SYNTHESIS AND CHARACTERIZATION OF POLYAMIDE (PA) FORWARD OSMOSIS MEMBRANE

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

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2015

ABSTRACT

This paper presents the synthesis and characterization of polyamide forward osmosis membrane. Forward osmosis (FO) is a process where the osmotic pressure difference occurs between two different concentration solutions is equalized by the transport of water through the semi permeable membrane from less concentrated region to a higher concentrated region. Forward osmosis can be used to solve the problem of yellowish water that is delivered to consumer. In this study, polyamide forward osmosis membrane was produced through interfacial polymerization by using m-phenylenediamene (2% wt) and trimesosyl chloride (0.15% wt) as active monomer. Humic acid was used as the feed solution and NaCl (0.5M, 1.0M, 1.5M, 2.0M and 2.5 M) as the draw solution. The weight of the humic acid was recorded for every 10 minutes to calculate it water flux. Humic acid and draw solution were measured using conductivity and UV-Vis to record it conductivity and absorption value. When the concentration of draw solution is 0.5 M, the water flux is 1.030×10^{-4} m^3/ m^2min while when the draw solution concentration is 2.5 M the water flux is 1.390×10^{-4} m^3/ m^2min.Humic acid rejection is 97.1 which were highest when the draw solution is 2.5M. When concentration of draw solution increases the water flux also increase. This increase is contributed by the increasing osmotic pressure. FO can be used in wastewater treatment, control drug release and food processing.

ABSTRAK

Kertas kerja ini membentangkan sintesis dan pencirian membran osmosis poliamida ke hadapan. Osmosis Hadapan adalah satu proses di mana perbezaan tekanan osmosis berlaku antara dua penyelesaian yang berbeza kepekatan menyamakan kedudukan oleh pengangkutan air melalui membran separa telap dari kawasan kurang pekat ke kawasan yang lebih tinggi pekat. Osmosis ke hadapan boleh digunakan untuk menyelesaikan masalah air kekuningan yang dihantar kepada pengguna . Dalam kajian ini, membran osmosis poliamida hadapan telah dihasilkan melalui pempolimeran antara muka dengan menggunakan m - phenylenediamene (2% berat) dan trimesosyl klorida (0.15 % berat) sebagai monomer aktif . Asid humik telah digunakan sebagai penyelesaian suapan dan NaCl (0.5m , 1.0M , 1.5M , 2.0m dan 2.5 M) sebagai larutan penarik. Berat asid humik dicatatkan untuk setiap 10 minit untuk mengira fluks air. Asid humik dan larutan penarik diukur menggunakan konduksi meter dan UV-Vis untuk mengetahui kekonduksian dan penolakan asid humik. Apabila kepekatan larutan penarik 0.5 M digunakan , fluks air adalah 1,030 × 10^{-4} m^3/m^2min manakala apabila larutan penarik 2.5 M digunakan fluks air adalah 1.390 × 10^{-4} m^3/m^2min^{-1}. Penolakan humic asid adalah 97.1 yang adalah paling tinggi apabila penyelesaian cabutan adalah 2.5M . Apabila kepekatan larutan penarik meningkat, fluks air juga meningkat. Peningkatan ini disumbangkan oleh tekanan osmosis yang semakin meningkat. FO boleh digunakan dalam rawatan air sisa, kawalan pelepasan dadah dan pemprosesan makanan.

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LIST OF ABBREVIATIONS

C_p	Draw Solution absorption
C_F	Feed Solution absorption
J_w	Water Flux
R	Rejection
τ	Tortuosity
t	Thickness
ε	Porosity
D_s	Diffusion coefficient
n	number of moles of solute
C	Solute molar concentration
R	Gas constant
MW	Molecular weight
T	Absolute temperature
K	Solute resistance

LIST OF ABBREVIATIONS

A	Effective area of membranes
AFM	Atomic Force Microscopy
CP	Concentration Polarization
CTA	Cellulose Triacetate
DS	Draw Solution
ECP	External Concentration Polarization
FESEM	Field Emission Scanning Electron Microscopy
FS	Feed Solution
FO	Forward Osmosis
FO-mode	Forward Osmosis Mode
ICP	Internal Concentration Polarization
LMH	Flux Rate
MNP	Magnetic Nanoparticles
MPD	M-phenylenediamine
PA	Polyamide
PRO-mode	Pressure-retarded osmosis mode (PRO-mode)
RO	Reverse Osmosis
TMC	Trimesoyl chloride

