{-}06x^2 – 1E\text{-}05x + 3E\text{-}05$	0.9545
Fructose	$y = 5E\text{-}06x^2 – 7E\text{-}06x + 3E\text{-}05$	0.9631

By referring to the regression coefficients of flux for each draw solutions, it is shown that the regression coefficients for each draw solution are higher than 0.95 where it is 0.9941 for calcium nitrate, 0.9723 for sodium chloride, 0.9545 for calcium chloride and 0.9631 for Fructose. Therefore, due to the regression coefficients being higher than 0.95, it is safe to conclude that the data obtained are valid and reliable where the change in water flux from feed side to permeate side can be explained by the change in molarity of draw solutions.

4.4 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.

Based on the data obtained by using UV-vis spectrometer, a series of absorption data based on humic acid concentration in draw solution is obtained, thus, the determination of the concentration of humic acid was done based on the calibration curve. The experimental data obtained is illustrated as shown in table 4-8 and figure 4-11.

Table 4-8: Table of humic acid absorption

Draw solution	Absorption Draw solution concentration (mol/L)				
	0.1	0.3	0.5	0.7	1
Calcium Nitrate	0.052	0.095	0.113	0.124	0.163
Sodium Chloride	0.033	0.083	0.101	0.134	0.152
Calcium Chloride	0.013	0.072	0.106	0.119	0.129
Fructose	0.002	0.024	0.048	0.061	0.083

