WATER RECOVERY FROM PRODUCED WATER VIA FORWARD OSMOSIS

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UNIVERSITI SAINS MALAYSIA

2017

WATER RECOVERY FROM PRODUCED WATER VIA FORWARD OSMOSIS

by

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

June 2017

ACKNOWLEDGEMENT

First and foremost, I would like to convey my sincere gratitude to my supervisor, Assoc. Prof. Dr. Ooi Boon Seng for his precious encouragement, guidance and generous support throughout this work.

I would also extend my gratitude towards my colleague, namely Beh Jyh Jiunn for his kindness cooperation and helping hands in guiding me carrying out the lab experiment. He is willing to sacrifice his time in guiding and helping me throughout the experiment besides sharing his valuable knowledge.

Apart from that, I would also like to thank all SCE staffs for their kindness cooperation and helping hands. Indeed their willingness in sharing ideas, knowledge and skills are deeply appreciated.

Once again, I would like to thank all the people, including those whom I might have missed out and my friends who have helped me directly or indirectly. Their contributions are very much appreciated. Thank you very much.

Lim Siow Yoke

June 2017

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Symbol	**Description**	**Unit**
A	Effective Membrane Area	m^2
C_p	Average initial and final oil concentration in the draw solution	ppm
C_f	Average initial and final oil concentration in the feed solution (synthetic produced water)	ppm
J	Water permeate flux obtained from forward osmosis of synthetic produced water	$L/ m^2.hr$
P	Pressure	Pa
R	Rejection of oil	%
t	Time taken for collection of permeated water	hr
V	Permeated water volume	L
$\Delta\pi$	Osmotic Pressure Difference	Pa

LIST OF ABBREVIATIONS

CFV	Cross Flow Velocity
DS	Draw Solution
FS	Feed Solution
FO	Forward Osmosis
FTIR	Fourier Transform Infrared Spectroscopy
MF	Microfiltration
RO	Reverse Osmosis
SEM	Scanning Electron Microscope
UF	Ultrafiltration
UV-Vis	UV-Visible Spectrophotometer

PEMULIHAN AIR DARI SINTETIK AIR SISA MINYAK MELALUI OSMOSIS HADAPAN

ABSTRAK

Pemulihan air dari sintetik air sisa minyak melalui osmosis hadapan dengan menggunakan membran komposit nipis telah dijalankan dalam kerja ini. Kesan-kesan kepekatan minyak, kepekatan rumusan menelap dan kadar aliran silang rumusan menelap terhadap prestasi membran telah dikajikan. Tiga kepekatan minyak dalam rumusan asal iaitu 10 ppm, 25 ppm dan 50 ppm telah digunakan dalam kajian ini manakala kepekatan rumusan menelap dan kadar aliran silang rumusan menelap telah masing-masing dimanipulasi kepada 1 M, 1.5 M, 2 M dan 6 GPH, 8 GPH, 10 GPH. Pengukuran sudut kenalan yang kurang daripada 90°, iaitu 60.3°, menunjukkan membran komposit nipis mempunyai ciri hidrofili. Kadar fluks menelap menjadi kurang dengan peningkatan kepekatan minyak daripada 10 ppm kepada 50 ppm adalah disebabkan formasi lapisan kek yang semakin tebal. Selain itu, peningkatan kepekatan menelap daripada 1 M NaCl kepada 2 M NaCl telah mempertingkatkan kadar fluks disebabkan kewujudan perbezaan tekanan osmosis yang lebih besar. Kadar fluks menelap meningkat apabila kadar aliran silang meningkat daripada 6 GPH ke 10 GPH disebabkan peningkatan ricih permukaan. Membran komposit nipis didapati mempunyai purata penolakan minyak sebanyak 99.76 % dan kadar fluks sebanyak 1.06 L/m^2.h.

WATER RECOVERY FROM PRODUCED WATER VIA FORWARD OSMOSIS

ABSTRACT

Water recovery from synthetic produced water via forward osmosis was performed in this work using thin film composite membrane. The effect of oil concentration, draw solution concentration and draw solution cross flow velocity on membrane performance were studied. Three oil concentrations in feed solutions which are 10 ppm, 25 ppm and 50 ppm were used in this forward osmosis process. Whereas, the draw solution concentrations and draw solution cross flow velocities were manipulated to 1 M, 1.5 M, 2 M and 6 GPH, 8 GPH, 10 GPH respectively. Contact angle measurement showed that the thin film composite membrane is hydrophilic with contact angle less than 90° which is 60.3°. With the increased of oil concentration from 10 ppm to 50 ppm, the permeate flux had been reduced due to the increased of cake layer. On the other hand, the increment of draw solution concentration from 1 M NaCl to 2 M NaCl had enhanced the membrane performance with improved permeate flux as greater driving force in term of osmotic pressure difference was created to draw the water from the feed side. When the cross flow velocity increase from 6 GPH to 10 GPH, the permeate flux was also increased due to the increasing surface shear. The thin film composite membrane was found to have an average oil rejection of 99.76 % and flux of 1.06 $L/m^2.h$.

