

**POTENTIAL OF CELLULOSE TRI ACETATE (CTA) MEMBRANE FOR
SEAWATER TREATMENT BY FORWARD OSMOSIS**

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**BACHELOR OF CHEMICAL ENGINEERING
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**POTENTIAL OF CELLULOSE TRI ACETATE (CTA) MEMBRANE FOR
SEAWATER TREATMENT BY FORWARD OSMOSIS**

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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**

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DEDICATION

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

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ABSTRACT

Nowadays, the increased of human population and rapid industrial growth in most parts of the world caused insufficient clean water supply and water scarcity. Therefore the depletion of resources of water encouraged us to find new resources for clean water supply. Forward osmosis (FO) which used in desalination of seawater by using low energy consumed and low cost needed become more potential process to treat in desalination of seawater. This research focused on the seawater treatment by forward osmosis by Cellulose Tri Acetate (CTA) Membrane. Sodium sulphate was used as draw solution because of less toxicity and easily recovery after forward osmosis process. Synthetic seawater, NaCl with concentration of 35g/L was used as feed solution. This research was conducted based on different concentrations of draw solution (1.0M, 1.25M, 1.50M, 1.75M and 2.0M) and pH (3, 7 and 9) which will impact the water flux and reverse salt flux (RSF). Besides that, the effect of orientation of CTA membrane in the mode of active layer face draw solution (AL-DS) and active layer face feed solution (AL-FS) were also investigated. After optimum parameters were obtained, treatment on real seawater was conducted and the results were compared with synthetic seawater. To observe that, 1.75M of sodium sulphate produced highest water flux at value $1.07 \text{ E-}04 \text{ m}^3/\text{m}^2.\text{min}$ and optimum RSF 6.44 GMH at pH 7. Good performance of FO were shown in the orientation AL-DS of CTA membrane. Besides that, real seawater treatment has lower water flux ($7.00 \text{ E-}05 \text{ m}^3/\text{m}^2.\text{min}$) and RSF (3.68 GMH) than synthetic seawater. In conclusion, 1.75M and pH 7 of sodium sulphate as draw solution in AL-DS orientation of CTA membrane showed the optimum performance of FO.

ABSTRAK

Pada masa kini, peningkatan populasi manusia dan pertumbuhan perindustrian yang pesat menyebabkan kekurangan bekalan air yang bersih. Oleh itu, kekurangan sumber air mendorong kita untuk mencari sumber-sumber baru. Osmosis hadapan yang digunakan dalam penyahgaraman air laut dengan menggunakan tenaga yang rendah dan kos rendah menjadikannya proses yang lebih berpotensi untuk penyahgaraman air laut. Kajian ini memberi tumpuan kepada rawatan air laut melalui osmosis hadapan yang menggunakan membran Cellulose Acetate Tri (CTA). Sodium sulfat digunakan sebagai larutan penarik kerana kurang toksik dan mudah medapatkan semula selepas proses osmosis hadapan dan NaCl dengan kepekatan 35g/L sebagai larutan suapan. Kajian ini dijalankan berdasarkan kepekatan yang berbeza iaitu (1.0M, 1.25M, 1.50M, 1.75M dan 2.0M) dan pH (3, 7 dan 9) yang akan memberikan kesan kepada fluks air dan penyebaran garam terbalik. Selain itu, kesan orientasi membran CTA dalam mod lapisan aktif terhadap larutan penarik dan lapisan aktif terhadap larutan suapan juga telah dikaji. Selepas parameter optimum diperolehi, eksperimen yang menggunakan air laut sebenar telah dijalankan dan keputusan telah dibandingkan dengan air laut sintetik. Keputusan kajian menunjukkan bahawa, 1.75M natrium sulfat menghasilkan fluks air tertinggi pada nilai $1.07 \text{ E-}04 \text{ m}^3/\text{m}^2.\text{min}$ dan optimum fluks garam berbalik pada nilai 6.44 GMH pada pH 7. Prestasi yang baik daripada osmosis hadapan ditunjukkan oleh orientasi membran CTA lapisan aktif menghadap larutan penarik. Selain itu, rawatan air laut sebenar mempunyai fluks air yang lebih rendah iaitu $7.00 \text{ E-}05 \text{ m}^3/\text{m}^2.\text{min}$ dan fluks garam berbalik dalam 3.68 GMH berbanding dengan air laut sintetik. Kesimpulannya, 1.75M dan pH 7 natrium sulfat dalam orientasi membran CTA lapisan aktif mengemuka larutan penarik menunjukkan prestasi optimum dalam proses osmosis hadapan.

TABLE OF CONTENTS

SUPERVISOR’S DECLARATION	IV
STUDENT’S DECLARATION	V
DEDICATION.....	VI
ACKNOWLEDGEMENT.....	VII
ABSTRACT	VIII
ABSTRAK	IX
TABLE OF CONTENTS	X
LIST OF TABLES	XIII
LIST OF FIGURES	XIV
LIST OF SYMBOL.....	XVI
LIST OF ABBREVIATIONS	XVII
1. INTRODUCTION	1
1.1 Background	1
1.2 Motivation	1
1.3 Problem statement	2
1.4 Objective	2
1.5 Scope of research	3
1.6 Organisation of this thesis	3
2. LITERATURE REVIEW	5
2.1 Introduction	5
2.2 Reverse Osmosis (RO).....	5
2.2.1 Fundamental of reverse osmosis	5
2.2.2 Advantages of reverse osmosis	7
2.2.3 Applications of reverse osmosis	7
2.3 Forward osmosis (FO).....	8

2.3.1	Fundamental of forward osmosis	8
2.3.2	Advantages of forward osmosis	9
2.3.3	Applications of forward osmosis	9
2.4	Forward osmosis membrane	11
2.4.1	Thin film composite (TFC) polyamide (PA) based membranes (Interfacial Polymerization)	12
2.4.2	Cellulose Triacetate (CTA) membrane (Phase Inversion)	13
2.5	Draw solutions	14
2.6	Selection of sodium sulphate (Na ₂ SO ₄) as draw solution	17
2.7	Challenges of forward osmosis	17
2.7.1	Concentration polarization	17
2.7.2	Membrane fouling	19
2.7.3	Reverse solute diffusion	19
2.8	Summary	20
3.	MATERIALS AND METHODS	21
3.1	Overview	21
3.2	Chemicals	21
3.3	Preparation of draw solutions (Na ₂ SO ₄)	22
3.4	Preparation of synthetic sea water	22
3.5	Permeation module	22
3.6	Methodology	22
3.6.1	Characterization of CTA membrane performance	22
3.6.2	Characterization of CTA membrane morphology	24
3.7	Treatment on real seawater	24
3.8	Summary	25
4.	RESULTS AND DISCUSSION	26
4.1	Overview	26

4.2	Morphology of CTA membrane.....	26
4.3	Water flux.....	27
4.3.1	Results.....	28
4.3.2	Discussion.....	29
4.4	Reverse salt diffusion.....	32
4.4.1	Results.....	33
4.4.2	Discussion.....	34
4.5	Treatment on real seawater.....	36
5.	CONCLUSION AND RECOMMENDATIONS.....	38
5.1	Conclusion.....	38
5.2	Recommendations.....	39
	REFERENCES.....	40
	APPENDICES.....	46

LIST OF TABLES

Table 2-1: Comparison between RO and FO process (Liu et al, 2009).....	10
Table 2-2: Comparison between TFC and CTA membrane.	14
Table 2-3: Overview of draw solutions used for FO process in the last two decades. (Linares et al. 2014)	15
Table 4-1: Water flux for draw solution in different concentrations and pH 3, 7 and 9 at active layer face draw solution (AL-DS).	28
Table 4-2: Water flux for draw solution in different concentrations and pH 3, 7 and 9 at active layer face feed solution (AL-FS).	29
Table 4-3: Reverse salt diffusion for draw solution in different concentrations and pH 3, 7 and 9 at active layer face draw solution (AL-DS).	33
Table 4-4: Reverse salt diffusion for draw solution in different concentrations and pH 3, 7 and 9 at active layer face draw solution (AL-FS).	33
Table 4-5: Comparison between water flux and reverse salt flux for synthetic and real seawater.	36
Table A-1: Table of change in feed solution volume with pH 3 for different concentration of draw solution at active layer face draw solution.	46
Table A-2: Table of change in feed solution volume with pH 7 for different concentration of draw solutions at active layer face draw solution.	46
Table A-3: Table of change in feed solution volume with pH 9 for different concentration of draw solutions at active layer face draw solution.	47
Table A-4: Table of change in feed solution volume with pH 3 for different concentration of draw solutions at active layer face feed solution.	48
Table A-5: Table of change in feed solution volume with pH 7 for different concentration of draw solutions at active layer face feed solution.	48
Table A-6: Table of change in feed solution volume with pH 9 for different concentration of draw solutions at active layer face feed solution.	49
Table A-7: Table of change in feed solution volume with pH 7 for concentration of 1.75M draw solutions at active layer face feed solution.	49

LIST OF FIGURES

Figure 2-1: Schematic diagram of RO process.	7
Figure 2-2: Schematic diagram of FO process.	9
Figure 2-3: Comparison between forward osmosis and reverse osmosis- Adapted from (Cath et al. 2006).....	11
Figure 2-4: Schematic diagram for thin film composite membrane.	13
Figure 2-5: Schematic diagram for asymmetric composite membrane.	14
Figure 2-6: Schematic diagram of membrane orientation in FO and PRO mode.....	19
Figure 3-1: Overall research flow.	21
Figure 3-2: Schematic diagram for bench-scale of forward osmosis (Achilin et al., 2010).	22
Figure 3-3: Lab scale unit	23
Figure 4-1: FESEM images of CTA membrane (a) at active layer before the FO process, (b) at active layer after the FO process, (c) at support layer before the FO process, (d) at support layer after the FO process.	27
Figure 4-2: Water flux for different concentrations in orientation AL-DS and AL-FS at pH 3.	29
Figure 4-3: Water flux for different concentrations in orientation AL-DS and AL-FS at pH 7.	29
Figure 4-4: Water flux for different concentrations in orientation AL-DS and AL-FS at pH 9.	30
Figure 4-5: Water flux at pH 3, 7 and 9 in different concentration of draw solution in AL-DS orientation.	32
Figure 4-6: Reverse salt flux for different concentrations in orientation AL-DS and AL-FS at pH 3.	34
Figure 4-7: Reverse salt flux for different concentrations in orientation AL-DS and AL-FS at pH 7.	34
Figure 4-8: Reverse salt flux for different concentrations in orientation AL-DS and AL-FS at pH 9.	34
Figure 4-9: Reverse salt flux at pH 3, 7 and 9 in different concentration of draw solution.	35
Figure 4-10: Comparison of water flux for synthetic and real seawater.	36
Figure 4-11: Comparison of reverse salt flux for synthetic and real seawater.	37

Figure A-1: Calibration curve of conductivity against concentration of NaCl solution.

.....50

LIST OF SYMBOL

J_w	Water flux
A	Water permeability
M	Molarity
J_s	Reverse flux of the solute
C_f	Final feed solution concentration
C_i	Initial feed solution concentration
ΔV	Volume of water which permeates through the membrane
A	Effective area of the membrane
Δt	Time taken for water permeation in minutes
R	NaCl rejection
C_p	Concentration of NaCl in draw solution
C_F	Concentration of NaCl in feed solution
Greek	
σ	Reflection coefficient
$\Delta\pi$	Osmotic pressure difference across the membrane
π	Osmotic pressure
π_D	Bulk osmotic pressure of the draw solution
π_F	Bulk osmotic pressure of the feed solution
η	Viscosity of the polyelectrolyte solution
η_r	Relative viscosity
η_0	Viscosity of the ionized water

LIST OF ABBREVIATIONS

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CTA	Cellulose Tri Acetate
DS	Draw solution
ECP	External concentration polarization
FESEM	Field Emission Scanning Electron Microscopy
FO	Forward osmosis
FS	Feed solution
HTI	Hydration Technology Inc.
ICP	Internal concentration polarization
IP	Interfacial polymerization
MD	Membrane distillation
NF	Nanofiltration
OER	Osmotic energy recovery
RO	Reverse osmosis
TFC	Thin film composite
TSS	Total suspended solids

1. INTRODUCTION

1.1 Background

With the development of economic around this world, clean water resources are greatly utilized. Desalination of seawater by forward osmosis technology becomes one of the important researches for clean water supply. Osmosis defined as the transfer of water particles through a selectively permeable membrane driven by a concentration gradient (McCutcheon et al., 2005). During the last four decades, many researches about FO osmosis have been studied but mainly focused on achieving high water flux by choosing the right draw solution. The draw solutions that have been chosen are glucose, sulphur dioxide (SO_2) and aluminium sulphate ($Al_2(SO_4)_3$) (Batchelder, 1965; Frank, 1972; Kravath, 1975; Stache, 1989). After this, a two stage FO process was patented by using draw solutions potassium nitrate (KNO_3) and sulphur dioxide (SO_2) in first stage and second stage respectively (McGinnis, 2002). However, performance data were either limited or not reported. Recently, based on the reports from various researches and patents, ammonium bicarbonate was introduced as new novel draw solution (McCutcheon et al., 2005) and new developed CTA membrane was used as the FO membrane. However ammonium bicarbonate was found that not stable in high temperature. In addition, there is a lack of mechanistic explanation on the effects of various factors on the performance of the FO process. To date, only two studies were reported on the impact of one of the affecting factors: membrane structure. Loeb et al. (1997) conducted a static osmosis study and discussed about the effects of membrane structure on osmosis using RO cellulose acetate asymmetric membrane. McCutcheon (2005) briefly mentioned that “internal concentration polarization” would adversely affect the performance of the cellulose ester FO membrane in the dynamic FO process.