1 INTRODUCTION

1.1 Background

Forward osmosis is a process where the osmotic pressure difference occurs between two different concentration solutions is equalized by the transport of water through the semipermeable membrane from less concentrated region to a higher concentrated region (Liu *et al.*, 2008). Since 1995, NASA had been doing the research on forward osmosis for the use in water treatment system. Forward osmosis can be used to help to minimize the membrane fouling that occurs in reverse osmosis for the water treatment (Kamiya *et al.*, 2013). The efficiency of forward osmosis is affected by the draw solution properties, membrane properties, feed solution properties, and operating condition (Phuntsho *et al.*, 2013). Forward osmosis is environmental friendly and it has low energy demand compared to the reverse osmosis that is harmful to environment and need high energy expenditure. Unlike the reverse osmosis, forward osmosis works based on the osmotic pressure where the draw solution must present to enable this process to occur (Liu *et al.*, 2008). Draw solution is important as it work as the driving force in forward osmosis. New forward osmosis membranes such as polyamide thin-film composite (PA TFC) membranes and cellulosic membranes have been developed extensively as membrane also affect the efficiency of forward osmosis (Cho *et al.*, 2013) .Forward osmosis has been used for brackish water, purification of contaminated water source and seawater desalination. Recently forward osmosis has attract interest in its potential area such as wastewater treatment, control drug release and food processing (Field & Wu, 2013)

1.2 Motivation

Fresh water is a daily basic need for living things. However 97% of water in earth is salt water leaving 3% fresh water (Sun *et al.*, 2014). Due to the increasing world population, the demand for the fresh water for drinking water supplies, food production, industrial and daily use also increases (Checkli *et al.*, 2012). The climate change around the world has causes frequent drought. This causes lacking of fresh water. Currently, certain area in Malaysia such as Pahang and Selangor face water shortages problem due to not receiving rain over a period of time. In Malaysia, we obtain fresh water from river.

However this river water must be treated before being delivered to consumer and sometimes the water that is delivered to consumer is yellowish in colour due the present of humic acid. Humic acid is a type of dissolved organic compound that causes colour in water. Research is conducted to find the solution to remove the humic acid in water supply (Lowe & Hossain, 2008). Osmosis is one of the methods that have been chosen in water treatment. Osmosis can be divided into reverse and forward osmosis. Forward osmosis is more preferable compare to reverse osmosis. Forward osmosis has high water recovery and helps to minimize membrane fouling (Kamiya *et al*., 2013). Membrane such as polyamide membrane can be synthesized using the interfacial polymerizations (La *et al*., 2013). The normal forward osmosis has problem in reverse salt diffusion. This type of problem occurs because the forward osmosis membranes used is not ideally semipermeable and large concentration difference between the draw and feed solution used. Hence the draw solute diffuse across the membrane to the feed solution (Ge *et al*., 2013) .This reverse salt problem cause the water flux to decrease and the process uneconomical due to the costs required to treat the feed solution before being discharge (Lutchmiah *et al.,* 2013 & Checkli *et al.,* 2012). Hence, suitable forward osmosis membrane and draw solution properties play an important role in improving the efficiency of forward osmosis process

1.3 Objectives

The following are the objectives of this research:

- To synthesis and determine the performance of polyamide membrane in forward osmosis.

1.4 Scope of this research

The following are the scope of this research:

i) Synthesis of polyamide membrane through interfacial polymerization method.

ii) Study on polyamide membrane performance in term of water flux, humic acid removal using sodium chloride as draw solution.

iii) Study the reverse salt diffusion mechanism

1.5 Organisation of this thesis

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

Chapter 2 provides a description of forward and reverse osmosis .General description about polyamide forward osmosis membrane, as well as characterization of polyamide membrane, and past research on synthesis of polyamide membrane. This chapter also provides details about draw solution properties, problems encounter in membrane and feed solution selection.

Chapter 3 gives a review of the methodology that includes the types of chemicals that are bought, draw and feed solution preparation, calibration curve for humic acid and NaCl, synthesis of polyamide membrane through interfacial polymerization and test the permeation of water flux through forward osmosis process

Chapter 4 is the detailed description of the preliminary lab work, which will include the calibration curve of sodium chloride and humic acid. This chapter also provide the water flux, humic acid rejection and reverse salt for different NaCl concentration.

2 LITERATURE REVIEW

2.1 Overview

This paper represents the comparison between reverse and forward osmosis, properties of draw solution, problems faced by membrane, types of draw solution, characterization of polyamide membrane and past research about interfacial polymerization. Draw solution properties such as concentration, molecular weight, temperature and osmotic pressure will determine the efficiency of the forward osmosis process. Membrane used in forward osmosis sometimes will encounter problems such as concentration polarization and fouling. Interfacial polymerization will determine the polyamide membrane towards water permeability rate and salt rejection ability.