CHAPTER ONE

INTRODUCTION

1.1 Research background

In recent years, fresh water scarcity has become one of the most severe global problems due to the increasing population, industrialization, expanding agricultural activities, increasing inequities between water supply and demand, water contamination and climate change (Qasim et al., 2015, Zhao et al., 2016). Statistical forecasts and predictions show that two-thirds of the world's population may be exposed to water stress by the year 2025 which will not only disrupt the socio-economic growth but also pose threats to our healthy ecosystem (Qasim et al., 2015). Therefore, it is very important to find other water sources to meet the demand of fresh water. Desalination and water reuse are found to be promising solutions. Therefore, huge research effort has been dedicated to the development of technologies to recover fresh water from seawater or wastewater (Zhao et al., 2016).

Large amount of oily wastewater has been produced from various industries. Oil exists in several forms in oily wastewater as classified into free oil (oil droplet size >150 μm), dispersed oil (20 μm <oil droplet size <150 μm) and emulsified oil (oil droplet size <20 μm) (Cheryan and Rajagopalan, 1998). Oily wastewater is one of the main pollutants to the environment in the world. Therefore, the recovery of fresh water from wastewater has received a great concern. The largest source of oily wastewater is the produced water which is co-produced during oil and gas manufacturing (Susan et al., n.d.)

and it is one of the largest waste streams in the oil and gas industry (Dickhout et al., 2017). The produced water is generated due to the hydraulic fracturing process in the production of crude oil and natural gas (Zhang et al., 2014). It contains various organic and inorganic fractions which include dissolved and dispersed oil compounds, dissolved minerals, production chemical compounds such as corrosion inhibitors and surfactants, production solids and dissolved gases (Susan et al., n.d.). The estimated amount of produced water in the US is 1.6 – 2.1 million gallons per day (Benko and Drewes, 2008). In addition, energy exploration and extraction continue to increase rapidly and lead to the rapid growth of oil and gas industries. Therefore, the amount of produced water is expected to be increased.

In order to meet the global demand of fresh water and overcome the environmental issue caused by the pollution of large amount of produced water, the urgency to treat produced water has emerged (Duong and Chung, 2014). The treatment of produced water and refinery waste water from the oil industry has been commonly done by physical as well as chemical processes (Munirasu et al., 2016). Conventional treatment methods, such as hydrocyclones, gas flotation, adsorption, media filtration and macro-porous polymer extraction (MPPE) can remove most of the oil and contaminants from the produced water but the smallest, stabilized oil droplets (<10 μm) still exist in the treated water (Dickhout et al., 2017). As compared to traditional physical and chemical treatment, the usage of membrane technology can better remove the low concentration, stable oil-in-water emulsions consisting oil particles of the size of less than 20 μm to meet the discharge requirement of 10 mg/L with no generation of precipitate sludge (Chakrabarty et al., 2008, Chakrabarty et al., 2010). Membrane technology does not need frequent replacement of filters and it was found that the water quality after membrane treatment is better (Dickhout et al., 2017). Moreover, membrane technology is more environmental friendly, practical and cost effective (Duong and Chung, 2014). Membrane technology has been applied for treating produced water by using microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO) and recently by forward osmosis (Cheryan and Rajagopalan, 1998). Forward osmosis (FO) membrane technology has been developed to overcome two major problems faced by conventional membrane technology namely membrane fouling and high energy consumption.

Since no hydraulic pressure is applied in forward osmosis process, the energy consumption in electrical pumping can be reduced. At the same time, this operation results in lower fouling propensity and higher fouling reversibility which prolong the membrane's service life-time and reduce overall operational cost (Cai and Hu, 2016). In conclusion, compared to pressure-driven membrane techniques, forward osmosis process can produce clean water with the quality as good as the reverse osmosis process with the additional advantages of no or low pressure operation, higher water flux and recovery rate, less fouling propensity and easy cleaning. Therefore, forward osmosis may be a promising technology to effectively and economically recover water from stable emulsified oily wastewater (Duong and Chung, 2014).

As a result, in this research, forward osmosis was applied to recover the water from produced water. The performance and efficiency of forward osmosis were investigated under different operating conditions. Figure 1.1 shows the schematic illustration of forward osmosis process. Forward osmosis (FO) is a naturally driven process that potentially separates clean water from contaminated sources via a semi-permeable membrane by the osmotic pressure difference across the membrane without applying external hydraulic pressure. Forward osmosis (FO) is an osmotic process that uses a semi-permeable membrane to effect separation of water from dissolved solutes. The driving force for this separation is an osmotic pressure gradient between a solution of high concentration, often referred to as a “draw” and a solution of lower concentration, referred to as the “feed”.