1.2 Motivation

Clean water play an important role in our daily life, we use water in drinking, cooking, bathing, industries and agriculture. About 97% of water in our earth covered by seawater therefore seawater considered the most potential clean water resources. However, desalination of seawater was considered as challenged process because of high energy and cost consumed.

Therefore, the introduced of forward osmosis (FO) as one of the technologies in desalination of seawater which is more valuable with low operating cost (McChutcheon et al., 2006). For this research, forward osmosis (FO) was chosen instead of reverse osmosis (RO) because RO is pressure-driven membrane separation processes which required more energy. In forward osmosis, selected a suitable draw solution and an optimum semi-permeable membranes are the crucial things to obtain a good result of FO system. The current available membrane which is commercialised is cellulose triacetate (CTA) membrane developed by HTI (Hydration Technologies Albany, OR). A suitable draw solution need to fulfil the requirements which are high water flux, low reverse salt diffusion and easy recovery of the diluted draw solution (Chekli et al., 2012; Ge et al.,2013).

In addition, nowadays there are a lot of studies that related to desalination of seawater by using reverse osmosis. Besides that, reverse osmosis is the technologies established in large scale and commercially around the world. However, researches for forward osmosis in desalination of seawater are scarce. In order to produce high quality of clean water, the research on forward osmosis for seawater should be investigated. This research also important to reduce the problem of water crisis by using a less energy and cost consumed technology.

1.3 Problem statement

Reverse osmosis (RO) is the technology which is commonly used in water treatment but cannot achieved high recovery of water flux due to hydraulic pressure limitation of the pumps and membrane fouling. Besides that, forward osmosis (FO) is a process that is more valuable but the challenged of this process is lack of optimised membrane and draw solution. Moreover, forward osmosis also met the problem which is the reverse salt diffusion which can influence its performance.

1.4 Objective

The objective of this research is to perform desalination of seawater by using cellulose triacetate (CTA) FO membrane with sodium sulphate as draw solution.

1.5 Scope of research

To achieve the objective in this research, three main scopes of research had been identified. The following are the scopes of this research:

1. First, the performance of CTA membrane was tested in terms of pure water permeability. This is done by determine the water flux by using different pH of draw solution (pH 3,7 and 9) and different concentration of draw solution (1.0M, 1.25M, 1.50M, 1,75M and 2.0M).
2. The second scope of this research is to study the effect of orientation of CTA membrane. There are two modes of membrane orientation in FO which are the porous layer facing the feed solution and the dense layer facing the draw solution and vice versa. This result will help in knowing the best orientation of membrane in desalination of seawater.
3. Finally the last scope is to study the effect of different of pH and concentration for the draw solution sodium sulphate on reverse salt flux (RSF).

1.6 Organisation of this thesis

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

Chapter 2 introduces the membrane technology used in water treatment and the fundamental principles of osmosis and forward osmosis (FO). Besides that, this chapter discusses on the advantages of using FO method and its applications. The differences between FO and the current most popular membrane process RO are also compared. In addition, this chapter provides a description on the different method of membrane technologies currently used in this era. Furthermore, this chapter discusses on the common membrane used for forward osmosis process known as cellulose triacetate (CTA) membrane. The selection of Na_2SO_4 draw solution and its properties that could influence the FO performance is also discussed on this chapter. Lastly, this chapter also looks into the current challenges of FO that can gravely affect the efficiency of the process which are concentration polarization, membrane fouling and reverse salt diffusion.

Chapter 3 provides description on the chemicals used and methodology of this research which includes the procedures to characterize CTA FO membrane in terms of physical

and chemical properties. The preparation of draw solution and feed solution will be described and the permeation module of the experiment will be demonstrated.

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

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

2. LITERATURE REVIEW

2.1 Introduction

Water crisis remained an issue for human all around the world including Malaysia. Freshwater is the most important fundamental needed for life as it is important for human daily lifestyle and the sustainability for our ecosystem. However, the resources are progressively strained by population growth, development, droughts, climate change and more. Seawater cover 97% of the total available water therefore it is the most suitable resources for fresh water. Most research done to find out the most optimum technologies for desalination of seawater to produce fresh water as it is expected that global water demand will increase by 53 % to 6.9 trillion m^3 until 2030 (Amarasinghe & Smakhtin 2014). While there are numerous ways to desalinate seawater, reverse osmosis (RO) is most commonly known. However, this technology has been criticised because consume a lot of energy cause the technology unsustainable (Chung et al. 2012). Therefore, forward osmosis has been introduced as the new technology for desalination of seawater which is environmentally safe technologies that would make use of unconventional water resources and promote beneficial water reuse.

2.2 Reverse Osmosis (RO)

2.2.1 Fundamental of reverse osmosis

Reverse osmosis (RO) is the current process used around the world to produce fresh water. This process normally used in desalination of sea water and brackish water. RO process is the process occurred by applying high pressure in a feed channel surrounded by a semi-permeable membrane. The pressure that applied in this process should be higher than the osmotic pressure of solution. The water flux or the clean water rate obtained is influenced by the concentration of salt concentration in the feed water and the properties of membrane such as permeability and solubility. The higher the values of permeability and solubility, the more possibility for the salt concentration polarization occur along the membrane surface. This is because when the selectivity and permeability of the membrane increase, the water permeation and the salt accumulation along the membrane surface will also increase. The salt concentration polarization occurred will influence the performance of the membrane. One of the influence is increased the osmotic pressure for the solution because of the increased in

salt concentration. Hence, the applied pressure will need more higher to achieve the same production of clean water rate. Another influence for the performance of the membrane is increased the fouling occurs on the membrane especially at the area where the salt concentration polarization occurred (Shenvi et al.,2015; Malaeb & Ayoub, 2011; Lee et al, 2011).

The performance of RO system is affected by several factors, such as feed pressure, feed salinity, and water flux. There have been many researches done to obtain an optimized RO process to find out the optimal size, configuration of process units, and also the optimal operation (Kotb et al, 2016). One of the research done by investigated various multistage of RO process by changing the parameters which are the concentrations of the feed solutions and products specification to reduce the total annual cost (Lu et al., 2007). Besides that, osmotic energy recovery (OER) was introduced to reduce the consumption of energy (Feinberg et al., 2013). OER involves harvesting the energy released during the controlled mixing of two solutions with different salt concentrations (i.e., a salinity gradient) but it has been reported that this technology is not commercially viable at present and the feasibility of using OER at seawater RO plants remains speculative.

The RO process is simple in design consists of four major systems which are pre-treatment system, high pressure pumps, membrane systems and post-treatment. Pre-treatment system is provided to remove all suspended solids so that salt precipitation or microbial growth does not occur on the membranes. High-pressure pumps supply the pressure needed to enable the water to pass through the membrane. Membrane systems consist of a pressure vessel and a semi-permeable membrane inside that permits the feed water to pass through it. Depending upon water quality of permeate and use of permeate; post treatment may consists of adjusting the pH and disinfection (Garud et al, 2011). Figure 2-1 showed the schematic diagram of reverse osmosis system.

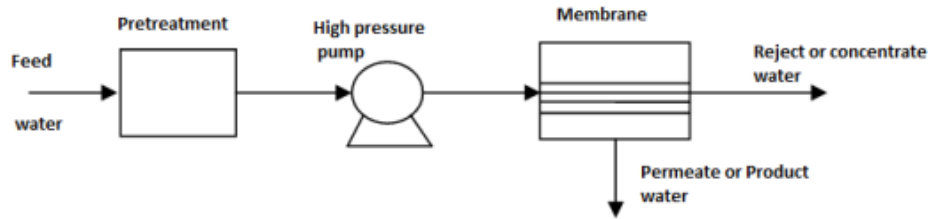


Figure 2-1: Schematic diagram of RO process.

2.2.2 Advantages of reverse osmosis

The advantages of reverse osmosis are it can remove the organic and inorganic pollutants simultaneously. Besides that, RO systems allow recovery/recycle of waste process streams with no effect on the material being recovered. RO process can considerably reduce the volume of waste streams so that these can be treated more efficiently and cost effectively by other processes such as incineration (Garud et al., 2011). RO plant can operate at ambient seawater temperatures of - 4 to 29 °C (25 to 85 °F). The process is electrically driven hence it is readily adaptable to powering by solar panels. In addition, RO systems can replace or be used in conjunction with others treatment processes such as oxidation, adsorption, stripping, or biological treatment (as well as many others) to produce high quality product water that can be reused or discharged (Garud et al., 2011).

2.2.3 Applications of reverse osmosis

Reverse Osmosis (RO) is a membrane based process technology to purify water by separating the dissolved solids from feed stream resulting in permeate and reject stream for a wide range of applications in domestic as well as industrial applications. RO process used in treatments of municipal wastewater by removing the dissolved solid which cannot be solved by conventional municipal wastewater treatment. RO is increasingly used as a separation technique in chemical and environmental engineering for the removal of organics and organic pollutants present in wastewater. A number of studies (Bellona et al., 2004; Xu et al., 2005) have been reported on the application of RO for the removal of organics such as endocrine disrupting chemicals, plastic additives, pesticides, pharmaceutically active compounds (PhaC's), benzene and toluene. Cellulose acetate and polyamide membrane has good salt rejection for

inorganic salts like sodium chloride ($NaCl$) and sodium sulphate (Na_2SO_4). Besides that, applicability of RO system for treating effluents from distillery spent wash. The spent wash in distillery is acidic having pH 3.94 -4.30, dark brown liquid with high BOD 45000– 100000 mg/ l and COD 90000 – 210000 mg/ l, and emits obnoxious odour but do not contain toxic substances, when this wastewater flow into other water stream for example river and sea will cause depletion of dissolved oxygen and bring threaten to the aquatic flora and fauna (Mane et al., 2006).

2.3 Forward osmosis (FO)

2.3.1 Fundamental of forward osmosis

According to the second law of thermodynamics, chemical potential tends to equilibrate in an isolated system (Ge et al., 2013). The FO process followed the second law of thermodynamics. Water transport from the low concentration solution (feed) to a relatively high concentration solution (draw) across the semi-permeable membrane which impermeable to salt particle. The FO utilizes an osmotic gradient instead of hydraulic pressure for the driving force for movement of water particles (McCutcheon et al., 2005). The water flux, J_w ($Lm^{-2}h^{-1}/LMH$), in an FO process can be described by the following equation (2-1) (Zhao et al., 2012):

$$J_w = A\sigma\Delta\pi \quad (2-1)$$

where A is the water permeability coefficient, and σ is the reflection coefficient. Generally, the effective $\Delta\pi$ across the selective layer of the membrane is lower than the bulk $\Delta\pi$, thus the real water flux across the membrane is lower than the theoretical value (Su et al., 2012). Because of concentration polarization, the effective osmotic pressure difference across the membrane declines as equation (2-2):

$$\pi_{D,a} - \pi_{F,a} < \pi_{D,b} - \pi_{F,b} \quad (2-2)$$

where $\pi_{D,a}$, $\pi_{F,a}$, $\pi_{D,b}$, $\pi_{F,b}$ represent the osmotic pressures of the draw and feed solutions at the membrane active layer surfaces and bulky solutions, respectively. As a result, equation (2-3) in real cases must be modified as (Su & Chung, 2011):

$$J_w = A\sigma (\pi_{D,a} - \pi_{F,a}) \quad (2-3)$$

The concept of desalination by the FO process for potable water is shown by the schematic diagram in Figure 2-2.