2.2 Introduction

Forward osmosis is a process where the osmotic pressure difference occurs between two different concentration solutions is equalized by the transport of water through the semipermeable membrane from less concentrated region to a higher concentrated region (Liu *et al*., 2008). Forward osmosis membranes, have a salt-rejecting, active layer and a porous support that have high water permeability rate and reduced salt diffusion (Tiraferri *et al.,* 2013). The diluted draw solution will undergo pre-treatment to separate the potable water from the draw solute before it is used by consumers. However there are some diluted draw solutions that can be used directly without post-treatment (Phunsto *et al.,* 2014).

2.3 Comparison between Reverse Osmosis (RO) and Forward Osmosis Process (FO)

The driven pressure of forward osmosis process is osmotic pressure difference while the reverse osmosis is high hydraulic pressure (Liu *et al*., 2008). The high hydraulic pressure in reverse osmosis causes the reverse osmosis process is more expensive than the forward osmosis process (McCutcheon *et al*., 2006). The water recovery of reverse osmosis is 30-50% which is lower compare to forward osmosis that has at least 75% water recovery. The reverse osmosis process is harmful to environment and this process has serious problem with membrane fouling. Forward osmosis is environmental friendly and has low membrane fouling problem. Reverse osmosis can be used in normal separation system. Forward osmosis process can be used in temperature and pressure sensitive system. Forward osmosis has low energy demands whereas the reverse osmosis has high energy expenditure (Liu *et al*., 2008).

2.4 Fundamental and Performance of Forward Osmosis

Forward osmosis a process that follows the second law thermodynamics where the water diffuses across a semi permeable membrane from a low concentration solution (feed solution) to high concentration solution (draw solution)(Ge *et al*., 2013). The performance of forward osmosis is affected by the draw solution properties, feed solution properties, operating condition and membrane properties. The feed solution and draw solution represent the low concentration solution and high concentration solution. The draw solution properties such as the molecular weight, temperature, osmotic pressure and concentration will determine the efficiency of the forward osmosis process. Besides that, the type of membrane used, and pH of the solution used also will determine the water flux and salt rejection ability in forward osmosis. The fundamental of the forward osmosis is shown in figure 2.1.

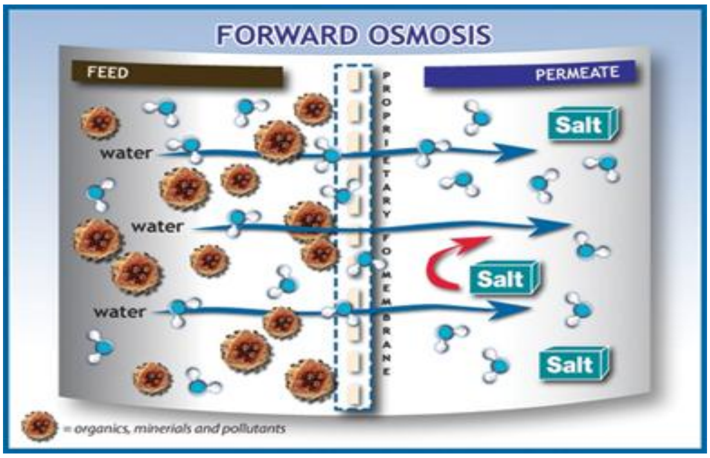


Figure 2-1: Fundamental of Forward osmosis process by Technology, 2010

2.5 *Draw Solution Properties*

2.5.1 *Concentration*

When concentration of draw solution increases, the water flux across the membrane will also increase. However this increase is not always constant as high draw solution concentration tends to cause concentration polarization (Checkli *et al*., 2012). The concentration polarization that occurs on membrane active layer is known as external concentration polarization (ECP) while the concentration polarizations that occur within the membrane support layer is known as internal concentration polarization (ICP) (Phuntsho *et al*., 2013). Concentration polarization will decrease the movement of water across the membrane and cause fouling to occur (Checkli *et al*., 2012). Increase in draw solution concentration also causes the possibility of reverse salt to occur increase (Hau *et al*., 2014).