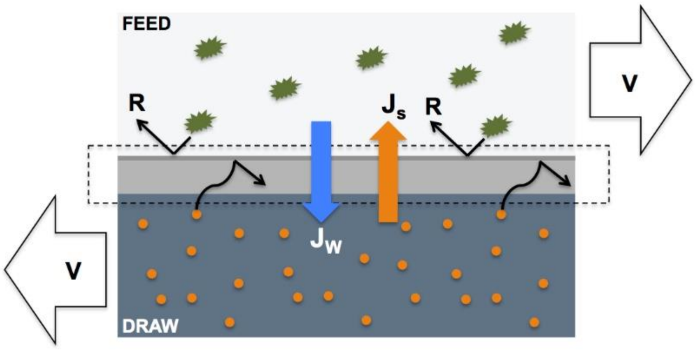

Figure 1.1 : Schematic illustration of the forward osmosis process

1.2 Problem statement

The conventional methods used to treat produced water, namely hydrocyclones, gas flotation, adsorption, media filtration and macro-porous polymer extraction (MPPE) cannot remove small and stabilized oil droplets (<10 μm) in the produced water. In order to improve the separation of oil from water, membrane technologies are used as they are proven for its ability to produce better quality of water. However, severe membrane fouling is inevitable and required high maintenance and cleaning costs. Forward osmosis which is naturally driven process without applying pressure is expected to have minimized fouling problem. Therefore, the general purpose of this work is to recover water by separating the oil from produced water via forward osmosis. For a better understanding about the forward osmosis process, a few objectives had been clarified. The fouling tendency of forward osmosis membrane is studied to show that the fouling problem of forward osmosis is exist but not serious.

Besides fouling tendency, the operating conditions such as oil concentration, draw solution concentration and draw solution cross flow velocity played important roles in separating the oil from produced water effectively. No separation process is ideal, include forward osmosis process. The efficiency of forward osmosis is limited by a few problems, namely internal concentration polarization, reverse solute flux and membrane fouling. Therefore, the performance of forward osmosis under different operating conditions is investigated and the efficiency of water separation from produced water via forward osmosis is studied.

1.3 Research objectives

Forward osmosis technology will be used for the water recovery by separating the oil from produced water. The experimental study will be carried out to observe the membrane performance and evaluate the fouling phenomenon. Below are the objectives aligned with this study:

1. To study the efficiency of water separation from produced water using forward osmosis.
2. To evaluate the fouling tendency of the membrane.
3. To investigate the performance of FO under different operating conditions.

1.4 Scope of study

In this work, thin film composite (TFC) membrane was used to recover water from synthetic produced water via forward osmosis. The efficiency of water separation from produced water by using different concentrations of synthetic produced water (10 ppm, 25 ppm and 50 ppm), different concentrations of draw solutions (1 M, 1.5 M and 2 M) and different cross flow velocity of draw solution (6 GPH, 8 GPH, 10 GPH) will be studied. The water flux and rejection of oil will be determined to study the efficiency and investigate the performance of membrane under different operating conditions. In addition, the fouling tendency of the membrane will be evaluated by using the graph of water flux against time.

1.5 Thesis organization

This work is organized into five chapters, this is the first one: the research background, problem statement and objectives of this project. In chapter two, some theoretical concepts are described and explained, for instance the membrane technology for produced water treatment such as microfiltration, ultrafiltration and reverse osmosis. Furthermore, the purpose of this project which is forward osmosis and its applications, advantages as well as challenges also discussed in this chapter. Chapter three presented the materials and methods used during the development of this work. The details of experimental procedures are described in this section. Results and discussion are reported in chapter four. Chapter five contains the conclusions deduced from the present work and recommendations for future work. In the end, there is a list of references used for this work and appendices that support the accomplished work.

CHAPTER TWO

LITERATURE REVIEW

2.1 Oily Wastewater

Large amounts of oily wastewater have been discharged from oil and gas (O&G) drilling processes and other industries operated onshore and offshore. The amount of wastewater increases rapidly as the demands of global energy and innovative O&G drilling technologies are continuously rise. Direct discharge of such oily wastewater is now prohibited by regulations since it will lead to severe water and soil pollution. Therefore, the disposal and treatment of oily wastewater have received worldwide attention (Han et al., 2015). The treatment of oily wastewater is an essential concern as oily wastewater pollution can affect drinking water and groundwater resources. Moreover, it endangers aquatic resources and human health. Furthermore, it affects crop production and destruct the natural landscape (Mardhiah et al., 2017). Therefore, a proper and effective oily wastewater treatment should be applied to minimize those environmental impacts and at the same time recover the water for usage purpose.