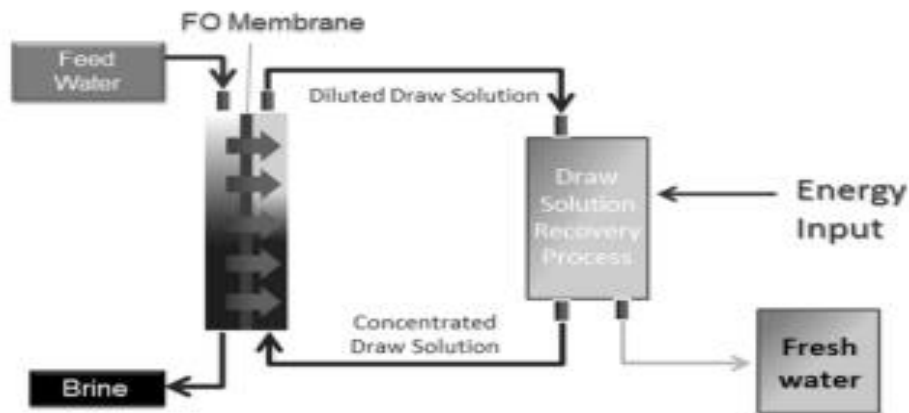


Figure 2-2: Schematic diagram of FO process.

2.3.2 Advantages of forward osmosis

Forward osmosis (FO) is the process of desalination of seawater at a notably reduced cost. Nowadays, forward osmosis technology is finding increasing use in desalination and water reuse. The absence of hydraulic pressure in FO process which use normal osmotic pressure which will occur on its own without any external pressure benefit in reduce the capital and operation cost. This is because, from the absence of the external high pressure, we can cut the cost for large pressure pumps and pressure exchanger systems. Besides that, FO process also potential in reduce fouling factor compared to other pressure-driven membrane process. In many cases, the fouling process is found that physically reversible which reduces the cleaning process (Lee et al., 2010; Boo et al., 2012, 2013). Forward osmosis has the small scale power generation.

2.3.3 Applications of forward osmosis

Recently, the applications of FO process increased steadily. Forward osmosis has been used in wastewater treatment. The feed stream is waste water with high amounts of total suspended solids (TSS) and other difficult-to-treat pollutants and the draw stream is tailored for the given application. Waste water with high TSS is difficult to treat with traditional pressure-driven membrane technologies due to continuous membrane clogging (fouling) and ensuing membrane performance decrease. In order to treat high TSS waste waters with pressure-driven membranes, pre-treatment processes are

necessary, which further increase CAPEX and OPEX costs. However, forward osmosis membranes are far less prone to fouling, which makes them ideally suited to treat high TSS waste water. During operation, the FO sub-system extracts fresh water from the high TSS waste water stream, thus reducing its volume, and at the same time the tailored draw is diluted and fed through a second membrane sub-system to produce potable fresh water permeate and a re-concentrated draw solution. Besides that, the continuous bench scale-system used FO as pre-treatment for RO process (Holloway et al., 2007). The applications also include food processing. Forward osmosis (FO) process was applied to concentrate the orange juice. The orange juice as feed solution, the difference of osmotic pressure will makes the water flow from orange juice to draw solution across a semi-permeable membrane without apply any energy. The draw solutions choose are salt solutions which are NaCl, $CaCl_2$, KCl, and $MgSO_4$ (Beaudry & Lampi, 1990). Moreover FO process used in pharmaceutical application for example recent developments in materials science have allowed the use of FO in controlled drug release in the body. Zero-order delivery (i.e., constant delivery rate) is the desired target product performance in many extended-duration drug delivery applications. Zero-order delivery assures that plasma or tissue drug concentrations will not fall below minimum efficacious thresholds nor will the maximum concentrations exceed levels that are toxic or provoke uncomfortable side effects. Drug delivery systems based on the principles of osmosis have demonstrated the capacity to provide zero-order delivery in a number of human, animal, and research applications. These include systems administered orally to the gastrointestinal tract (oral osmotic systems), systems administered intraruminally to cattle, systems implanted in laboratory and food-producing animals, and systems implanted for human therapy (Wright et al., 2003). Table 2-1 and Figure 2-3 showed the comparison between RO and FO process.

Table 2-1: Comparison between RO and FO process (Liu et al, 2009).

Sort	Reverse osmosis	Forward osmosis
Pressure driven	Hydraulic pressure	Osmotic pressure
Energy consumed	High	Low
Membrane fouling	High percentage	Low percentage
Environmental effect	Harmfully	Friendly

Challenges	Feed pressure, feed salinity, and water flux	Draw solution and membrane
Application	Treatment in municipal wastewater, separation of organic and inorganic pollutants, treating effluents from distillery spent wash	Wastewater treatment, food processing, controlled drug released

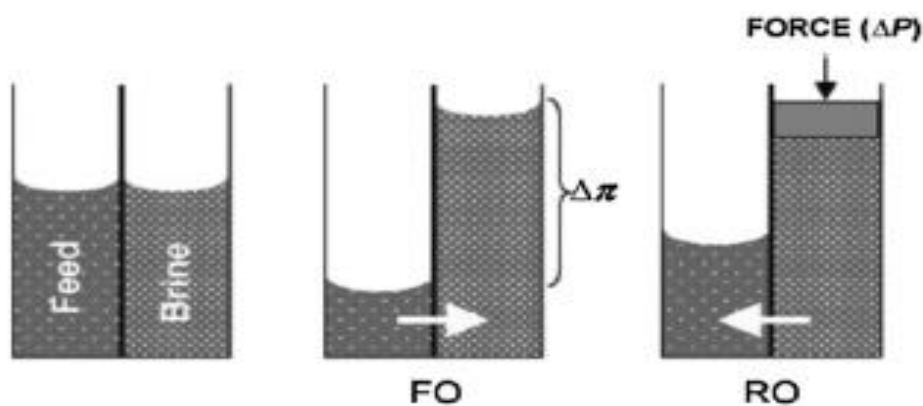


Figure 2-3: Comparison between forward osmosis and reverse osmosis- Adapted from (Cath et al. 2006)

2.4 Forward osmosis membrane

There are three parameters used to describe FO membrane properties which are the pure water permeability, solute permeability and the resistance to salt diffusion within the support layer. These three parameters used as the standard criteria for FO membrane characterization (Kim et al., 2014). The parameters pure water permeability and solute permeability which related to the active layer of the FO membrane are measured by applying hydraulic pressure in RO mode experiments. Another parameter, the resistance to salt diffusion within the support layer is measured by FO mode experiments. These all parameters evaluated by using two different types of experiment (Cath et al., 2013). Besides that, the support layer of the membrane in FO process must be thinner, less tortuous and more porous if compare with membrane of RO process which can decrease the physical resistance (Yip et al., 2010). A porous support layer,

nevertheless, is necessary to sustain desirable mechanical strength of the membrane. New explorations and developments in phase inversion and membrane formation processes, therefore, are urgently needed to fabricate membranes with a thin and fully porous support layer that can minimize ICP effect, while at the same time maintaining a thin and dense selective layer for sufficient water flux and salt rejection. The current membranes used for FO include conventional RO membranes made from thin-film polymerization on a polysulfone layer supported by nonwoven fabrics, HTI (Hydration Technologies Inc., OR, USA) FO membranes made of cellulose triacetate coated on polyester mesh, both of which have flat sheet configurations.

2.4.1 Thin film composite (TFC) polyamide (PA) based membranes (Interfacial Polymerization)

A typical TFC membrane comprises a top skin layer mostly made from polyamide formed by an interfacial polymerization (IP) reaction at the surface of a micro porous substrate (Khorsidi et al., 2015). The support substrate usually consists of polysulfone (PSf) or polyethersulfone (PES) cast over a polyester fabric, typically polyethylene terephthalate (PET), using a phase inversion technique (Sadrzareh et al., 2013). The composite structure of the TFC membranes provides beneficial flexibility in their design, as both the top active and the bottom support layers can be tailored separately to optimize the final performance (Klaysom et al., 2013). Although the TFC membranes are very popular in pressure-driven separation processes like reverse osmosis (RO) and nanofiltration (NF), their application in FO is at the early stage (Wei et al., 2011). TFC-RO and TFC-NF membranes typically have a dense active layer to provide high selectivity and a thick support layer to offer mechanical stability when external hydraulic pressure is applied. But these membranes exhibit low permeation flux when tested for the FO process, as in the absence of hydraulic pressure, the dense active layer hinders the permeation flux through the membrane. Additionally, the thick and dense support layer provides a large resistance against the diffusion of the draw solute to the back side of the active layer, contributing to internal concentration polarization (ICP) phenomenon, thereby adversely affecting the water permeation of the membranes (McCutcheon et al., 2006). The ICP generally occurs inside the pores of the porous support layer and depends mainly upon the thickness, porosity and tortuosity of the support layer rather than the hydrodynamics of the flow. Figure 2-4 showed the schematic diagram for thin film composite membrane.

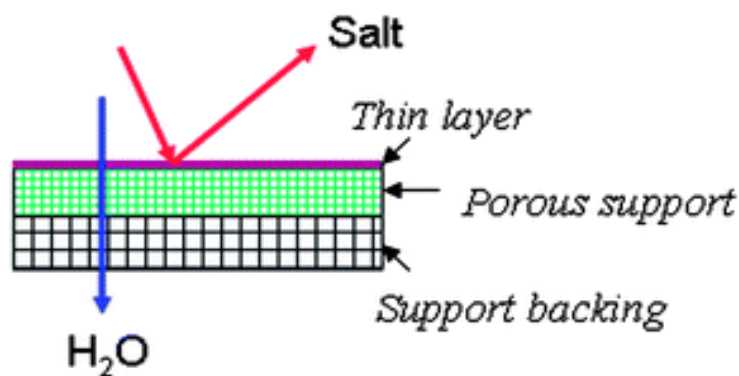


Figure 2-4: Schematic diagram for thin film composite membrane.

2.4.2 Cellulose Triacetate (CTA) membrane (Phase Inversion)

Ever since Loeb and Sourirajan invented the phase inversion process to fabricate asymmetric polymeric membranes more than 40 years ago, cellulose triacetate (CTA) has been a popular material for various separation applications. Cellulose triacetate (CTA) membranes are the current available commercial membranes for forward osmosis process which were developed by HTI (Hydration Technologies Albany, OR). CTA membranes were prepared by immersion precipitation. Casting composition and preparation conditions — 1,4-dioxane/acetone ratio, CTA/CA ratio, substrate type, casting thickness, evaporation time and annealing temperature — were tested for their effects on formation and subsequent performance of membranes. Membranes were characterized by various methods, and their performances were tested against commercially available membranes (Nguyen et al., 2013). The structure of the CTA membrane is asymmetric which combined of one functional dense layer and another side is porous support layer with an embedded polyester mesh (Zhang et al., 2013). The embedded polyester mesh provides mechanical support (Cath et al., 2006). CTA membranes are in hydrophilic nature enhance these membranes readily wettable. Therefore, CTA membrane have ability in high permeable for water particle and resistance for fouling (McCutcheon & Elimelech, 2008). In a world where environmental protection becomes important, it is also notable that CTA is a green polymer as it derives from acetyl substitution of cellulose, which is one of the most common natural organic compounds on earth. Figure 2-5 showed the schematic diagram for asymmetric composite membrane. Table 2-2 showed the comparison between TFC and CTA membrane.