2.5.2 *Osmotic Pressure*

Draw solution with higher osmotic pressure tends to draw more water from the feed solutions that have lower osmotic pressure across the membrane. A small molecular weight solute with high solubility has high osmotic pressure. The osmotic pressure of the ideal dilute solution is given by Van't Hoff's equation (Checkli *et al*., 2012)

$$\pi = n\left(\frac{c}{\mathrm{MW}}\right)RT \qquad \text{...} \ (2.1)$$

Where

n is the number of moles of solute in the solution
C is the solute molar concentration in g/L
R is the gas constant (R = 0.0821)
MW is the molecular weight of the solute
T is the absolute temperature of the solution

2.5.3 *Molecular Weight*

A draw solution that has small molecular weight solute and low viscosity can reduce concentration polarization that often occurs in forward osmosis process. When solute molecular weight and solution viscosity increase, the diffusion coefficients of the draw solution decrease. The decrease in the diffusion coefficient caused the concentration polarization especially internal concentration polarization to occur (Ge *et al*., 2013). Small molecular weight solutes help to induce higher osmotic pressure compare to the larger molecular weight solute for same volume draw solution. However smaller molecular weight draw solute tends to have reverse salt problems (Checkli *et al*., 2012). A high molecular weight solute has high probability to deposit on the membrane porous layer. This will prevent back diffusion in the porous structure. This will help to reduce external polarization (Nayak *et al*., 2011).

2.5.4 *Temperature*

Increase in draw solution temperature can help to initiate higher water flux and water recovery. However it also causes more negative impacts to the membrane fouling and cleaning (Checkli *et al*., 2012). At lower temperature solution increase water viscosity. This will decrease the diffusion rate, water recovery and water flux across the membrane and increase the concentration polarization. Hence increasing temperature is benefit in improving flux performance (Liu *et al*., 2009). Diffusion coefficient of solutes and the water molecules increases with the increase in temperature. The increase of the diffusion coefficient will decrease the solute resistivity within the membrane support layer that helps to decrease ICP (Phunsto *et al*., 2012). However, the increase in temperature should be controlled because concentration polarization will become more severe at higher fluxes (Liu *et al*., 2009). The fouling effect will increase when the temperature increase and causes negative effect to the membrane cleaning (Zhao & Zou, 2011). The effect of temperature on water flux is varying with the draw solution concentration (Phunsto *et al*., 2012).

2.5.5 Diffusion Coefficient

A high diffusion coefficient draw solution will have higher water flux. A high diffusion coefficient draw solution has lower resistance to diffusion within the membrane support layer. Hence more solvent can pass through the membrane. This can be seen through the equation

$$K = \frac{t\tau}{\varepsilon D_S} \text{..............................} \quad (2.2)$$

K is the solute resistance for the diffusion within the porous support layer

τ is tortuosity

t is thickness

ε is porosity

D_s is diffusion coefficient

Low molecular weight solutes have a high diffusion coefficient. High molecular weight solutes have low diffusion coefficient and tend to cause ICP effects (Checkli *et al.*, 2012).

2.5.6 Recovery of Draw Solution

The draw solution reconcentration and recovery after the draw solution is diluted through the flow of water from feed to draw solution should done under low cost energy. The reconcemtration process chosen should have high recovery of draw solution and produce high quality water. The water product after the separation should not have the draw solution solute.Thus, right recovery processes need to be selected for specific draw solution to reduce cost and energy. For example, volatile draw solution can be reconcentrated by heating while alcohol, SO_2 can be regenerated through distillation. However there is some diluted draw solution can be used directly without undergo reconcentration and recovery process(Checkli *et al.*, 2012 and Achilli *et al.*, 2010).

2.5.7 Other Characteristics

The draw solution must be easily separated from the drinking water (McCutcheon *et al.*, 2006).A high solubility draw solutions also induces high osmotic pressure and therefore can achieve high water flux and high recovery rates. The draw solutions should not degrade the membrane chemically or physically (Liu *et al.*, 2008 & Checkli *et al.*, 2012). A good draw solution should have high water flux, inert, minimum reverse flux, nontoxic, low cost and easy recovery (Ge *et al.*, 2013).

2.6 Types of Draw Solution

Draw solution can be a organic, inorganic based draw solution and magnetic nanoparticles (Checkli *et al.*, 2012).