2.1.1 Produced Water

Produced water is one of the largest waste streams in the oil and gas industry. The daily global production of produced water is 250 million barrels which is three times than that of the produced oil (Susan et al., n.d.). This means that produced water has a 3:1 volume-to-product ratio. The produced water is left over after the phase separation of oil and gas (Dickhout et al., 2017). Generally, produced water can be classified as oil field produced water, natural gas produced water and coal bed methane (CBM) produced water depending on the source. Oilfields are responsible for more than 60% of daily produced water generated worldwide. Produced water is composed of various organic and inorganic fractions which include dissolved and dispersed oil components, dissolved formation minerals, production chemicals (corrosion inhibitors and surfactants, dissolved gases (including CO_2 and H_2S) and produced solids (Igunnu, 2014). Table 2.1 lists typical composition and properties of oilfield produced water (Igunnu, 2014).

Produced water can cause pollution on the ground water and poses serious environment threats. Therefore, proper treatment of produced water is required in order to meet the stringent regulations on the discharge and disposal of produced water in the environment (Susan et al., n.d.). An effective treatment is needed so that the water can be safely discharged or re-used for other purposes by separating the oil from water. Produced water is an oil-in-water emulsion, where the oily phase is dispersed in the aqueous phase, stabilized by surfactants (Dickhout et al., 2017). The traditional methods are not efficient enough for treating the stable oil-in-water emulsions (size ≤ 10 μm) especially when the oil droplets are finely dispersed and the concentration is very low. This is because very long residence time is required by the emulsion droplets, which are of micron and submicron size, to rise onto the top for enabling gravity separation and even addition of chemicals cannot break the emulsions effectively.

Table 2.1：Composition of oil field produced water (Igunnu, 2014).

Parameter	**Minimum value**	**Maximum value**	**Heavy metal**	**Minimum value (mg/l)**	**Maximum value (mg/l)**
Density (kg/m^3)	1014	1140	Calcium	13	25 800
Conductivity (µS/cm)	4200	58 600	Sodium	132	97 000
Surface tension (dyn/cm)	43	78	Potassium	24	4300
pH	4.3	10	Magnesium	8	6000
TOC (mg/l)	0	1500	Iron	<0.1	100
TSS (mg/l)	1.2	1000	Aluminium	310	410
Total oil (IR; mg/l)	2	565	Boron	5	95
Volatile (BTX; mg/l)	0.39	35	Barium	1.3	650
Base/neutrals (mg/l)	—	<140	Cadmium	<0.005	0.2
Chloride (mg/l)	80	200 000	Copper	<0.02	1.5
Bicarbonate (mg/l)	77	3990	Chromium	0.02	1.1
Sulphate (mg/l)	<2	1650	Lithium	3	50
Ammoniacal nitrogen (mg/l)	10	300	Manganese	<0.004	175
Sulphite (mg/l)	—	10	Lead	0.002	8.8
Total polar (mg/L)	9.7	600	Strontium	0.02	1000
Higher acids (mg/l)	<1	63	Titanium	<0.01	0.7
Phenol (mg/l)	0.009	23	Zinc	0.01	35
Volatile fatty acids (mg/l)	2	4900	Arsenic	<0.005	0.3
			Mercury	<0.005	0.3
			Silver	<0.001	0.15
			Beryllium	<0.001	0.004

Those conventional techniques cannot efficiently remove oil droplets below 10 µm size and can only reduce oil concentration to hardly 1% by volume of the total wastewater. The water phase obtained from conventional treatment is usually required to be further purified to meet the accepted effluent standard for discharge into the river (Chakrabarty et al., 2010). In addition, the treated water cannot meet the quality to be reused for other purposes. In view of this, membrane technology has been considered as a promising method to treat the micron sized produced water due to its suitable pore size and its capability to remove emulsified oil droplet without any de-emulsification processes (Susan et al., n.d.). It was found that the water quality after membrane treatment has better quality for discharge or even direct usage.

2.2 Membrane Technology for Produced Water Treatment

Due to the limitation of conventional treatment methods, membrane technology which is more environmental friendly, practical and cost effective (Duong and Chung, 2014) is used to treat produced water and it was found that the water quality after membrane treatment is better (Dickhout et al., 2017). Membrane technology has been applied for treating produced water by using microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO) and recently by forward osmosis (Cheryan and Rajagopalan, 1998).