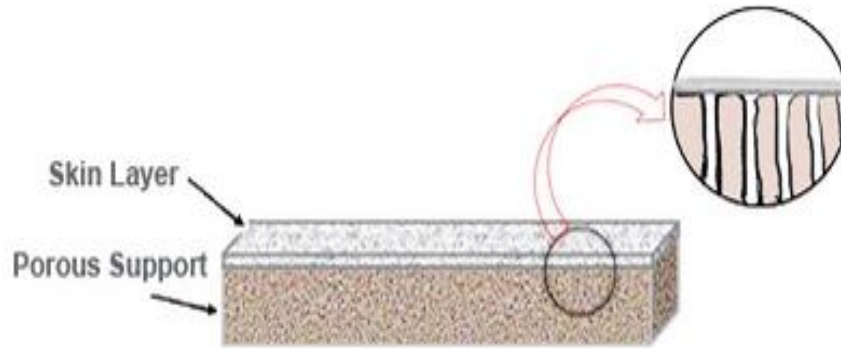


Figure 2-5: Schematic diagram for asymmetric composite membrane.

Table 2-2: Comparison between TFC and CTA membrane.

Sort	Thin film composite (TFC) polyamide (PA) based membranes	Cellulose Triacetate (CTA) membrane
Process	Interfacial polymerization	Phase inversion
Status	New stage	Commercialise membrane
Support layer	Thick	Thin
Water permeability	Low	High

2.5 Draw solutions

A draw solution is the solution which has the higher osmotic pressure than feed solution which as a driving force for water particle to pass through a semi-permeable membrane. At the end of the process, draw solution becomes dilute and feed solution become concentrated. An optimised draw solution must have the characteristics of high water flux, low reverse salt diffusion, easy recovery of the diluted draw solution, less toxicity and reasonable low cost (Ge et al., 2013). In addition, any trace concentration of the draw solutes in the final desalted water should meet the WHO Guidelines for drinking-water quality (Duranceau, 2012). Nowadays many of the research draw solutions met the problem of high salt leakage and high energy consumption in recovering the diluted draw solution. The draw solution which most commonly used in FO process is ammonium bicarbonate, NH_4HCO_3 . This draw solution formed by mixing ammonium carbonate and ammonium hydroxide to form three different salt species: ammonium bicarbonate, ammonium carbonate and ammonium carbamate (McCutcheon et al., 2005, 2006; McGinnis & Elimelech, 2007). Besides that, Polyelectrolytes of IBMA-Na were explored as new draw solution in the FO process. The characteristics of high

solubility in water and flexibility in structural configuration ensure the suitability of IBMA-Na as draw solutes and their relative ease in recycle through pressure-driven membrane processes. IBMA-Na was produced by hydrolysis reaction of poly (isobutylene-alt-maleic anhydride) with sodium hydroxide. The hydrolysis of poly (isobutylene-alt-maleic anhydride) is arguably the most important reaction in terms of their application given their widespread use as polyelectrolytes (Johnson et al., 2010). Strong polyelectrolyte draw solution can dissolve well in water, which ensures the high osmotic pressure and high water flux created by the resultant aqueous solution. Besides that, strong polyelectrolytes have various molecular weights and structural sizes, which enable them to be separated readily from water by low pressure-driven processes depending on the selected system. Meanwhile, their expanded structure would be expected to minimize the reverse salt diffusion (Ge et al., 2012). In FO osmosis process, polyelectrolyte has a friendly pH value with ester bond CTA membrane and can generate high osmotic pressure and produced high water flux. Besides that, polyelectrolyte as draw solution also easily to recovery by using simple method (Wang et al., 2016). The overall performance demonstrates that IBMA-Na is promising as new draw solution, and the new concept of using polyelectrolytes as draw solution in FO processes is applicable. Table 2-3 showed the overview of draw solutions used for FO process in the last two decades.

Table 2-3: Overview of draw solutions used for FO process in the last two decades. (Linares et al. 2014)

Year	Draw solution	Post-treatment
1992	Sugar cane	Reverse osmosis
2002	$KNO_3, SO_2, and NH_4NO_3$	Precipitation (cooling) and separation through thermal waste heat
2005-2011	Ammonia-carbon dioxide solution (ammonium bicarbonate and ammonium hydroxide)	Thermal decomposition

2006	Magnetoferritin particles	Magnetic field
2010	Crosslinked superabsorbent polymer	Microfiltration
2011-2013	Ionic polymer hydrogels	Dewatering hydrogels via external pressure
2011	Hydrophilic nanoparticles	Ultrafiltration
2012	Divalent salts (Na_2SO_4 , $MgSO_4$)	Nanofiltration
2012	Cloud point solutes (polyethylene glycols)	Cloud point extraction (thermal process)
2012	Retrograde soluble solutes (polyoxy-random copolymer)	Coalescer (thermal process) and nanofiltration
2013	Thermally responsive hydrogels with a semi-interpenetrating network	Dewatering hydrogels via thermal process
2013	$CuSO_4$	Metathesis precipitation
2013	Thermoresponsive magnetic nanoparticles	Magnetic field
2013	NaCl 0.2-1 M	Solar-powered electro dialysis

2.6 Selection of sodium sulphate (Na₂SO₄) as draw solution

Three parameters were used to evaluate the performance of the draw solutions tested. Water flux, reverse salt diffusion, and cost. In the term of water flux, sodium sulphate (Na₂SO₄) has a high water flux because it has high osmotic pressure (driving force) than other material studied. This can be explained by the osmotic pressure equation (2-4) below:

$$\pi_i = \phi_i m_i RT c_i \quad (2-4)$$

Osmotic pressure (π_i) depends on the molecular weight of solute (m_i), sodium sulphate has large molecular weight therefore has higher osmotic pressure (Wahab et al., 2015). Besides that, sodium sulphate contains larger-sized hydrated anions showed the lowest reverse salt diffusion, regardless of their paired cations. Na₂SO₄ has relatively low solute costs which is \$0.003/L (Achilli et al., 2010). Therefore, sodium sulphate was selected as draw solution because of high water flux, low reverse salt flux and low cost.

2.7 Challenges of forward osmosis

FO does not operate with hydraulic pressure but with osmotic pressure difference. There are several challenges faced by FO that need to find the optimum solutions. This challenges will limit its application in large scale processes. Some of these limiting factors include concentration polarization, membrane fouling, and reverse solute diffusion.

2.7.1 Concentration polarization

Concentration polarization (CP) arising in pressure driven and osmotically driven membrane separation processes. CP develops due to occurrence of concentration difference at the membrane-solution interface arising from selective transfer of species through a semi-permeable membrane (Hoek et al., 2013). In membrane processes that are osmotically driven such as FO and PRO, CP arises due to concentration gradient between draw and feed solutions through an asymmetric FO membrane. CP arising in FO process can be further classified as internal concentration polarization (ICP), which occurs within the membrane support layer, and external concentration polarization (ECP), which exists at the membrane active layer surface. In FO, the transmembrane osmotic pressure is chiefly responsible for controlling the water flux and recovery. Based on the extensive research conducted on CP, it was found that the occurrence of CP on both sides of FO membrane greatly reduces the effective transmembrane osmotic

pressure; therefore, it is one of the major factors that contributes to declining water flux and recovery across the semi-permeable membranes.

2.7.1.1 External concentration polarization (ECP)

ECP can happen in both FO and RO process. This phenomenon occurs because the difference in the concentration of the solution at the membrane surface from that of the bulk solution in the active layer of the membrane. Unlike pressure-driven membrane process where only concentrative ECP can occur, both concentrative and dilutive ECP can take place in membrane processes driven by osmotic pressure in accordance with membrane orientation. Concentrative ECP takes place when the dense active faces the feed (FO mode) whereas, dilutive ECP occurs when the dense active layer faces the draw solution (PRO mode) due to diffusion of water from the side of the feed to that of the draw solution (Puguan et al., 2014). ECP plays a substantial role in decreasing the osmotic gradient; hence, inhibiting the flux of water across the membrane. However, the extent of ECP is considerably smaller than ICP during FO.

2.7.1.2 Internal concentration polarization (ICP)

It is evident from experimental studies that the diminution of water flux in FO is mainly caused by ICP. ICP refers to the occurrence of CP layer within the porous layer of the membrane due to the inability of the solute to penetrate the dense selective layer of the membrane easily (Zhou et al., 2014). Depending on the orientation of asymmetric membranes, two types of ICP can occur: concentrative ICP and dilutive ICP. When the draw solution is against the support layer, dilutive ICP occurs. Varying the concentration of the feed solution produces a linear relationship between net osmotic pressure and flux. When the draw solution is against the active layer, concentrative ICP occurs. Now, a non-linear relationship between bulk osmotic pressure difference and flux exists. Figure 2-6 showed the schematic of FO and PRO mode.

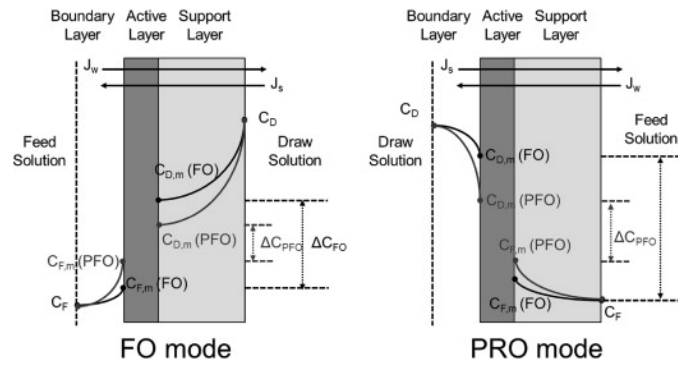


Figure 2-6: Schematic diagram of membrane orientation in FO and PRO mode.

2.7.2 Membrane fouling

Membrane fouling is significantly associated with all membrane processes and can adversely affect the performance of membranes and decrease the water flux across the membrane. However, membrane fouling is less prominent in osmotically driven membrane processes compared to pressure-driven processes because the former processes operate with low or no hydraulic pressure. Hence, FO or PRO can be attractive choices over other pressure-driven processes because lower fouling membranes require less cleaning and maintenance, have a longer membrane life, and can produce more product water over time; hence lowering the operational and capital costs (Lee et al., 2010).

2.7.3 Reverse solute diffusion

Reverse solute flux across the membrane from the draw to the feed solution seems to be unavoidable in FO due to the concentration gradient. According to Cath et al., the influence of reverse salt diffusion will influence the efficiency of FO process. Recently, many researches have been conducted to study the effect of reverse diffusion of the draw solute on membrane fouling. It has been shown by Lee et al. and Lay et al. that draw solute's reverse flux can worsen membrane fouling by heightening the CEOP effect. Hence, solutions containing multivalent ions with lower diffusion coefficients may be desirable in situations where considerable salt rejection is desired. However, after reverse solute diffusion, some multivalent ions like calcium and magnesium ions may intensify membrane fouling by interfering with the fouling agents in the feed. Additionally, more severe ICP can be caused due to the lower solution diffusion coefficients and larger ion sizes of multivalent ion solutions.

2.8 Summary

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

3. MATERIALS AND METHODS

3.1 Overview

This chapter discusses on how the experiment was carried out. It includes the chemicals needed for the draw solution and feed solution. Besides that, this chapter includes the membrane used in the experiment, known as cellulose triacetate (CTA) membrane. The methodology were divided into two parts which are the characterization of CTA membrane in terms of physical and chemical properties. In addition, the permeation module for the forward osmosis process is demonstrated in this chapter. Lastly, the method for which the data was tabulated and also the way of discussion of results are discussed in this chapter. The whole process is summarized in Figure 3-1.