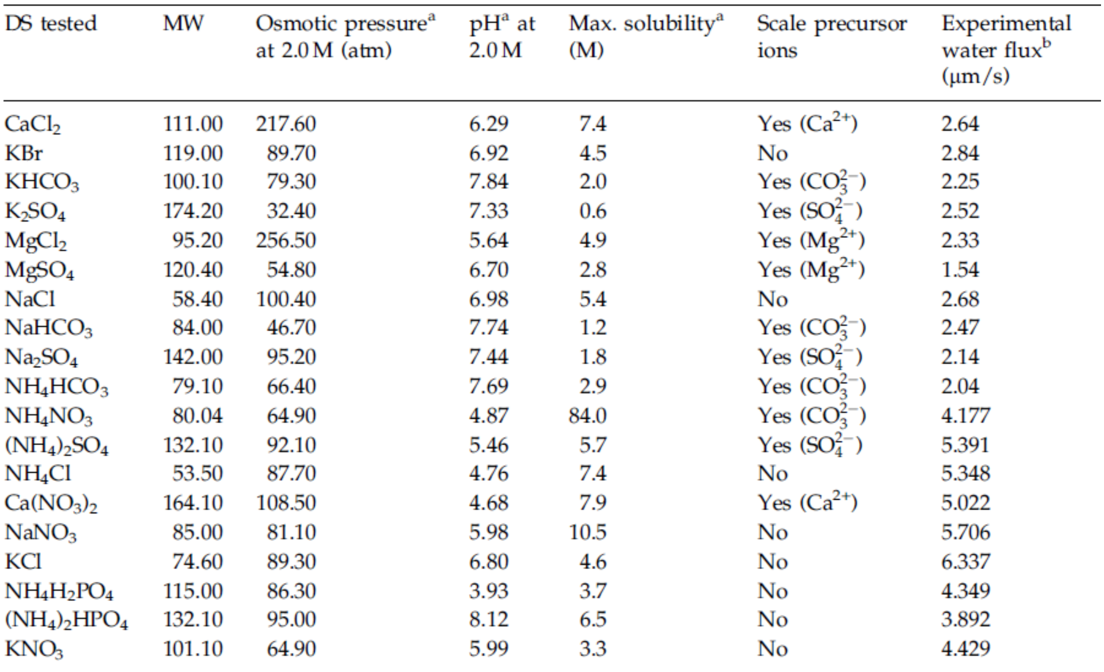
2.6.1 Organic based Draw Solution

Organic draw solution used is normally non-electrolyte compound and has high solubility that can generate high osmotic pressure (Checkli *et al*., 2012). A former organic compound has less internal concentration polarization compare to the latter due to the higher diffusion coefficient. Hence an organic compound with a short carbon chain has a better performance than the organic compound with long carbon chain while both of them have the same cation species under same osmotic pressure. The forward osmosis that uses the organic draw solution has lower water flux than those inorganic analogs produced at same condition. According to Ge *et al*., 2013, organic sodium salt has water flux that range from 8.7 – 9.4 LMH while NaCl produce 14 LMH at the same condition. This is due to larger size of the organic sodium salt have lower diffusion coefficient compare to the smaller size NaCl (Ge *et al*., 2013).

2.6.2 Inorganic Salt

Inorganic based draw solution is normally comprise of electrolyte solutions and there is also possibility of non-electrolyte solution categorised under inorganic salt. Different types of inorganic-based compounds is selected as draw solution and tested in forward osmosis process. These solutions were selected due to their high water solubility, osmotic pressure, low cost and toxicity,that are important factor that can help to increase forward osmosis performance (Checkli *et al*., 2012). According to Achilli *et al* and Liu et al, three draw solutions such as $KHCO_3$, $MgSO_4$, and $NaHCO_3$ was ranked high due to its high performance with low refilling costs. $CaCl_2$ and $MgCl_2$ was also ranked high considering the water flux, reverse salt diffusion but not considering the refilling costs because of their relatively high solute costs and in opposite the NaCl and Na_2SO_4 ranked low considering the water flux, reverse salt performance but high considering of the replenishment costs due to their relatively low solute costs (Achilli *et al*., 2010). The type of inorganic draw solution used by past researchers is shown in table 2.1.

Table 2-1: Types of inorganic draw solutions with osmotic pressure, pH and solubility by Checkli *et al*., 2012