2.2.1 Microfiltration (MF)

Microfiltration (MF) has been used and it is considered as successful treatment of oily wastewaters as it can produce high quality of permeate. Microfiltration (MF) membranes are characterized by their functioning pores between 0.1 and 10 μm and have been studied to separate water from oily wastewater. Based on a study done by Mueller et al. (1997), they used cross flow microfiltration to treat oily wastewater with different concentration of heavy crude oil droplets of 1–10 μm diameter. In this study, Mueller et al. (1997) used a-alumina ceramic membranes (0.2 and 0.8 μm pore sizes) and a surface-modified polyacrylonitrile membrane to study the performance of membrane to treat oily wastewater, the results showed that the membranes produce high quality permeate. Typical final flux values for membranes at 250 ppm oil in the feed at the end of experiments with 2 hours of filtration are approximately 30 - 40 kg m $^{-2}$ h $^{-1}$.

Although MF membranes can successfully treat produced waters, they experience a decline in permeate throughput or flux as a result of fouling. This flux decline is due to the adsorption and accumulation of rejected oil, suspended solids, and other components of produced water on the membrane surface (external fouling) or in the membrane pores (internal fouling). This fouling can be irreversible or resistant to cleaning, cause the original flux to be unrecoverable (Mueller et al., 1997). Another major limitation of MF is the lack of removal of dissolved component (Munirasu et al., 2016).

MF can be used as cost effective pre-treatment for the produced water treatment. It can be applied after removing the bulk of the oil component by using the primary treatment of sedimentation, coagulation, flocculation & sedimentation process. The MF process can effectively remove the dispersed oil droplets and other particulates with the size of more than 100 nm. However, the smaller droplets and particulates can pass though the MF membrane. Consequently, for more effective removal of smaller size, the UF membrane can be employed (Munirasu et al., 2016).

2.2.2 Ultrafiltration (UF)

Ultrafiltration (UF) membranes are characterized by their functioning pores between 0.2–100 nm and have been widely studied to remove emulsified oil and suspended solids from produced water. UF process is one of the initial methods attempted along with MF for the oil removal from the produced water. Most of the studies showed that smaller droplets and particulates still can pass though the MF membrane, therefore UF membrane is employed for more effective removal of smaller size particulates (Munirasu et al., 2016). However, UF membranes were easily susceptible to the fouling due to high permeation flux. Based on a study done by Chakrabarty et al. (2010) who used polysulfone membranes to treat oily wastewater via cross-flow mode of ultrafiltration, the results showed that the oil content in the permeate has not met the discharge standard of 10 mg L^{-1}. The oil rejection was found to be below 80% although the flux was reasonably high. This suggests that the UF operational unit should be followed by another operational unit, for example nanofiltration or reverse osmosis in order to meet the discharge standard of 10 mg L^{-1} (Chakrabarty et al., 2010). Moreover, the UF process for oil in water separation suffered from severe fouling on membrane surface. Therefore, additional membrane modification was made to decrease fouling (Zhang et al., 2014).

UF process is an effective membrane technology for the produced water treatment especially for the low saline and less toxic produced water. The UF treatment can stand alone to achieve the discharge standard if the produced water is more benign in nature, for example in offshore oil field. In more practical terms, the UF process can be ultimate pretreatment for the nanofiltration or reverse osmosis membrane where purified water with reasonably acceptable quality can be obtained for the beneficial use like irrigation or live stocks. The challenge of ultrafiltration membrane is fouling problem and therefore fouling resistance, smart UF membrane development will be the ongoing and future research development in membrane technology (Munirasu et al., 2016).

2.2.3 Reverse Osmosis (RO)

Reverse osmosis (RO) has been widely applied in various water and wastewater treatment processes as a promising membrane technology. However, RO membrane fouling is a global issue, which limits its operating flux. Fouling reduces the recovery of water, increases the power consumption and requires periodical membranes Cleaning-in-Place (CIP) procedure. This may result in low effectiveness of membrane, high cost and adds environmental issues related to the CIP solutions disposal (Qin et al., 2009). RO membranes can achieve high rejections towards contaminants with 99.9% oil rejection, however high energy consumption and severe fouling have been encountered. In addition, due to the use of extremely high hydraulic pressure, the compacted and tightly held fouling layer on the RO membrane surface cannot be cleaned easily. Therefore, treating highly contaminated oily wastewater by RO still exhibit serious limitations such as the short membrane life time and low recovery rate due to the high membrane fouling propensity, high operation and equipment costs (Duong and Chung, 2014). In conclusion, there are three major drawbacks of using RO membrane to recover water (Valladares Linares et al., 2014) which are:

i. energy intensive operation due to high hydraulic pressure used to drive the process (≈60 bar)
ii. extensive pretreatment needed to maintain long-term operation of membrane modules
iii. membrane fouling, resulting in decreasing membrane permeability and in feed channel pressure drop increase

2.3 Forward Osmosis Membrane for Produced Water Treatment

Due to the problems encountered by conventional membrane technology, a more economical and practical process which is forward osmosis has been developed for the treatment of stable emulsified produced water.