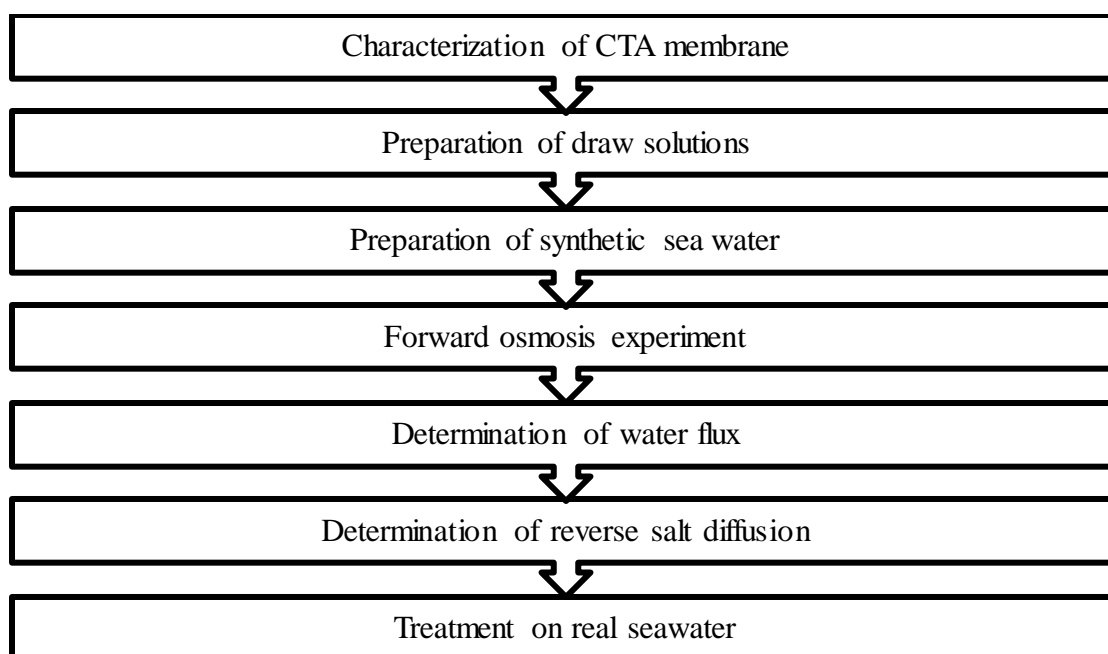


Figure 3-1: Overall research flow.

3.2 Chemicals

Sodium sulphate was purchased from Merck Co. for preparation of draw solutions. Solid sodium hydroxide and sulphuric acid used in control the pH of draw solutions were purchased from Merck Co. Sodium chloride, $\geq 99.5\%$ used in preparation of synthetic sea water purchased from Merck Co. Deionized water used for rinsing and preparation. Besides that, deionized water (DI) water was used for all of the reactions and DS preparation. Membrane used was cellulose triacetate (CTA) membrane (HTI technology). CTA membrane was used to separate the sodium chloride (NaCl) feed solution from the draw solution and allowed forward osmosis to occur.

3.3 Preparation of draw solutions (Na_2SO_4)

Five different concentrations of draw solutions (Na_2SO_4) in (1.0M, 1.25M, 1.50M, 1.75M and 2.0M) were prepared by dissolved 71g, 88.78g, 106.53g, 124.29g and 142.04g of sodium sulphate into 500ml of deionised water. The draw solution for five different concentrations were adjusted in pH 3, 7 and 9 by adding different drops of diluted sodium hydroxide and sulphuric acid. The solutions were stir to maintain in homogeneous solution.

3.4 Preparation of synthetic sea water

A 35g/L NaCl feed solution was prepared as synthetic sea water to be used as the feed solution for the forward osmosis experiment. 35g/L of NaCl was used as it is the average salt concentration in the real sea water. The volume of the salt solution was 500ml.

3.5 Permeation module

The permeation module is shown in figure 3-2.

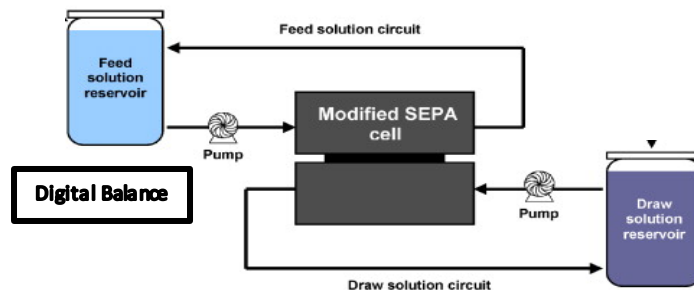


Figure 3-2: Schematic diagram for bench-scale of forward osmosis (Achilin et al., 2010).

3.6 Methodology

3.6.1 Characterization of CTA membrane performance

The forward osmosis experiment was conducted on a lab scale unit. The lab scale unit is shown in figure 3-3.



Figure 3-3: Lab scale unit

First, the Cellulose Tri Acetate (CTA) Membrane was inserted between two chambers to separate the feed solution from the draw solution. The membrane was orientated such that its active layer faced the draw solution (AL-DS). Then, 500ml of 1.0M of draw solution with 500ml of 35g/L of NaCl solution were prepared in respective beakers. The feed solution was placed on a digital balance and weight changes were recorded for 1 hour in 5 minutes interval after the peristaltic pump was turned on to calculate the permeate flux. Peristaltic pump was used to circulate the feed and draw solutions in the process. Before the experiment starts, the pH of draw solution was determined by using pH meter to make sure in pH 7. Besides that, the conductivity of the feed solutions were measured and recorded using conductivity meter before and after the experiment. Temperature was maintained at room temperature and the pressure was 1 atm. After running the experiment for 1 hour, all the apparatus was cleaned by using deionized water and the experiment was repeated by using the same cellulose triacetate (CTA) membrane for concentration 1.25M, 1.50M, 1.75M and 2.0M. After that, the whole experiment was repeated by manipulated the pH of draw solution to 3 and 9 by using diluted hydrochloric acid and sodium hydroxide. After finished the three sets, the whole three sets were repeated by changing the orientation of CTA membrane to active layer faced feed solution (AL-FS). The reverse salt flux was determined by measuring the initial conductivity and final conductivity after 1 hour of feed solution and recorded. A calibration curve was plotted to determine the amount of reverse salt flux based on different concentration of draw solution.

After the experiment, the volume of water permeated was calculated by using equation (3-1) as shown below:

$$\Delta V = \frac{\Delta Mass}{Density\ of\ water} \quad (3-1)$$

where ΔV is the volume of water permeated, $\Delta mass$ is the changes in mass of feed solution and density of water is $1000\ kg/m^3$. After that, the water flux of each draw solution at different concentration was calculated by using equation (3-2):

$$\Delta J_w = \frac{\Delta V}{A\Delta t} \quad (3-2)$$

where J_w is the water flux, ΔV is volume of water which permeates through the membrane, Δt is time taken in minutes and A is the effective area of the membrane. The reverse salt diffusion was calculated by using equation (3-3):

$$\Delta J_s = \frac{\Delta(C_f V_f - C_i V_i)}{A\Delta t} \quad (3-3)$$

where J_s is the reverse salt diffusion, $\Delta(C_f V_f - C_i V_i)$ is concentration and volume of feed solution changed, Δt is time taken in minutes and A is the effective area of the membrane.

3.6.2 Characterization of CTA membrane morphology

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

3.7 Treatment on real seawater

After determination the optimum concentration and pH of draw solution and the orientation of CTA membrane, the parameters were used in the treatment of desalination of real seawater as feed solution. Water flux and reverse salt flux were determined and discussed.

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

4. RESULTS AND DISCUSSION

4.1 Overview

This chapter discussed about the results obtained from forward osmosis experiment done in lab scale unit by manipulating five different concentrations of Na_2SO_4 draw solution. Besides that, three different pH of Na_2SO_4 draw solution also manipulated by adding different amount of diluted NaOH or H_2SO_4 at two different orientation of membrane. Therefore, in this chapter the effect of different concentration and pH of draw solution at two different orientation of membrane on the performance of FO process were discussed. In addition, reverse salt diffusion will be discussed to determine which concentration of Na_2SO_4 draw solution will caused highest reverse salt diffusion which will decrease the efficiency of forward osmosis performance. The effect of draw solution pH on reverse salt diffusion will be discussed too. Based on these discussion, the optimal condition of concentration and pH of Na_2SO_4 draw solution will be obtained at optimal orientation of CTA membrane for the treatment of synthetic seawater using FO. After this, treatment of real seawater will perform with these optimal condition to compare the FO performance for synthetic sea water and real seawater.

4.2 Morphology of CTA membrane

As shown in the micrographs in Figure 4-1, there were no obvious changes for CTA membranes at both active and support layer before and after the forward osmosis experiment. According to Alsvik & Hägg (2013), foulant deposition occurs on the relatively smooth active layer in FO mode. However, the result obtained can be supported by Mi and Elimelech (2010) who stated that CTA membranes showed almost no natural organic matter (NOM) fouling and were easier to clean. The low fouling tendency of the CTA membrane confirms prior literature reports that CTA based commercial FO membranes have low fouling tendency (Jin et al., 2012; She et al., 2012).

The uneven active layer surface of CTA membrane as shown in Figure 4-1(a) and Figure 4-1(b) is caused by the drying process of the membranes in oven which has caused the shrinking of membrane pores (Ji & Wei, 2009). CTA membranes were cast with an embedded polyester mesh for membrane support as shown in Figure 4-1(c) and Figure 4-1(d). Due to the presence of such woven meshes, the thickness of the

membranes was highly non-uniform, and regions away from the mesh fibers were thinner than regions where fibers were located (Fane et al., 2012).

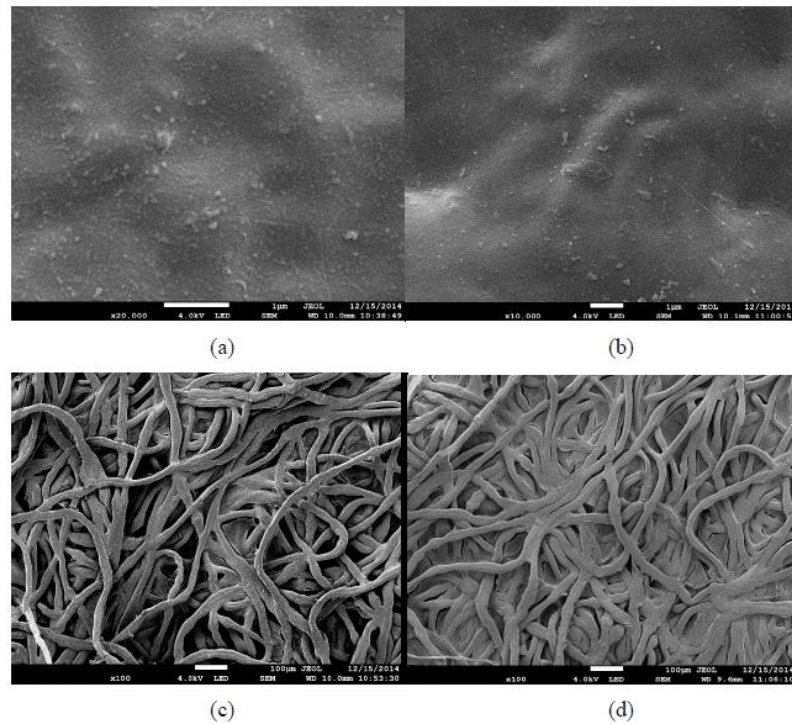


Figure 4-1: FESEM images of CTA membrane (a) at active layer before the FO process, (b) at active layer after the FO process, (c) at support layer before the FO process, (d) at support layer after the FO process.

4.3 Water flux

Benchmark forward osmosis experiments were conducted with synthetic seawater to determine the water flux permeate through CTA forward osmosis membrane. Experiments were conducted with Na_2SO_4 draw solution at various concentrations to elucidate the relationship between water flux and driving force. The draw solutions concentration are in 1.0M, 1.25M, 1.5M, 1.75M and 2.0M. The pH of draw solution Na_2SO_4 was at pH 3, 7 and 9 by adjusting using few drops of diluted sodium hydroxide and sulphuric acid. The orientation of the membrane are active layer faced draw solution (AL-DS) and active layer face feed solution (AL-FS). The mass and volume change of feed solution which is synthetic seawater were recorded for 1 hour in 5 minutes interval. Water flux data were used to determine the water permeability of the forward osmosis membrane and the effect of concentration polarization on the performance of the process. The method of calculating flux was derived in the following equation (4-1) and (4-2) (You et al., 2012).

$$\Delta J_w = \frac{\Delta V}{A \Delta t} \quad (4-1)$$

Where J_w is the water flux, ΔV is volume of water which permeates through the membrane, Δt is time taken in minutes and A is the effective area of the membrane.

$$\Delta V = \frac{\Delta Mass}{Density\ of\ water} \quad (4-2)$$

Where ΔV is the volume of water permeated, $\Delta mass$ is the changes in mass of feed solution and density of water is $1000\ kg/m^3$. Based on the formula, the water flux is inversely proportional to the area of the membrane and the time taken. In this experiment, the area of the membrane is constant which is $0.0042\ m^2$ and the time taken is 60 minutes. Therefore, the water flux is manipulated by volume of water which permeates through the membrane. By using the data obtained from the experiment, a series of flux was calculated to determine the efficiency of the different concentrations of Na_2SO_4 draw solution with different draw solution pH and two orientations of CTA membrane.