DS tested	MW	Osmotic pressure[a] at 2.0 M (atm)	pH[a] at 2.0 M	Max. solubility[a] (M)	Scale precursor ions	Experimental water flux[b] (μm/s)
$CaCl_2$	111.00	217.60	6.29	7.4	Yes (Ca^{2+})	2.64
KBr	119.00	89.70	6.92	4.5	No	2.84
$KHCO_3$	100.10	79.30	7.84	2.0	Yes (CO_3^{2-})	2.25
K_2SO_4	174.20	32.40	7.33	0.6	Yes (SO_4^{2-})	2.52
$MgCl_2$	95.20	256.50	5.64	4.9	Yes (Mg^{2+})	2.33
$MgSO_4$	120.40	54.80	6.70	2.8	Yes (Mg^{2+})	1.54
NaCl	58.40	100.40	6.98	5.4	No	2.68
$NaHCO_3$	84.00	46.70	7.74	1.2	Yes (CO_3^{2-})	2.47
Na_2SO_4	142.00	95.20	7.44	1.8	Yes (SO_4^{2-})	2.14
NH_4HCO_3	79.10	66.40	7.69	2.9	Yes (CO_3^{2-})	2.04
NH_4NO_3	80.04	64.90	4.87	84.0	Yes (CO_3^{2-})	4.177
$(NH_4)_2SO_4$	132.10	92.10	5.46	5.7	Yes (SO_4^{2-})	5.391
NH_4Cl	53.50	87.70	4.76	7.4	No	5.348
$Ca(NO_3)_2$	164.10	108.50	4.68	7.9	Yes (Ca^{2+})	5.022
$NaNO_3$	85.00	81.10	5.98	10.5	No	5.706
KCl	74.60	89.30	6.80	4.6	No	6.337
$NH_4H_2PO_4$	115.00	86.30	3.93	3.7	No	4.349
$(NH_4)_2HPO_4$	132.10	95.00	8.12	6.5	No	3.892
KNO_3	101.10	64.90	5.99	3.3	No	4.429

2.6.3 Magnetic Nanoparticles

Magnetic nanoparticles such as Polyacrylic acid magnetic nanoparticles (PAA MNPs), 2-Pyrrolidonemagnetic nanoparticles (2-Pyrol MNPs) and triethyleneglycol magnetic nanoparticles (TREG MNPs) can be used as draw solution. The benefits of magnetic nanoparticles are having a high surface area to volume ratio and have large particle sizes compared to inorganic and organic draw solutions that induce the water recovery through magnetic fields and low pressure membrane processes. Magnetic nanoparticles draw solutions also have high osmotic pressure (Checkli *et al.,* 2013).

This osmotic pressure also can be increased by enhancing MNPs surface hydrophilicity and decrease their particle sizes. Magnetic nanoparticles don’t have reverse salt problem due to their large particle size. MNPs draw solution recovery can be done using different method depending on their particles size .Magnetic field, electric field and others method can be used. However, magnetic nanoparticles have lower osmotic pressure and have significant concentration polarization problems due to their large particle sizes (Ge *et al.*, 2013)

2.6.4 Ionic polymer hydrogel particles

Hydrogels is a type of polymer chains that are connected to each other by the chemical bonds and have high concentrated hydrophilic groups that can attract large amount of water. Hydrogels with ionic groups can attract more volume of water which help to increases the osmotic pressures. The water recovery is very easy and low energy cost (Checkli *et al.*, 2013). Polymer hydrogels can draw and release water through temperatures, pressure or light stimulus by incorporates the light absorbing carbon particles. They can draw water from the feed solution and undergo a reversible changes in volume when it is exposed to the environmental stimulus. However polymer hydrogels has low performance under room temperature. Better performance can only be achieved when temperature is increase until 50^{o}C and need high hydraulics pressure during water removal which causes high energy consumption and costs (Ge *et al.*, 2013).

2.6.5 Dendrimers

Dendrimers are symmetrical spherical that carries molecules. These macromolecules provide a high osmotic pressure. They can be easily regenerated by conventional membrane processes. Two types of dendrimers that can be used as draw solution are ethylenediaminecore dendrimers with sodium succinamate terminal groups and pentaerythrityl core dendrimer with sodium carboxylate terminal groups (Checkli *et al.*, 2013).

2.7 Parameter Effect on Forward Osmosis

2.7.1 Effect of Feed Solution Concentration

When the feed solution concentration increases, the water flux from the feed to draw solution will decrease (Zhao *et al.*, 2011). This is because the driving force in forward osmosis is the osmotic pressure difference between the draw solution and the feed solution across the membrane used. Hence the osmotic pressure of the feed solution must lower than the draw solution to get a higher water flux. Increase the feed solution concentration decrease the osmotic pressure between the feed and draw solution (Ge *et al.*, 2013).