2.3.1 Fundamental Principle of Forward Osmosis

Forward osmosis (FO) is a naturally driven process that potentially separates clean water from contaminated sources via a semi-permeable membrane by the osmotic pressure difference across the membrane without applying external hydraulic pressure (Duong and Chung, 2014). In FO, water is permeated from a lower osmotic pressure feed solution (FS) into a higher osmotic pressure draw solution (DS) and this results in the concentration of the FS and dilution of the DS (Valladares Linares et al., 2014). The osmotic pressure difference is the driving force of water transport (Lutchmiah et al., 2014). The more concentrated solution on the permeate side of the membrane is the source of the driving force in the FO process and it is DS (Cath et al., 2006). The DS and related osmotic pressures in the FO process are important factors influencing mass transport and overall process performance. NaCl is the most commonly employed DS (approximately 40% of experiments), due to its high solubility but low cost and relatively high osmotic potential. In most of the studies, NaCl has been used as a DS in concentrations between 0.3 and 6 M (Qasim et al., 2015).

There are two important criteria where a DS must have. Firstly, DS must be a highly-concentrated salt concentration with low water chemical potential (high osmotic pressure), so that it has enough driving force to draw the water molecules from a feed solution (produced water) with higher water chemical potential (lower osmotic pressure). This is in agreement with the 2nd law of thermodynamics, since transport of water molecules will lead chemical potentials in the feed and the draw solution to equilibrium (Qasim et al., 2015). Secondly, the draw solute must be easily separated from the diluted DS in the subsequent process to regenerate the draw solute for reuse and to produce purified water (Cai and Hu, 2016). In short, the process of FO desalination can be divided into two steps. In the first step, water molecules are permeated from the feed to the draw solution across the semipermeable membrane. After that, the DS is subsequently recovered by separating pure water from the diluted draw solution obtained in the first step of the process (Qasim et al., 2015). Figure 2.1 illustrates the water flow pattern in forward osmosis process.

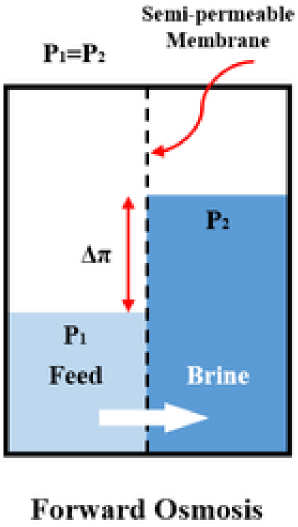

Figure 2.1: Schematic illustration of water flow pattern in Forward Osmosis process.

2.3.2 Application of Forward Osmosis in Produced Water Treatment

Forward osmosis technology has been widely studied and applied for many purposes such as food processing, desalination, wastewater treatment, power generation, and pharmaceutical applications (Yang et al., 2016). In this thesis, only wastewater treatment related applications are discussed.

Based on a study done by Duong and Chung (2014), they used a thin film composite membrane (TFO) to investigate the effectiveness of forward osmosis (FO) processes to treat the stable oil–water emulsions by separating the stable emulsified oil particles from water. Results showed that the FO technique has been successfully applied for the treatment of a wide range of oil–water emulsions from a low to a very high concentration up to 200,000 ppm. Water can be separated from oily feeds with concentration of 500 ppm or 200,000 ppm emulsified oil at a relatively high flux of

16.5±1.2 LMH or 11.8±1.6 LMH respectively by using a thin film composite membrane and 1 M NaCl as the draw solution. Moreover, the membrane can produce water with a negligible oil level with an oil rejection of 99.88 % (Duong and Chung, 2014).

In addition, Han et al. (2015) had demonstrated that the TFC membranes can be effectively used for sustainable water reclamation from emulsified oil/water streams via forward osmosis (FO) under the pressure retarded osmosis (PRO) mode. The newly developed TFC-FO membrane exhibits a high water flux of 37.1 L m^{-2} h^{-1} with an oil rejection of 99.9 % using a 2000 ppm soybean oil/water emulsion as the feed and 1 M NaCl as the draw solution under the PRO mode. Remarkable anti-fouling behaviors have also been observed (Han et al., 2015).

Another useful application of forward osmosis was reported by Coday et al. (2015), he used asymmetric cellulose triacetate versus polyamide thin-film composite to evaluate the performance of FO membranes for desalination of produced water for the Niobrara shale formation. Results from this study indicate that FO can achieve high rejection of organic and inorganic contaminants which is above 90 %. Furthermore, membrane fouling can be mitigated with chemical cleaning and long-term FO system performance might be better controlled with optimized hydrodynamic conditions near the membrane surface (i.e., feed flow velocity, module design, membrane packing) (Coday et al., 2015).