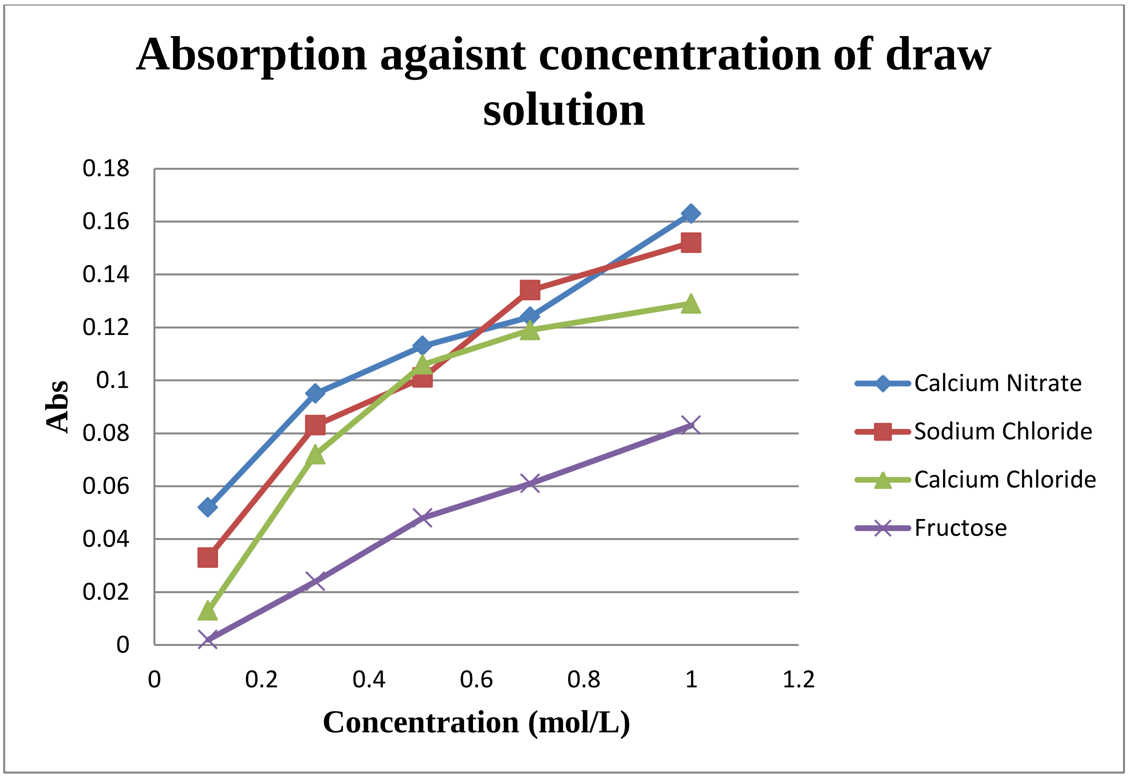

Figure 4-11: Absorption against concentration of draw solution

By referring to figure 4-11, it can be seen that at each concentration, calcium nitrate draw solution holds the highest value of humic acid absorption with the reading of 0.163 at 1mol/L, 0.113 at 0.5mol/L, 0.093 at 0.3mol/L and 0.052 at 0.1mol/L. Whereas, fructose shows the lowest value of humic acid absorption at each concentration intervals with the reading of 0.083 at 1mol/L, 0.061 at 0.7mol/L, 0.048 at 0.5mol/L, 0.024 at 0.3mol/L and 0.002 at 0.1mol/L. Sodium chloride draw solution on the other hand shows an erratic value of absorption with the highest absorption value of 0.134 at 0.7 mol/L which is the highest among all absorption value at that particular draw solution concentration. Similarly, the absorption values of calcium chloride draw solution are the third lowest for almost all concentration except for the concentration at 0.5mol/L where it has a value 0.106 which is higher than the absorption value of sodium chloride draw solution with the value of 0.101. The concentration of humic acid present in the draw solutions are then determined by using the data at of calibration curve and also the data at figure 4.11. The result can be seen at table 4-9 and figure 4-12.

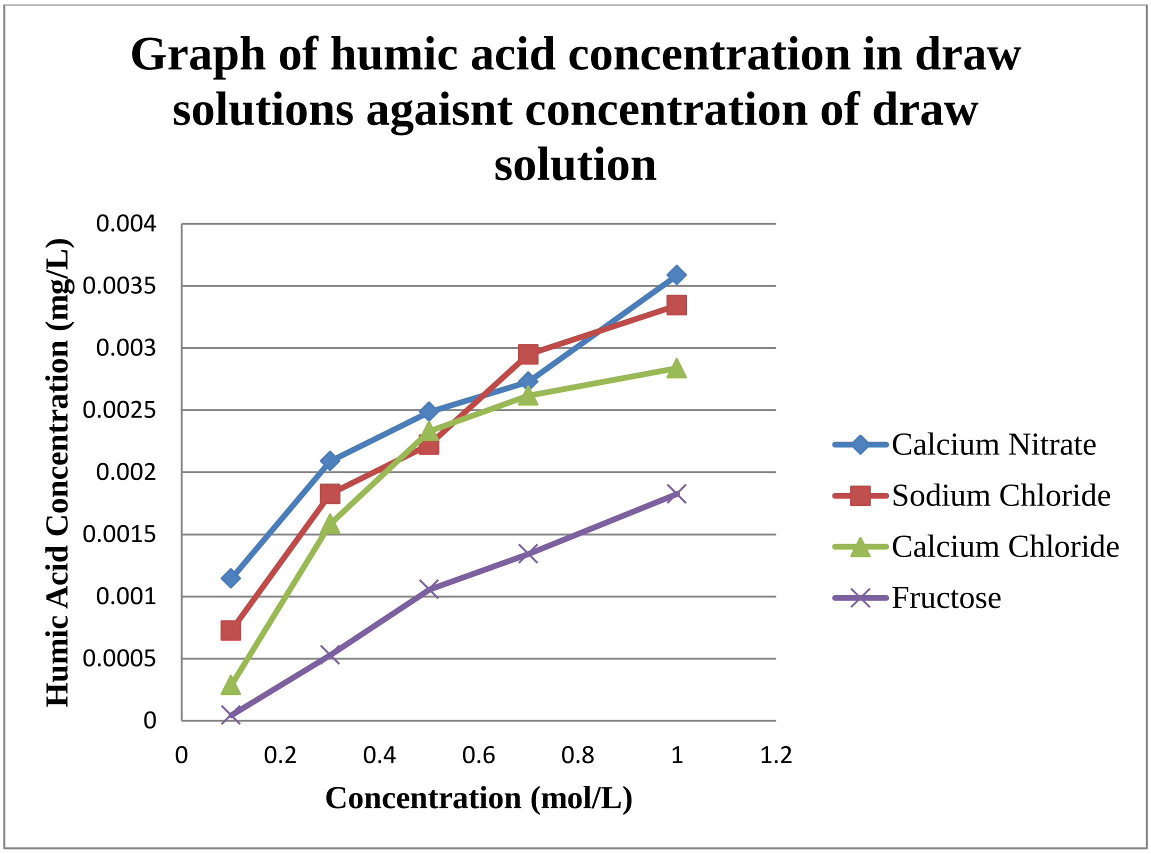

Figure 4-12: Graph of humic acid concentration in draw solutions against concentration of draw solution