2.7.2 Influence of Feed and draw Solution Temperature

The increase in both draw and feed solution temperature will result high water flux. Decreasing the solution temperature leads to increase in viscosity while the diffusion coefficient decrease (Phunsto *et al.,* 2012). When the feed solution temperature increases, it causes the membrane pores to enlarge and the water permeability rate increase (Wong *et al.,* 2012). Increase in feed solution temperature will increase the feed solution osmotic pressure across the membrane which is unfavourable. However this increase is not significant since draw solution has higher osmotic pressure. In Phunsto *et al*., research, when they increase both the draw and feed solution from 25 ^{0}C to 35^{0}C and 45^{0}C. The osmotic pressure increases from 85.4 atm to 88.1 atm and 90.6 atm. When a temperature difference between draw solution and feed solution is introduced by heating the draw solution to 35^{0}C or 45^{0}C and the temperature of the feed solution is remain at 25 ^{0}C. A slightly higher osmotic pressure is recorded when only draw solution is heated rather than heating both solutions (Phunsto *et al*., 2012).

2.7.3 Solution Flow Rate

The changes in the solution flow rate change the thickness of mass transfer boundary layer of membrane surface. At lower flow rate, the membrane boundary is thicker, which results in low rate of mass transfer and, consequently, increase concentration polarization. Feed and draw solution flow rates did not seriously affect the water flux across the membrane (Wong *et al*., 2012).

2.7.4 Concentration Polarization

Concentration polarization occurs due to the effect of the dilution of the draw solution and the concentrative effect of the feed solution. This causes the draw solute concentration at the membrane surface become lower than its bulk concentration, while the feed concentration at the membrane surface is higher than its bulk concentration with water diffusing from the feed solution to the draw solution. Concentration Polarization can be classified into internal and external concentration polarization (Ge *et al*., 2013).

2.7.5 External Concentration Polarization (ECP)

External concentration polarization can be classified into dilutive and concentrative external concentration polarization. ECP happens on both sides of the membrane surface. At the draw solution side, the solute is diluted on the membrane surface whereas at the feed solution side the solute concentrate at the surface of the membrane. This results in decrease of water permeability rate across the membrane due to the decrease of the osmotic pressure of the draw solutions side (Suh & Lee, 2013). Concentrative ECP exists on the feed solution side of a membrane. Dilutive ECP occurs in at the membrane surface that facing the draw solution when the convective water flow is replacing and bringing the dissolved draw solute from the membrane surface at the permeate side. In concentrative ECP, solute and solvent of the feed solution will flow to the surface of the membrane and the solvent will diffuse through the membrane and enter draw solution side. The solute of the feed solution will remain and accumulate at the membrane surface. According to McChuteon and Elimelech, concentrative ECP reduces the osmotic pressure due to the increase in concentration of feed solution and decrease in the draw solution concentration. Hence the water flux of forward osmosis will decrease. High water flux occur when the at lowest feed solution concentration. ECP more often occur under high water flux (McCutcheon & Elimelech, 2006). The impact of the external CP phenomenon on osmotic pressure can be reduced by using the cross flow filtration with hydrodynamics designed to create the adequate shear and turbulence on the membrane surface (McCutcheon *et al*., 2006).

2.7.6 Internal Concentration Polarization (ICP)

Internal concentration polarization can be divided into dilutive and concentrative ICP. ICP occur between the feed solutions or draw solution with membrane porous surface Concentrative ICP occurs when the membrane support layer is facing the feed solution, water will enter the porous support layer and diffuse through the active layer and enter the draw solution site. The solute in feed will enter the open structure when it flows to the membrane. This solute cannot pass through the active layer from the support layer site. Hence, the concentrations of solute in the porous layer increase (McCutcheon *et al*., 2006). Dilutive ICP occurs when the feed solution faces the active layer. The draw solution becomes less concentrated when water diffuse from the feed solution. Dilutive ICP causes the osmotic pressure gradient across the membrane decreases and water diffusion across the membrane decrease. (Suh & Lee, 2013). ICP causes more significant effect on the decease of water flux than the ECP effect caused by the axial flow of the salt solution into the porous layer of FO membrane. The solutes enter and leaves the porous layer through the advective water flux and direct diffusion, very small amount of solute can pass through the active layer, which resulting in back diffusion and the accumulation of solute within the porous layer that causes the ICP effect to occur (Tan & Ng, 2013). ICP becomes more serious for a thicker and lesser porous support layers membrane due to the increase of the mass transfer resistance (Tang *et al*., 2010)