2.3.3 Challenges of Forward Osmosis

Forward osmosis (FO) is a promising technology for treating oily wastewater thanks to its high rejection and high water recovery. However, there are few challenges faced by FO technology and leads to the major problem which is decline in water flux. Those challenges include concentration polarization, reverse solute flux and membrane fouling.

2.3.3(a) Concentration Polarization

As permeate water moves across the membrane, it delivers solutes and particles toward the membrane via advective transport. If these materials are rejected by the membrane, they may start to accumulate on or near the membrane surface and lead to the formation of additional layers of materials where permeate water must pass. These materials achieve higher concentrations near the membrane surface than the bulk in a flowing concentration boundary layer which is the concentration polarization (CP) layer (Yang et al., 2016). CP develops due to existence of concentration difference at the membrane-solution interface arising from selective transfer of species through a semi-permeable membrane (Akther et al., 2015).

CP due to water permeation is not only limited to pressure-driven membrane processes but also occurs during osmotic-driven membrane processes, on both the feed and permeate sides of the membrane. In FO, CP arises as concentration gradient between draw and feed solutions through an asymmetric FO membrane. Membranes used in FO show unexpected low flux and this is credited to concentration polarization. CP arising in

FO process can be further classified as internal concentration polarization (ICP), which occurs within the membrane porous support layer, and external concentration polarization (ECP), which occurs at the membrane active layer surface (Akther et al., 2015).

When the feed solution flows on the active layer of the membrane, solutes build up at the active layer. This is called concentrative ECP. Simultaneously, the draw solution in contact with the permeate side of the membrane is being diluted at the permeate–membrane interface by the permeating water. This is called dilutive ECP. The effective osmotic driving force can be reduced by both concentrative and dilutive ECP phenomena. The adverse effect of ECP on osmotic-driven membrane processes can be minimized by increasing flow velocity and turbulence at the membrane surface. Due to the low hydraulic pressure used in FO, membrane fouling induced by ECP has smaller effects on water flux compared to the effects in pressure-driven membrane processes. It has been shown that ECP plays a minor role in osmotic-driven membrane processes and is not the major cause for the lower-than-expected water flux in such processes. In most flux models for FO, ECP is assumed to be negligible due to low fluxes and a high mass transfer, however ECP has severe impact when the feeds are with high total dissolved solids (TDS) (Lutchmiah et al., 2014, Cath et al., 2006).

ICP is more significant in FO and has more influence on flux compared to ECP. ICP is considered as a major problem in FO, it can reduce the water flux and increase reverse solute transport. ECP can be mitigated by hydraulic means, such as increasing cross flow velocity. However, ICP, a unique CP phenomenon occurring inside the porous support layer of the FO membrane, is much more unfavorable to the FO processes due to the difficulty to control it. Severe ICP leads to the reduction of the effective driving force and thus the permeate flux. ICP refers to the occurrence of CP layer within the porous layer of the membrane when the solute unable to penetrate the dense selective layer of the membrane easily. When the solute in the porous support layer is transported solely by hindered diffusion in the stagnant zone of the support, and the concentration of draw solution is commonly diluted by the permeating water from the feed solution, this kind of diluted concentration layer is called dilutive ICP (Wang et al., 2016). Figure 2.2 illustrates the phenomena of ICP and ECP across an asymmetrical FO membrane.

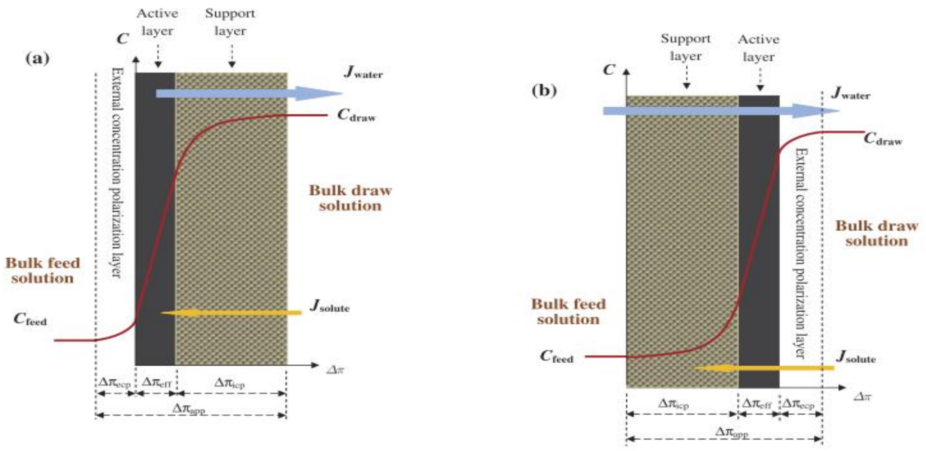

Figure 2.2: Diagram of internal (ICP) or external concentration polarization (ECP) across an asymmetrical FO membrane: (a) Dilutive ICP and concentrative ECP when the feed is on the active layer side, (b) Concentrative ICP and dilutive ECP when the feed is on the support layer side.