Table 4-9: Table of humic acid concentration in permeate side

Draw solution	Humic acid concentration(mg/L) Draw solution concentration (mol/L)				
	0.1	0.3	0.5	0.7	1
Calcium Nitrate	0.001144	0.00209	0.002486	0.002728	0.003586
Sodium Chloride	0.000726	0.001826	0.002222	0.002948	0.003344
Calcium Chloride	0.000286	0.001584	0.002332	0.002618	0.002838
Fructose	0.000044	0.000528	0.001056	0.001342	0.001826

The data generated as shown in figure 4-12 provides the data for humic acid concentration present in each draw solution at different draw solution concentrations. This set of data generated shares the similar trend and explanation to the data obtained in figure 4-12. This set of data is used to calculate the rejection value of humic acid by using formula (11).

$$R = \left(1 - \frac{C_a}{C_b}\right) x\ 100\% \ (11)$$

Where R is the humic acid rejection value in %, C_a is the concentration of humic acid present in draw solution while C_b is the initial humic acid concentration in feed solution. The values of R obtained can be seen in table 4-10 and figure 4-13.

Table 4-10: Table of humic acid rejection

Draw solution	Humic Acid Rejection(%) Draw solution concentration (mol/L)				
	0.1	0.3	0.5	0.7	1
Calcium Nitrate	99.99237333	99.98606667	99.98342667	99.98181333	99.97609333
Sodium Chloride	99.99516	99.98782667	99.98518667	99.98034667	99.97770667
Calcium Chloride	99.99809333	99.98944	99.98445333	99.98254667	99.98108
Fructose	99.99970667	99.99648	99.99296	99.99105333	99.98782667