4.3.1 Results

The results obtained are tabulated in terms of calculation of water flux to compare the efficiency of FO in terms of concentrations at pH 3, 7 and 9 in two different orientation. Water flux for concentration 1.0, 1.25, 1.50, 1.75 and 2.0 M at pH 3, 7 and 9 by CTA membrane active layer faced draw solution (AL-DS) and active layer faced feed solution (AL-FS) were compared in Table 4-1 and Table 4-2.

Table 4-1: Water flux for draw solution in different concentrations and pH 3, 7 and 9 at active layer face draw solution (AL-DS).

Concentration of Draw Solution (M)	Water flux, J_w ($\frac{m^3}{m^2 \cdot min}$)		
	DS pH 3	DS pH 7	DS pH 9
1.00	6.58E-05	2.99E-05	4.05E-05
1.25	2.49E-05	5.08E-05	5.42E-05
1.50	2.85E-05	6.07E-05	6.46E-05
1.75	4.36E-05	1.07E-04	7.65E-05
2.00	6.90E-05	1.05E-04	8.37E-05

Table 4-2: Water flux for draw solution in different concentrations and pH 3, 7 and 9 at active layer face feed solution (AL-FS).

Concentration of Draw Solution (M)	Water flux, J_w ($\frac{m^3}{m^2 \cdot min}$)		
	DS pH 3	DS pH 7	DS pH 9
1.00	3.19E-05	3.21E-05	3.17E-05
1.25	3.17E-05	5.23E-05	3.15E-05
1.50	5.59E-05	5.28E-05	6.30E-05
1.75	8.06E-05	5.42E-05	4.85E-05
2.00	6.22E-05	6.05E-05	7.43E-05

4.3.2 Discussion

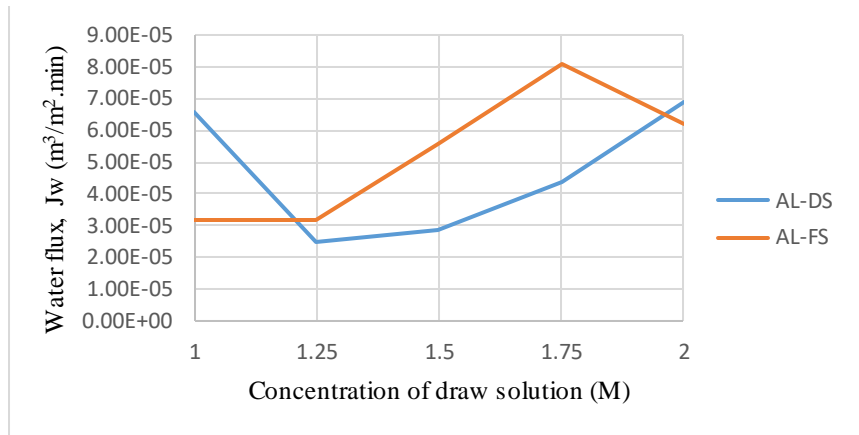


Figure 4-2: Water flux for different concentrations in orientation AL-DS and AL-FS at pH 3.

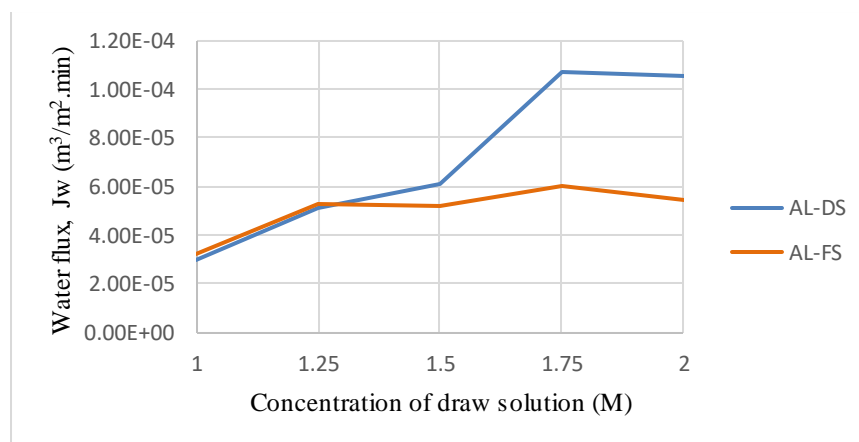


Figure 4-3: Water flux for different concentrations in orientation AL-DS and AL-FS at pH 7.

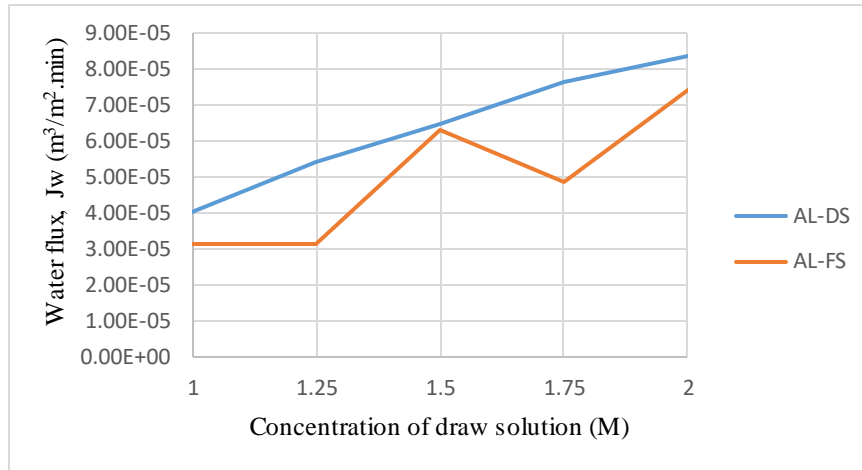


Figure 4-4: Water flux for different concentrations in orientation AL-DS and AL-FS at pH 9.

Effect of concentration of draw solutions

Firstly, the discussion will be about the relationship of the water flux and the concentrations of draw solution 1.0, 1.25, 1.50, 1.75 and 2.0 M. From the Figure 4-2, Figure 4-3 and Figure 4-4, the trend of the overall result for water flux at pH 3, 7 and 9 showed that the higher the concentration of draw solution, the higher the water flux. The concentration is an important factor for a draw solution since it directly affects its osmotic pressure and viscosity, and determines its FO performance and the relative investment cost. Morse equation derived from the van't Hoff equation, the osmotic pressure of a solution, π , can be expressed as equation (4-3) below:

$$\pi = iMRT = i\left(\frac{n}{V}\right)RT \quad (4-3)$$

where i is the Van't Hoff factor, M is the molarity of the solute which is equal to the ratio of the number of solute moles (n) to the volume of the solution (V), R is the gas constant of $8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$, and T is the absolute temperature. Hence, to achieve a high osmotic pressure, a good solubility of the draw solute in water is required to get a high n or M value. Therefore, osmotic pressure is directly proportional to molar concentration of the solution. When concentration of the draw solution increases, the osmotic pressure increases and the water flux permeate through membrane also increases. Although the higher the concentration, the higher the osmotic pressure but the growth is non-linear, and exorbitant draw solution concentration may bring adverse effects, like increasing solution viscosity, intensifying concentration polarization.

Effect of CTA membrane orientation

Generally, two membrane orientation modes exist in the FO process: one with the active layer facing the feed solution (FO mode) and the active layer facing the draw solution (PRO mode). Membrane orientation is important because water flux behaviours are different for different membrane orientations, even with identical concentrations of draw solution (i.e., identical osmotic pressure).

As compare the water flux result from the Figure 4-3 and Figure 4-4, the water flux for AL-DS (PRO) are higher than AL-FS (FO). From Table 4-1 and Table 4-2, showed that the highest water flux in AL-DS orientation is $1.07 \text{ E-}04 \text{ m}^3 / \text{m}^2 \cdot \text{min}$ being 46% higher than that of AL-FS orientation which the highest water flux in AL-FS orientation is $8.06 \text{ E-}05 \text{ m}^3 / \text{m}^2 \cdot \text{min}$.

The result obtained same as the FO studied. ICP is more severe in FO mode where dilutive ICP occurs compared to the concentrative ICP that occurs in PRO mode (Ong, 2014). Besides that, dilutive ICP will be more severe with larger molecular weight solutes that cannot diffuse as quickly through the porous support, sodium sulphate that used as draw solution has large molecular weight. Furthermore CTA membrane has gradient density of membrane materials, which is high in active layer side and low in the support layer (Wei et al., 2011). This gradient density composes the asymmetric structure of the membrane with a tight layer (active layer) to reject salts, and a porous layer (support layer) to enable high water penetration causing a better water flux when bottom layer is faced towards the draw solution due to the less severe ICP phenomenon in this orientation.

Effect of pH of draw solution

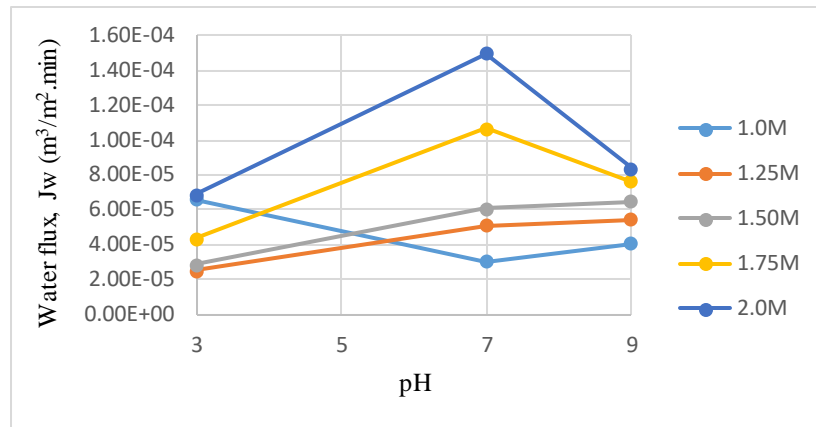


Figure 4-5: Water flux at pH 3, 7 and 9 in different concentration of draw solution in AL-DS orientation.

From the Figure 4-5, as compare the pH for draw solution at pH 3, 7 and 9, the water flux permeate through CTA membrane is the highest at pH 7 which is $1.07 \text{ E-}04 \text{ m}^3/\text{m}^2 \cdot \text{min}$ and for the overall trend, the water flux are higher at pH 7. Related to pH, it is hypothesized that the electrostatic repulsion between ionisable functional groups of the membrane polymeric matrix increases as the solution pH increase, thereby leading to an increased average pore size and higher permeate flux. Indeed, both the active layer and the supporting layer became more negatively charged with increasing feed solution pH (Esparra-Alvarado, 2014). Under basic conditions, the number of deprotonated hydroxyl groups (with negative charge) in the membrane matrix increased notably, which probably forced adjacent polymers apart, thus increasing water permeability (Wang et al., 2016). However, because osmotic pressure is the driving force in FO, and this pressure was relatively stable under different pH conditions, the overall variation of membrane flux with pH was slight.

4.4 Reverse salt diffusion

The calibrated conductivity meter was used to measure the conductivity in the feed tank. All the conductivities measured from the feed solution were converted in the range of the standard curve which was built from a series of single solutions and indicated the relationship of conductivity and concentration in the Figure A-1. The concentration of the draw solution transporting to the feed solution was thereafter obtained directly from the standard curve. The reverse solutes flux (J_s (GMH)) was determined from the concentration increase of the feed solution as follow Equation (4-4)

$$J_s = \frac{V_t C_t - V_0 C_0}{At} \quad (4-4)$$

where, C_0 (g/L) and V_0 (L) are the initial concentration and initial volume of the feed solution, respectively, and C_t (g/L) and V_t (L) are the solutes concentration and the volume of the feed solution measured at time of t , respectively.

4.4.1 Results

The results obtained are tabulated in terms of calculation of reverse salt flux to compare the efficiency of FO in terms of concentrations at pH 3, 7 and 9 in two different orientation. Reverse salt flux for concentration 1.0, 1.25, 1.50, 1.75 and 2.0 M at pH 3, 7 and 9 by CTA membrane active layer faced draw solution (AL-DS) and active layer faced feed solution (AL-FS) is compare in Table 4-3 and Table 4-4.