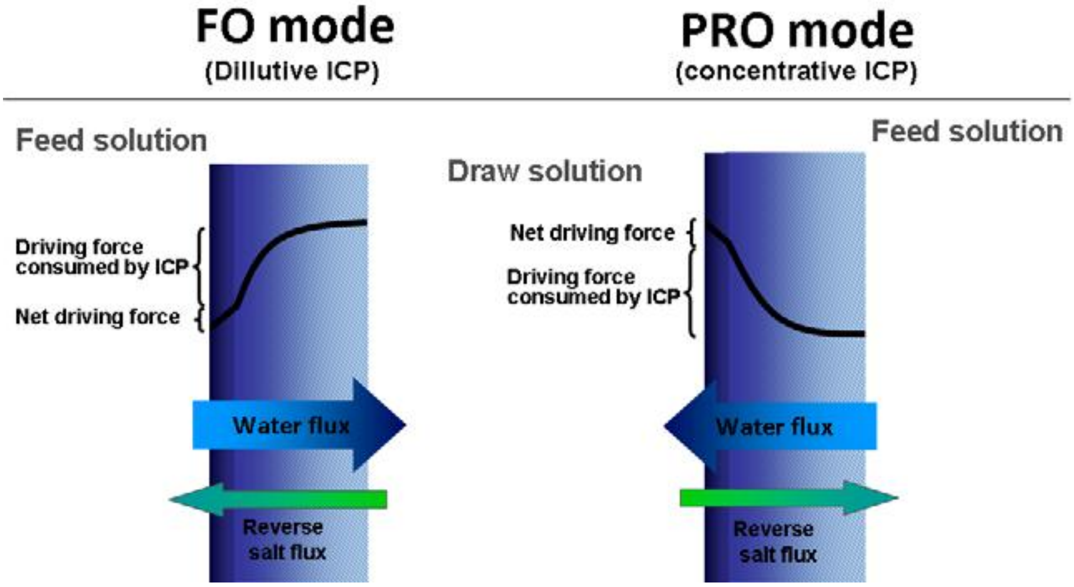


Figure 2-2: Illustration on dilutive and concentrative ICP at FO and PRO mode by Alsvik& Hägg, 2013.

2.8 Forward Osmosis Membrane

An ideal FO membrane is able to provide high water flux across it, high feed and draw solution rejection ability, low internal concentration polarization (ICP), and has high chemical stability and mechanical strength (Shaffer *et al*., 2014).

2.8.1 Effect of pH on Polyamide Membranes Performances

The molecular weight of the membranes is constant in acidic and neutral conditions. When the pH is greater than 11 the molecular weight of the membranes increase and the membrane permeability towards water decrease. This is due to the membrane has a higher effective average pore and effective thickness versus porosity in alkaline conditions as compared to the other pH level (Dalwani *et a*l., 2011).According to Tang *et al*, increase in feed solution pH will lead to decrease in water flux. When the pH decrease the amino group on the active layer will change into into RH_3N^+ or R_3HN^+ that will lead to the increment in the hydrophilicity and enlargement of the pore surface of the polyamide membrane. Besides that at high pH, the electrostatic repulsion will occur between -COO- and OH group on the membrane surface that lead to reduction in pores size. Polyamide membrane experience more significant fouling in lower pH condition than at more alkali environment (Dalwani, 2011). Hwang *et al* used humic acid as the feed solution and sodium chloride as the draw solution. When they increase the pH from 5 to 11, water flux and salt rejection increase. At high pH membrane fouling can be reduced. This will help to increase water flux.

2.8.2 Past research on Interfacial Polymerization of Polyamide Membrane

Polyamide membrane can be synthesized through interfacial polymerization using m-phenylenediamene (MPD) and trimesosyl chloride (TMC) (Wei *et al*., 2013).Interfacial polymerization strongly influences the performance of the polyamide membrane in forward osmosis. According to Klaysom *et al*, monomer concentrations, drying time, drying temperature and reaction time affecting the polyamide membranes performance in salt rejection ability and water permeability rate (Klaysom *et al.*, 2013).

I. Effect of M-phenylenediamine Concentration

In a research, the trimesoyl chloride concentration is fixed at 0.1% w/v and increase the m-phenylenediamine concentration from 1 to 2% wt, the permeability of the membrane towards water was slightly reduce while the salt rejection increase. When the MPD concentration increase, the driving force for MPD to diffuses into the organic phase also increase. Hence, the barrier layer thickness increase causes the water flux to decrease and salt rejection ability increase (Xie *et al*., 2012). However further increase the MPD concentration causes negative effect to the salt rejection and the water permeability rate remain constant. Wei et al use 0.5 of NaCl as draw solution and the membrane is in pressure retarded osmosis mode, the water flux increase from 11 to 22 L/m^2 when the MPD concentration decrease from 2 till 1 wt % (Wei *et al*., 2011).