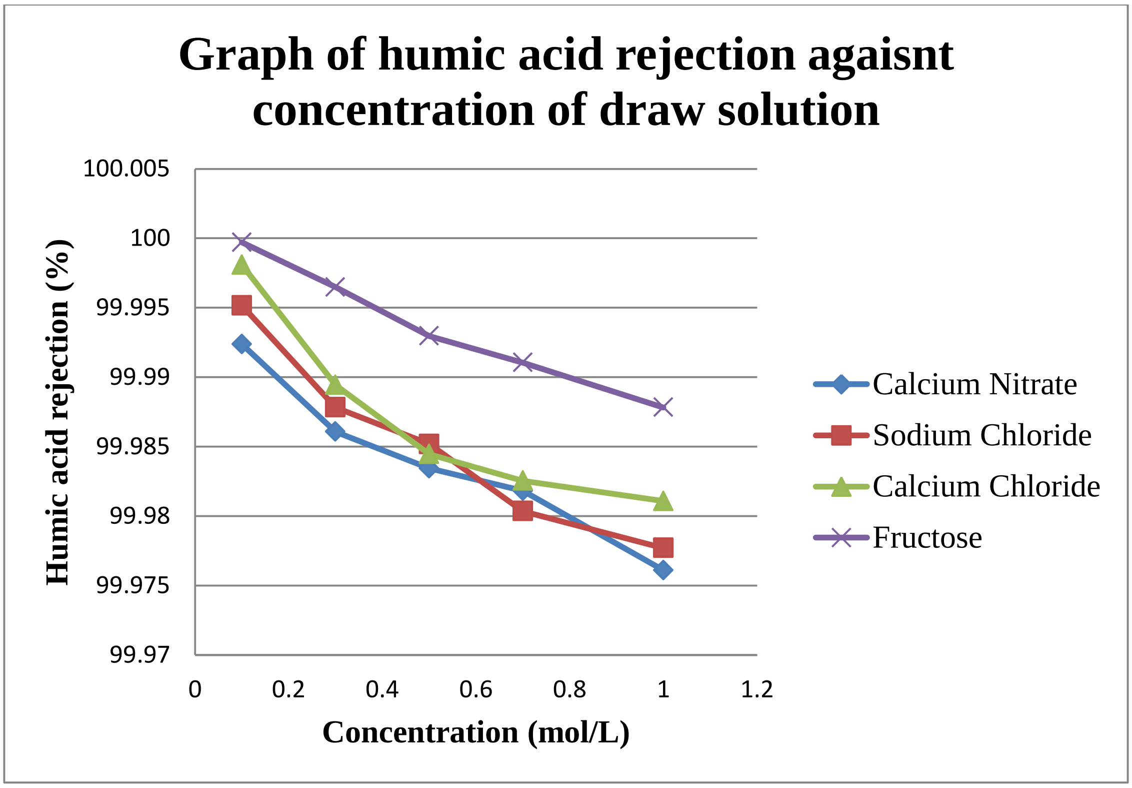

Figure 4-13: Graph of humic acid rejection against concentration of draw solution

Based on the data graph obtained in figure 4-13, the trend where increase in molarity causes an increase in humid acid rejection can be seen. At 0.1mol/L, fructose draw solution is shown to have the highest humic acid rejection of 99.999% at whereas the lowest humid acid rejection is shown by calcium nitrate with the reading of 99.992% followed by sodium chloride at 99.995% and lastly calcium chloride at 99.998%.

However, at the concentration of 1mol/L the humic acid rejection decreases where fructose shows rejection of 99.987%, followed by calcium chloride with the rejection of 99.981%, sodium chloride at 99.977% and lastly calcium nitrate at the rejection of 99.976%. This phenomenon and trend is explained by Xie et al. (2013) who stated that the increase in flux of water from feed side to permeate side caused by draw solution 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 penetrate through the membrane into the draw solution side. Thus, it is reasonable to have fructose with the lowest flux to have the highest rejection as the driving force is not strong enough to pull along a large quantity of humic acid solute to penetrate across the polyamide membrane into the draw solution side. On the other hand, the erratic rejection value of sodium chloride which shows the lowest rejection value at 0.7mol/L can is probably due to the lower scaling factor by sodium ions compared to fructose or calcium ion which eventually enable humic acid to pass through the membrane more easily compared to blockage which might be caused by scaling factors of calcium ions (Checkli et al., 2012).

However, the values of humic acid rejection for each draw solution is very high which implies that the amount humic acid particles that passed through the polyamide membrane is negligible. This occurs because the pore size of polyamide membrane is not large enough to allow the humic acid solutes to pass through the membrane and instead, causing adsorption of humic acid on the membrane surface to occur due to the structure of the polyamide membrane (Molinari, Argurio, & Romeo, 2001). Besides that, according to Gu et al. (2013), polyamide membrane is usually more hydrophilic with contact angle of approximately 45^o and is negatively charged with zeta potential of approximately 10mV, thus enable it to pull more water and increase water flux from feed side to permeate side instead of humic acid which at the very end, results in a big rejection of humic acid solutes.

4.5 *Reverse salt diffusion*

Table 4-11: Table of conductivity for sodium chloride draw solution feed side

	Conductivity (μS/m)		
Sodium Chloride(mol/L)	Initial	Final	Change
0.1	81.23	300.14	218.91
0.3	81.23	320.31	239.08
0.5	81.24	333.25	252.01
0.7	81.22	345.83	264.61
1	81.25	367.45	286.2

Table 4-12: Table of conductivity for calcium nitrate draw solution feed side

	Conductivity (μS/m)		
Calcium Nitrate (mol/L)	Initial	Final	Change
0.1	83.45	100.42	16.97
0.3	83.41	110.33	26.92
0.5	83.45	131.25	47.8
0.7	83.44	155.66	72.22
1	84.25	167.88	83.63

Based on the conductivity of feed side for draw solutions obtained, it can be seen that the change in conductivity after and before process of forward osmosis occurs proportionally to the concentration of draw solution which also means reverse salt diffusion increases as concentration of draw solution increases. This phenomenon can be explained by Checkli et al. (2012), who states 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. The highest recorded reverse salt diffusion is achieved by sodium chloride at the reading of 286.2 μS/m at 1.0mol/L compared to calcium nitrate at 83.63 μS/m at 1.0mol/L. This condition occurs similarly to the forward osmosis research on brackish water by Achilli et al. (2010), who found out that the reverse flux for sodium chloride is much higher with the value of 9.1 $g/m^2.h$ at 1.0mol/L compared to calcium nitrate at 6.6 $g/m^2.h$ at 1.0mol/L. The occurrence of this phenomenon is explained by Checkli et al. (2012), who states that solutes with lower molecular weight, for this case being sodium chloride, usually have higher salt diffusion coefficient as it can pass through the pores of the membrane more easily as compared to the solutes with larger molecular weight, for this case, calcium nitrate.