Table 4-3: Reverse salt diffusion for draw solution in different concentrations and pH 3, 7 and 9 at active layer face draw solution (AL-DS).

pH	Reverse salt diffusion ($g/m^2 \cdot h$)				
	1.0M	1.25M	1.50M	1.75M	2.00M
3	1.31	3.54	4.43	6.56	8.00
7	1.86	3.22	3.66	6.44	9.08
9	1.73	2.91	1.78	5.52	5.62

Table 4-4: Reverse salt diffusion for draw solution in different concentrations and pH 3, 7 and 9 at active layer face draw solution (AL-FS).

pH	Reverse salt diffusion				
	1.0M	1.25M	1.50M	1.75M	2.00M
3	1.61	3.50	4.19	5.74	7.94
7	2.31	3.88	5.40	6.50	7.06
9	3.76	4.34	4.65	6.21	7.52

4.4.2 Discussion

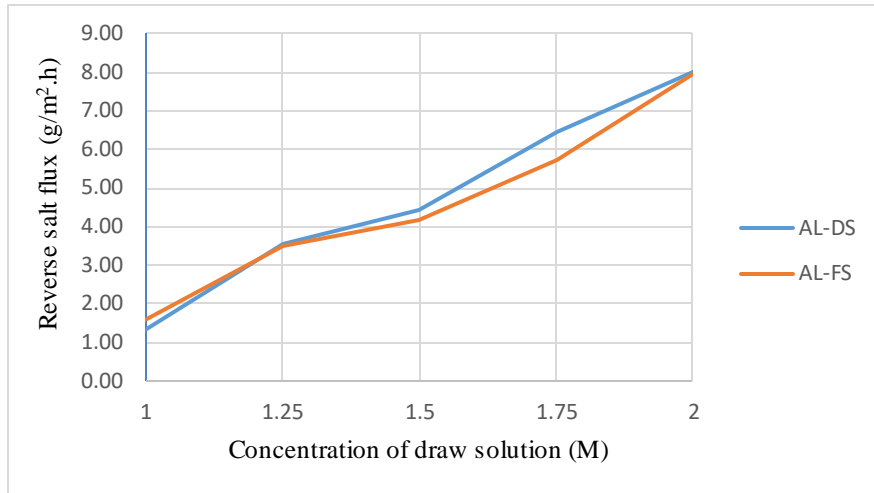


Figure 4-6: Reverse salt flux for different concentrations in orientation AL-DS and AL-FS at pH 3.

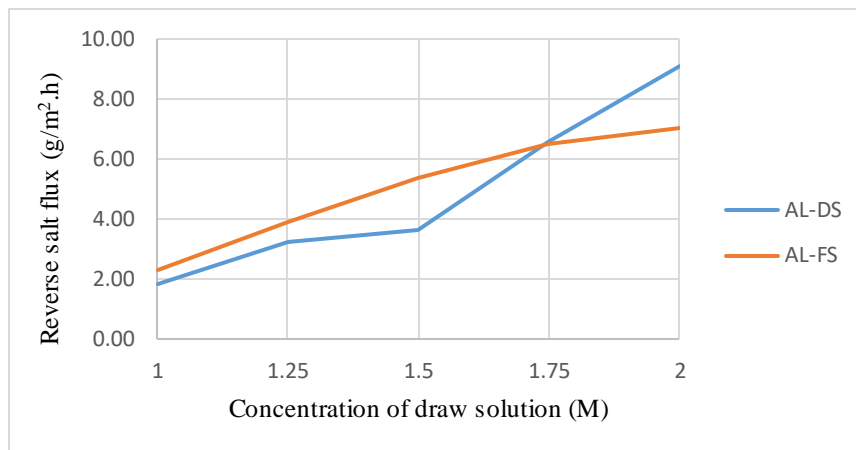


Figure 4-7: Reverse salt flux for different concentrations in orientation AL-DS and AL-FS at pH 7.

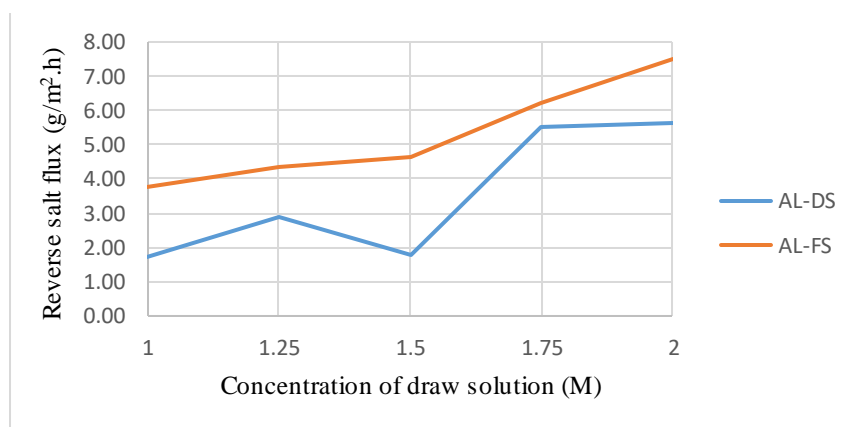


Figure 4-8: Reverse salt flux for different concentrations in orientation AL-DS and AL-FS at pH 9.

Effect of concentration of draw solutions

From the Figure 4-6, 4-7 and 4-8, the trend for the reverse salt flux increased when the concentration of draw solution increased from 1.0M to 2.0M. At high concentration of draw solute at membrane interface is necessary to generate a large osmotic gradient, which drive a high water flux. However, when the concentration of draw solution increase, the concentration gradient across the active layer also increase which will increase the reverse salt flux (Philip et al., 2010). Besides that, the higher the concentration of draw solution, the higher the amount of solutes, therefore the higher the possibility of more solutes at the draw solution side to permeate through the membrane into the feed side of the system (Chekli et al., 2012).

Effect of orientation of CTA membrane

From Figure 4-6 and Figure 4-7, as compare the reverse salt flux between the two orientation of membrane in AL-DS and AL-FS, the reverse salt flux between the two orientations at pH 3 and 7 were comparable. Furthermore, for the reverse salt flux at pH 9 from Figure 4-8, the reverse salt flux for AL-FS was higher than the orientation of CTA membrane in AL-DS. The highest RSF in pH 9 in orientation AL-FS was 7.52 GMH, which is 25% higher than RSF in orientation AL-DS. This can be discussed through the dilutive interaction concentration polarization (DICP). When the active layer faced feed solution, the solute will easily passed through the active layer therefore the reverse salt flux increased.

Effect of pH of draw solution

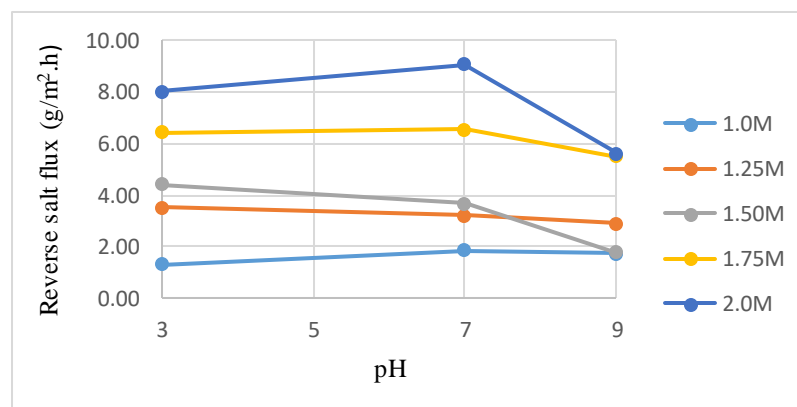


Figure 4-9: Reverse salt flux at pH 3, 7 and 9 in different concentration of draw solution.

From the Figure 4-9, the overall result trend for the reverse salt flux showed decrease from the pH 3 to pH 9. This result proved by Hancock & Cath (2009) stated that while the pH increase the reverse salt flux is suppressed. This condition is because when the pH of the draw solutions increased, the negative charged of the membrane will also increase. This will prevents the ions by repulsion from the draw side to permeate to the feed side.

4.5 Treatment on real seawater

After considered the water flux and reverse salt flux, the optimum parameters of draw solution chosen are. 1.75M of draw solution which has the highest water flux $1.07 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{min}$. Besides that, 1.75M of draw solution has optimum reverse salt flux which is $6.44 \text{ g}/\text{m}^2.\text{h}$ if compare with the highest reverse salt flux $9.08 \text{ g}/\text{m}^2.\text{h}$. Besides that, the pH for the draw solution chosen was in pH 7 in the orientation AL-DS (PRO) mode which is less severe to the forward osmosis performance. Therefore, 1.75M of Na_2SO_4 in pH 7 was used as draw solution and real seawater was used as feed solution. Lab scale forward osmosis experiment was done to test the water flux and reverse salt diffusion. Table 4-5 showed the comparison between water flux and reverse salt flux for synthetic and real seawater.

Table 4-5: Comparison between water flux and reverse salt flux for synthetic and real seawater.

	Synthetic seawater	Real seawater
Water flux ($\text{m}^3/\text{m}^2.\text{min}$)	1.07 E-04	6.97 E-05
Reverse salt flux ($\text{g}/\text{m}^2.\text{h}$)	6.44	3.68

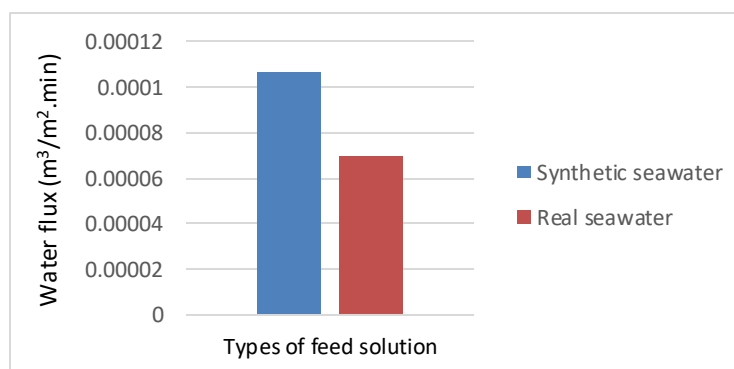


Figure 4-10: Comparison of water flux for synthetic and real seawater.

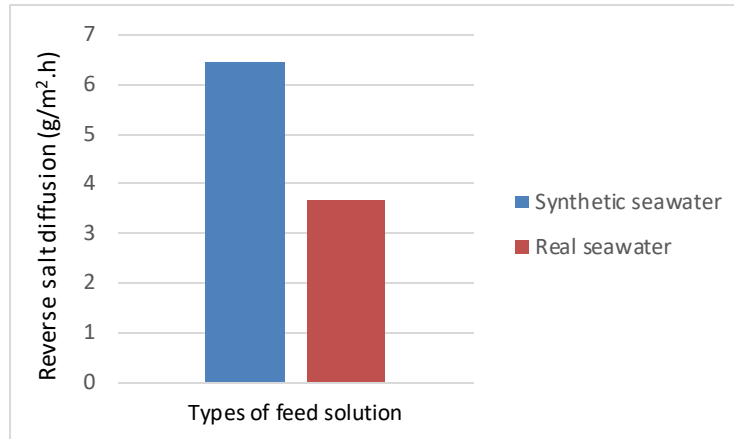


Figure 4-11: Comparison of reverse salt flux for synthetic and real seawater.

The water flux obtained is $6.97 \text{ E-}05 \text{ m}^3/\text{m}^2 \cdot \text{min}$. The positive water flux showed that the draw solution chosen are suitable as draw solution in desalination of seawater. From the Figure 4-10, water flux for synthetic seawater was higher than real seawater. This is because the real seawater contained other components. Chemical elements in sea water do not exist on their own but are attracted to preferential ions of opposite charge: sulphur will occur mainly as sulphate, sodium as sodium chloride, and so on. This chemical elements influenced the water flux in real seawater. In terms of reverse salt flux, from the Figure 4-11, the reverse salt flux for synthetic seawater which is 6.44 GMH was higher than real seawater which is 3.68 GMH.

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The performance of CTA membrane was characterized in terms of water flux and reverse salt diffusion. It was found that increase in both draw solution concentration and pH increase the water flux. The positive water flux and optimum reverse salt flux showed that the draw solution chosen are suitable as draw solution in desalination of seawater. Apart from that, the CTA membrane morphology before and after the experiment was identified and it was found that the changes on the membrane surfaces are negligible which showed that CTA has low fouling tendency.