2.3.3(b) Reverse Solute Flux

Ideally, the draw solute will not permeate across the semipermeable membrane into the feed solution in FO process. Unfortunately, no membrane is perfectly semipermeable and some draw solutes will permeate across the membrane from the draw to the feed solution due to the difference in solute concentrations (Qasim et al., 2015). Recently, many researches have been conducted to study the effect of reverse diffusion of draw solute on membrane fouling. It has been shown by Lee et al. (2010) and Lay et al. (2010) that draw solute's reverse flux can worsen membrane fouling by enhancing the concentration polarization effect. Hence, solutions containing multivalent ions with lower diffusion coefficients may be required in situations where considerable salt rejection is desired. However, some multivalent ions like calcium and magnesium ions may enhance membrane fouling by interfering with the fouling agents in the feed after reverse solute diffusion. In addition, more severe ICP can be caused due to the lower solution diffusion coefficients and larger ion sizes of multivalent ion solutions (Akther et al., 2015).

Phillip et al. (2010) has established that specific reverse solute flux is dependent on the membrane selectivity but is unaffected by the membrane support layer structure and the draw solution concentration. This result also suggests the importance for the development of a new FO membrane with a highly selective membrane active layer so that the reverse solute diffusion can be minimized to improve FO performance. Moreover, it has also been proposed that the use of draw solution consisting of multivalent ions might reduce reverse solute flux, which will in turn lessen membrane fouling but the resulting higher ICP can increase the potential risk of fouling (Akther et al., 2015).

Most of the research have shown that there are few things to be concerned in order to improve the performance of FO process which are new membrane development, draw solutions to enhance wastewater treatment and water recovery as well as operating conditions to optimize the FO process. Optimization of these parameters are essential to mitigate fouling, decrease concentration polarization and reverse solute flux so that FO performance can be improved. Those issues all closely related to one another. (Lutchmiah et al., 2014).

2.3.3(c) Membrane Fouling

Membrane fouling is significantly encountered by 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 low or no hydraulic pressure was applied in osmotically driven membrane processes. It can be said that FO or PRO are more 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. In addition, the operational and capital costs are lower for membrane with less fouling. Unlike fouling in RO membranes, most fouling (organic and inorganic fouling) in FO membranes is reversible and can be easily cleaned by osmotic backwashing and the need for any chemical reagents for cleaning may be reduced or completely eliminated (Akther et al., 2015).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Chemicals and Materials

Synthesized thin film composite membrane which supported by polyester with total thickness of 200 µm was used in the forward osmosis study. All other chemicals used in this study are listed in Table 3.1 with specified purposed of use.

Table 3.1 : List of chemicals used

Chemical	**Supplier**	**Purpose of Use**
Sodium Chloride	Merck	For the preparation of draw solution.
Sea Salt	Sigma Aldrich	For the preparation of sea salt solution.
Crude Oil	Petronas	Dispersed in the sea salt solution for synthetic produced water preparation.
Triton X-100 Surfactant	Sigma Aldrich	As stabilizer for oil droplets in the synthetic produced water.
Deionized water (pH ca. 6.3) with resistivity of 18.2MΩ produced by Purelab Flex	ELGA, Buckinghamshire, UK	For the preparation of feed and draw solutions.

3.2 Overall Experimental Flow Chart

Figure 3.1 illustrated the flow chart of the experimental works done in the study. At the beginning of the experimental works, characterization of the neat TFC membrane was done prior membrane filtration process. Then, feed and draw solutions were prepared at predetermined concentrations. Next, the cross flow forward osmosis (FO) was carried out to investigate the effect of oil concentration, draw solution concentration, and draw solution cross flow velocity on the membrane performance. The flux of the FO process was determined to analyze the efficiency of the water separation and evaluate the fouling tendency of the membrane. The characterization of the membrane after FO process was conducted to analyze the cake layer formation on the membrane. Finally, the initial and final concentration of feed (produced water) and draw solutions were determined to find out the rejection of the membrane.

3.3 Characterization of Membrane

3.3.1 Contact Angle Measurement

Contact angle can be known as the measurement of the hydrophilicity of composite membranes. The contact angle between water and membrane was measured using contact angle goniometer (Model: 300 Advanced Goniometer, Rame-Hart) at temperature 27 °C to evaluate membrane hydrophilicity based o sessile drop method. Accurately measured 10 µl water was carefully dropped using the motor-driven syringe on the top surface of the membrane. The acquired images were analysed using DROPimage software to obtain the measurement of contact angles. The contact angle of each membrane sample was measured for ten times at different locations to minimize experimental errors.