4.6 Selection and characterisation of best draw solution

Based on the discussions on the results obtained, it can be concluded that calcium nitrate is the best draw solution to be used in the forward osmosis process where humic acid is the feed solution. This is because it provides the highest flux value compared to calcium chloride, sodium chloride and fructose. The comparison of humic acid rejection value can be neglected even though calcium nitrate showing the lowest humic acid rejection value which is not ideal for a forward osmosis process because the despite showing the least humic acid rejection value, the rejection value is still very high at approximately 100%. Moreover, the in terms of reverse salt diffusion, as compared to sodium chloride, calcium nitrate shows lesser reverse salt diffusion value which can reduce the adverse impact on forward osmosis performance, especially when high quality product water is required. Besides that, in order to characterize the best draw solution, the draw solution has to be at high concentration as high concentration provides larger water potential thus increasing water flux compared to draw solution at lower concentration. However, higher concentration of draw solution will also cause higher reverse salt diffusion which can cause adverse effect to gaining high quality water through forward osmosis process. The osmotic potential also plays a large role in characterizing the draw solution where higher osmotic pressure will provide larger water potential, therefore, the larger the difference in between the osmotic pressure of draw solution and the osmotic pressure of feed solution, the larger and higher is the flux of water from feed side to permeate side. In terms of draw solution category, which are fertilizers, inorganic and organic draw solution, it is found that fertilizers provide the highest water flux compared to inorganic salts and organic salts. Despite so, based on this research, sodium chloride which is an inorganic salt, provides promising flux compared to calcium chloride and also a promising water rejection value which is approximately 100%. However, the high reverse salt diffusion of sodium chloride draw solution caused it to be least ideal of a choice to be fertilizers as high salt diffusion can cause adverse effects onto forward osmosis process. Organic salts at this case, is the least efficient draw solution as it gives very low flux even at high concentration due to its low osmotic pressure. Thus, despite providing high humic acid rejection value, it is not ideal or efficient to choose fructose as the draw solution due to its low water flux value. Based on everything which was discussed, it can be concluded that calcium nitrate at is the best performing draw solution as it provides highest flux in all concentration and also high reverse salt diffusion at each concentration compared to other draw solution. Besides that, it has much lower reverse salt diffusion value as compared to sodium chloride which will reduce any adverse effect on obtaining high quality water in forward osmosis process. In addition to that, based on treating 2L of synthetic river water, 0.7mol/L of calcium nitrate should be characterized as this concentration provides high flux but reasonable amount of reverse salt diffusion compared to 1.0mol/L of calcium nitrate which provides high flux but at the same time, very high reverse salt diffusion.