As a conclusion, it was found that the optimum condition for treating seawater by using CTA membrane can be achieved at high concentration of draw solution (1.75M) with optimum pH of draw solution (pH7) in AL-DS orientation. The objective of the research was achieved. From this research, it can be seen that CTA membrane exhibited a high potential of treating seawater in Malaysia by forward osmosis process which is a good option of water treatment in order to overcome the problem of water depletion in Malaysia.

5.2 Recommendations

In order to improve the research, there are several aspects should be remarked. First, it is recommended to extend the time taken for the experiment to longer time so that the influence of pH and concentration of draw solution on water flux and reverse salt flux more obvious. Besides that, it is also recommended that polyamide membrane is used together with CTA membrane in order to compare which membrane would be the better performing membrane in forward osmosis process. Furthermore, to maintain the temperature of the forward osmosis process at room temperature, insulation made by covering the beakers of feed and draw solution is recommended to reduce heat transfer. Moreover, it is recommended that other types of draw solution should be used together with Na_2SO_4 draw solution to determine the most suitable draw solution in FO process by using CTA membrane.

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APPENDICES

Active layer face draw solution

The data for concentrations (1.0, 1.25, 1.50, 1.75 and 2.0) and pH (3, 7 and 9) of draw solutions at active layer of CTA membrane faced draw solution are tabulated in Table A-1, A-2 and A-3.

Table A-1: Table of change in feed solution volume with pH 3 for different concentration of draw solution at active layer face draw solution.

	Volume of Water Permeates/m ³				
Orientation	Active : Draw Solution				
Time (min)/ Concentration of Draw Solution (M)	1.00	1.25	1.50	1.75	2.00
0	7.72E-04	7.70E-04	7.90E-04	7.76E-04	7.64E-04
5	7.71E-04	7.70E-04	7.89E-04	7.76E-04	7.63E-04
10	7.71E-04	7.70E-04	7.89E-04	7.75E-04	7.61E-04
15	7.70E-04	7.70E-04	7.88E-04	7.74E-04	7.60E-04
20	7.70E-04	7.69E-04	7.88E-04	7.73E-04	7.58E-04
25	7.69E-04	7.69E-04	7.88E-04	7.72E-04	7.58E-04
30	7.69E-04	7.69E-04	7.88E-04	7.71E-04	7.56E-04
35	7.69E-04	7.68E-04	7.87E-04	7.70E-04	7.55E-04
40	7.68E-04	7.67E-04	7.87E-04	7.69E-04	7.54E-04
45	7.67E-04	7.66E-04	7.86E-04	7.68E-04	7.52E-04
50	7.66E-04	7.65E-04	7.85E-04	7.67E-04	7.50E-04
55	7.66E-04	7.64E-04	7.85E-04	7.66E-04	7.49E-04
60	7.55E-04	7.63E-04	7.84E-04	7.65E-04	7.47E-04

Table A-2: Table of change in feed solution volume with pH 7 for different concentration of draw solutions at active layer face draw solution.

	Volume of Water Permeates/m ³				
Orientation	Active : Draw Solution				
Time (min)/ Concentration of Draw Solution (M)	1.00	1.25	1.50	1.75	2.00
0	7.55E-04	7.69E-04	7.59E-04	7.70E-04	7.59E-04

5	7.54E-04	7.68E-04	7.57E-04	7.68E-04	7.57E-04
10	7.53E-04	7.66E-04	7.56E-04	7.66E-04	7.56E-04
15	7.53E-04	7.65E-04	7.55E-04	7.64E-04	7.54E-04
20	7.52E-04	7.64E-04	7.53E-04	7.63E-04	7.52E-04
25	7.51E-04	7.63E-04	7.52E-04	7.58E-04	7.51E-04
30	7.51E-04	7.62E-04	7.51E-04	7.55E-04	7.48E-04
35	7.50E-04	7.61E-04	7.50E-04	7.52E-04	7.47E-04
40	7.50E-04	7.60E-04	7.48E-04	7.50E-04	7.45E-04
45	7.49E-04	7.59E-04	7.47E-04	7.48E-04	7.43E-04
50	7.48E-04	7.58E-04	7.55E-04	7.46E-04	7.41E-04
55	7.48E-04	7.57E-04	7.45E-04	7.44E-04	7.27E-04
60	7.47E-04	7.56E-04	7.43E-04	7.43E-04	7.22E-04

Table A-3: Table of change in feed solution volume with pH 9 for different concentration of draw solutions at active layer face draw solution.

Orientation	Volume of Water Permeates/m ³				
	Active : Draw Solution				
Time (min)/ Concentration of Draw Solution (M)	1.00	1.25	1.50	1.75	2.00
0	7.51E-04	7.49E-04	7.68E-04	7.58E-04	7.72E-04
5	7.50E-04	7.48E-04	7.67E-04	7.57E-04	7.70E-04
10	7.50E-04	7.47E-04	7.66E-04	7.55E-04	7.68E-04
15	7.49E-04	7.46E-04	7.64E-04	7.53E-04	7.67E-04
20	7.49E-04	7.44E-04	7.63E-04	7.52E-04	7.65E-04
25	7.48E-04	7.43E-04	7.62E-04	7.50E-04	7.63E-04
30	7.47E-04	7.42E-04	7.60E-04	7.49E-04	7.61E-04
35	7.44E-04	7.41E-04	7.59E-04	7.47E-04	7.60E-04
40	7.44E-04	7.40E-04	7.58E-04	7.45E-04	7.58E-04
45	7.43E-04	7.39E-04	7.56E-04	7.44E-04	7.56E-04
50	7.42E-04	7.38E-04	7.55E-04	7.42E-04	7.54E-04
55	7.41E-04	7.37E-04	7.54E-04	7.41E-04	7.53E-04
60	7.41E-04	7.35E-04	7.52E-04	7.39E-04	7.51E-04

Active layer face feed solution

The data for concentrations (1.0, 1.25, 1.50, 1.75 and 2.0) and pH (3, 7 and 9) of draw solutions at active layer of CTA membrane faced feed solution are tabulated in Table A-4, A-5 and A-6.

Table A-4: Table of change in feed solution volume with pH 3 for different concentration of draw solutions at active layer face feed solution.

	Volume of Water Permeates/m³				
Orientation	Active : Draw Solution				
Time (min)/ Concentration of Draw Solution (M)	1.00	1.25	1.50	1.75	2.00
0	7.60E-04	7.69E-04	7.68E-04	7.62E-04	7.71E-04
5	7.60E-04	7.70E-04	7.66E-04	7.61E-04	7.69E-04
10	7.59E-04	7.69E-04	7.65E-04	7.60E-04	7.67E-04
15	7.58E-04	7.68E-04	7.64E-04	7.58E-04	7.66E-04
20	7.58E-04	7.68E-04	7.62E-04	7.57E-04	7.65E-04
25	7.57E-04	7.67E-04	7.61E-04	7.56E-04	7.64E-04
30	7.56E-04	7.66E-04	7.60E-04	7.47E-04	7.62E-04
35	7.56E-04	7.65E-04	7.59E-04	7.46E-04	7.61E-04
40	7.55E-04	7.65E-04	7.58E-04	7.45E-04	7.60E-04
45	7.54E-04	7.64E-04	7.57E-04	7.44E-04	7.59E-04
50	7.54E-04	7.63E-04	7.56E-04	7.44E-04	7.57E-04
55	7.53E-04	7.62E-04	7.55E-04	7.43E-04	7.56E-04
60	7.52E-04	7.61E-04	7.54E-04	7.42E-04	7.55E-04

Table A-5: Table of change in feed solution volume with pH 7 for different concentration of draw solutions at active layer face feed solution.

	Volume of Water Permeates/m³				
Orientation	Active : Draw Solution				
Time (min)/ Concentration of Draw Solution (M)	1.00	1.25	1.50	1.75	2.00
0	7.45E-04	7.64E-04	7.61E-04	7.68E-04	7.68E-04
5	7.44E-04	7.62E-04	7.60E-04	7.66E-04	7.66E-04
10	7.43E-04	7.61E-04	7.58E-04	7.65E-04	7.65E-04
15	7.43E-04	7.60E-04	7.57E-04	7.64E-04	7.64E-04
20	7.42E-04	7.59E-04	7.56E-04	7.62E-04	7.62E-04
25	7.42E-04	7.58E-04	7.55E-04	7.61E-04	7.61E-04
30	7.41E-04	7.57E-04	7.54E-04	7.60E-04	7.60E-04
35	7.41E-04	7.56E-04	7.53E-04	7.58E-04	7.58E-04
40	7.40E-04	7.54E-04	7.52E-04	7.57E-04	7.57E-04
45	7.39E-04	7.53E-04	7.51E-04	7.56E-04	7.56E-04

50	7.39E-04	7.53E-04	7.50E-04	7.55E-04	7.55E-04
55	7.38E-04	7.52E-04	7.49E-04	7.54E-04	7.54E-04
60	7.37E-04	7.50E-04	7.48E-04	7.52E-04	7.52E-04

Table A-6: Table of change in feed solution volume with pH 9 for different concentration of draw solutions at active layer face feed solution.

	Volume of Water Permeates/m³				
Orientation	Active : Draw Solution				
Time (min)/ Concentration of Draw Solution (M)	1.00	1.25	1.50	1.75	2.00
0	7.77E-04	7.78E-04	7.61E-04	7.62E-04	7.94E-04
5	7.77E-04	7.77E-04	7.56E-04	7.61E-04	7.91E-04
10	7.76E-04	7.76E-04	7.56E-04	7.60E-04	7.90E-04
15	7.75E-04	7.76E-04	7.55E-04	7.59E-04	7.88E-04
20	7.74E-04	7.75E-04	7.54E-04	7.58E-04	7.87E-04
25	7.73E-04	7.74E-04	7.52E-04	7.57E-04	7.85E-04
30	7.73E-04	7.74E-04	7.52E-04	7.56E-04	7.84E-04
35	7.72E-04	7.73E-04	7.51E-04	7.55E-04	7.83E-04
40	7.71E-04	7.72E-04	7.49E-04	7.54E-04	7.81E-04
45	7.71E-04	7.72E-04	7.48E-04	7.53E-04	7.80E-04
50	7.70E-04	7.71E-04	7.47E-04	7.52E-04	7.78E-04
55	7.70E-04	7.70E-04	7.46E-04	7.51E-04	7.77E-04
60	7.69E-04	7.70E-04	7.45E-04	7.50E-04	7.76E-04

Treatment on seawater

Table A-7: Table of change in feed solution volume with pH 7 for concentration of 1.75M draw solutions at active layer face feed solution.

	Volume of Water Permeates/m³
Orientation	Active : Draw Solution
Time (min)/ Concentration of Draw Solution (M)	1.75
0	0.00074071
5	0.0007392
10	0.00073764
15	0.00073618

20	0.00073474
25	0.0007333
30	0.00073191
35	0.00073034
40	0.00072892
45	0.00072735
50	0.00072603
55	0.00072459
60	0.00072314

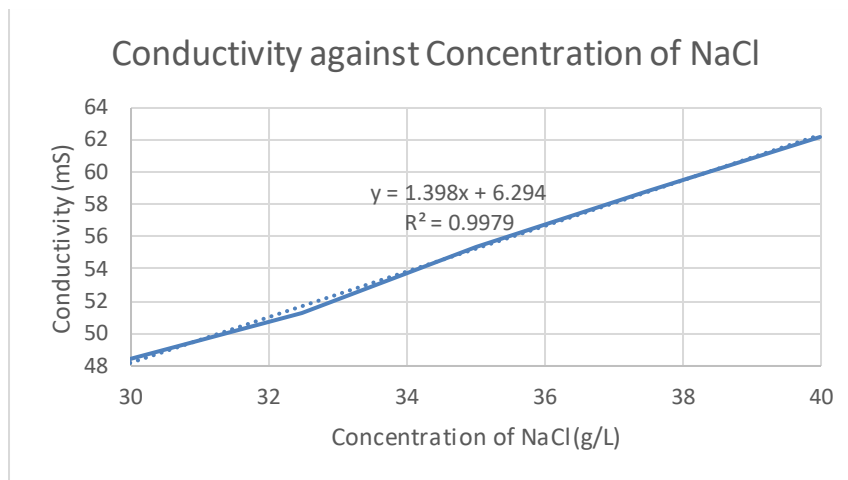


Figure A-1: Calibration curve of conductivity against concentration of NaCl solution.