4.7 Chapter summary

This chapter discusses on the relationship of flux, humic acid rejection and reverse salt diffusion with concentration of draw solution. This chapter also discusses on the reasoning on the type of trend obtained through the experiment. Besides, this chapter also compares the flux, humic acid rejection and also reverse salt diffusion data obtained between the draw solutions in order to select the best performing draw solution which can be used to treat river water. Moreover, this chapter also shows the validity of data obtained by using regression coefficient and also compares the data obtained by this research and also the data obtained by past researches.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the experimental data obtained and the discussions of the data, it can be concluded that every objectives of this research was reached. Firstly, the objective to obtain the water flux of each draw solution was obtained as the experiment was successful where every single flux for each draw solution at 5 different concentrations was obtained. Besides that, the objective of obtaining final concentration of humic acid in the draw solution or also known as humic acid rejection was achieved as the humic acid concentration was determined by UV-Vis spectrometer and the results were discussed where high rejection values were found. In addition to that, by using conductivity meter, the reverse salt diffusion for sodium chloride and calcium nitrate was determined and discussed where calcium nitrate is shown to have lower salt diffusion than sodium chloride even though the reverse salt diffusion increases with concentration thus achieving the third objective which is to determine the reverse salt diffusion of different draw solution. Lastly, by discussing the experimental data obtained and comparing it with previous research, 0.7mol/L of calcium nitrate was found to be the best performing draw solution which can be used to treat 2L of river water by forward osmosis process. Therefore, last objective of obtaining the best performing draw solution in treating river water was achieved. Thus, in conclusion, this research proved that fertilizers can provide high flux with high humic acid rejection and relatively low reverse salt diffusion compared to organic or inorganic salt in forward osmosis for the treatment of river water. Ultimately, this research can assist any future research with regards to forward osmosis in the treatment of river water as the selection of best draw solution could be made easier as compared to the situation before this research was done. Besides that, conventional forward osmosis process can also consider fertilizers as the draw solution in treating river water to provide clean water with minimum energy and a short amount of time which is very beneficial in to society and also the field of forward osmosis.

5.2 Recommendation

In order to improve the experimental result, it is recommended that the size of the module is decreased to enable repetition of experiment as smaller size module requires lesser amount of chemicals to be made into draw solution. Drainage system should also be built in the module to ease the process of withdrawing the draw and feed solution after the experiment. In addition, the measuring tube of the module is recommended to be built at the same size to ease the decrease and increase in water volume in feed solution and draw solution side respectively. Besides that, it is also recommended that more types of fertilizers, inorganic salts and also organic salts to be tested and compared in the forward osmosis of treating river water to indentify better draw solutions and also advantages and disadvantages of using these draw solutions. Moreover, it is also recommended that cellulose triacetate membrane is used together with polyamide membrane in order to compare which membrane would be the better performing membrane in forward osmosis process.

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APPENDICES

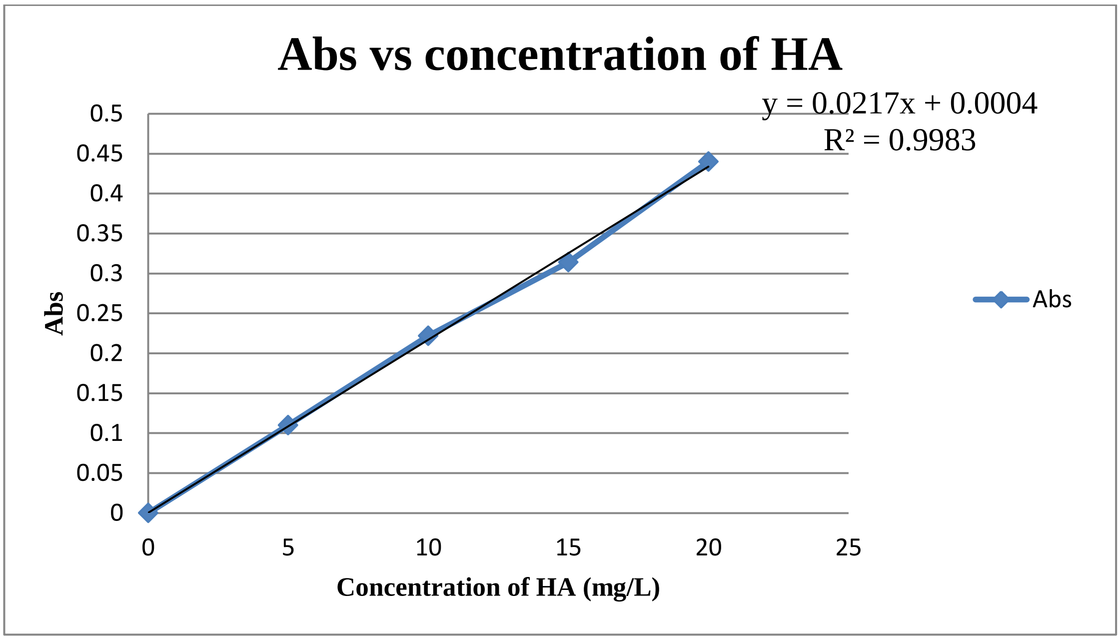

Figure: Calibration curve for absorption against concentration for humic acid