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COLLEGE OF ENGINEERING

ENGINEERING A FERTILIZING DRAW SOLUTION FOR IRRIGATION USING FORWARD OSMOSIS / REVERSE OSMOSIS HYBRID SYSTEM

BY

MHD AMMAR NABIL HAFIZ

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COMMITTEE PAGE

The members of the Committee approve the Thesis of
Mhd Ammar Nabil Hafiz. defended on 16/04/2019.

Dr. Alaa H. Hawari
Thesis/Dissertation Supervisor

Dr. Sayed Zayedi
Committee Member

Approved:

Abdel Magid Hamouda , Dean, College of Engineering

ABSTRACT

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Title: Engineering a Fertilizing Draw Solution for Irrigation Using Forward Osmosis / Reverse Osmosis Hybrid System

Supervisor of Thesis: Alaa, H, Hawari.

Large volumes of fresh water are consumed in the human's daily activities, producing large volumes of highly contaminated wastewater which exhibits a major environmental problem. Wastewater is treated using multiple technologies to produce Treated sewage effluent (TSE) which is considered to be less contaminated but unusable by human daily activities.

This work investigates the application of a hybrid system that combines forward osmosis (FO) and reverse osmosis (RO) processes for the supply of a fertilizing solution that could be used directly for irrigation purposes. In the forward osmosis process, treated sewage effluent (TSE) is used as the feed solution and two different types of draw solutions were investigated namely, 0.5M NaCl solution and 0.5M NaCl and 0.01M diammonium phosphate ((NH4)2HPO4) solution. The impact of the feed solution and the draw solution flowrates and the membrane orientation on the membrane flux were investigated in the forward osmosis process. In the reverse osmosis process, seawater RO membrane (SW30HR) and brackish water RO membrane (BW30LE) were tested for the regeneration of the draw solution. In the forward osmosis process, it was found that the highest membrane flux was 13.2 LMH achieved at a flow rate of 2 LPM for the feed solution and the draw solution and when the 0.5M NaCl and 0.01M diammonium phosphate solution was used as the draw solution in the FO mode membrane orientation. The FO process had high rejection rates for total phosphorus and ammonium which were 99% and 97%, respectively. Reverse osmosis achieved 99% total salts rejection rate using the seawater RO membrane. The final product water had high quality in terms of total dissolved solids and nutrients concentration. The final product meets the irrigation water quality.

DEDICATION

“ This work is dedicated to my parents. "

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LIST OF ABBREVIATIONS

AL	Active Layer
AL-DS	Active Layer Facing Draw Solution
AL-FS	Active Layer Facing Feed Solution
CECP	Concentrative External Concentration Polarization
CICP	Concentrative Internal Concentration Polarization
CP	Concentration Polarization
CTA	Cellulose Triacetate
DECP	Dilutive External Concentration Polarization
DI	Deionized
DICP	Dilutive Internal Concentration Polarization
DS	Draw Solution
ECP	External Concentration Polarization
FO	Forward Osmosis
FS	Feed Solution

ICP	Internal Concentration Polarization
PRO	Pressure Retarded Osmosis
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
SL	Support Layer
TDS	Total Dissolved Solids
TFC	Thin Film Composite
TS	Total Solids
TSE	Treated Sewage Effluent

CHAPTER 1: INTRODUCTION

1.1 Overview

Irrigation water constitutes over 75% of the fresh water consumption and it is expected to increase in the future because of the population growth.(Shaffer, Yip, Gilron, & Elimelech, 2012) World population is approximated to be 9 billion by 2050 which will increase the demand on the fresh water and food resources. The current fresh water resources are under significant strain due to the contamination of groundwater, climate change and increasing demands on fresh water supply. Agriculture in many regions has been suffered from the limited water supply which even worsened by the inconsistent rainfalls. Impaired-quality waters such as wastewater have been used in farming but several ethical and health issues prevented their wide application. Tertiary treated wastewater contains trace concentration of nitrogen and phosphorus compounds which are required for plant nutrition. However, some crops such as vegetables do not tolerate salinity even at low concentration (A. Altaee, G. J. Millar, A. O. Sharif, & G. Zaragoza, 2016).

Many countries suffer water shortage rely on saline water treatment for fresh water supply to irrigation(Ge, Ling, & Chung, 2013). Reverse Osmosis (RO) has been used for seawater desalination to supply freshwater for domestic application. The Total Dissolved Solids (TDS) of desalinated water is less than 500 mg/L which makes it good fit for plants irrigation. As a matter of fact, RO seawater desalination is a common approach for irrigation water supply in an attempt to encourage agriculture industry despite the high cost desalinated water. Often, RO desalinated water is mixed with other chemical compounds to form the fertilizing solution used for the plant irrigation.(Phuntsho, Shon, Hong, Lee, & Vigneswaran, 2011) Different compounds are used in the formulated water but most commonly are nitrogen and phosphorus compounds.

Seawater desalination is expensive for irrigation water supply in countries where natural fresh water resources are scarce such as Qatar. RO and thermal desalination processes are the main technologies for seawater desalination in Qatar with average cost about 1 USD/m3.(Peñate & García-Rodríguez, 2012) The product water also requires further post-treatment for pH and minerals adjustment before it can be used. Furthermore, fertilizing chemicals should be added for application of desalinated water in farming and agriculture.

In the recent years, forward osmosis (FO) has gained interest for the dilution of different types of draw solutions.(Phuntsho, Hong, Elimelech, & Shon, 2013) This is due to several advantages of the process such as; economical energy consumption, high salts rejection, low fouling possibility and reversible fouling property. This study evaluates the performance of using hybrid FO-RO process to produce engineered fertilizing solution applicable for irrigation purposes. The FO process was carried out using a real treated sewage effluent (TSE) as the FS and a tailor-made DS in order to produce a high-quality fertilizing solution to be used directly for irrigation purposes. The draw solution was a mixture of NaCl and Diammonium phosphate ((NH4)2HPO4). Seawater RO membrane (SW30HR) and brackish water RO membrane (BW30LE) were tested for the regeneration process of the draw solution. The study investigated the impact of the RO membrane type on the quality of the fertilizing solution and the desalination energy. (NH4)2HPO4 concentrations of 0.01M and 0.5M were tested in the FO process under different operating conditions, namely, flow rate and membrane orientation.

1.2 Objectives

The purpose of this study is the production of engineered fertilizing draw solution by using hybrid FO-RO system.

The impact of different parameters was studied in forward osmosis (FO):

- Flow rate of draw and feed solution.
- Membrane orientation.
- Concentration of draw solution.

In reverse osmosis (RO) system, different membranes types were evaluated.

1.3 Thesis Structure

Water challenges in Qatar and challenges to treat wastewater were demonstrated in the first part of this thesis. Then, a literature review of existing fertilizer drawn forward osmosis systems is prepared in addition to a summary for the most recent research done in FO and RO technologies. Later, methods and materials used in FO/RO process were described. Characterization and testing procedures were described. In chapter 4, the results of each system; FO and RO are presented and described. Moreover, the performance of the hybrid FO-RO system is discussed. Lastly, conclusions of the work done were stated along with recommendations.

CHAPTER 2: LITERATURE REVIEW

2.1 Water statistics in Qatar

With a booming economy, the need for fresh water is increasing every day in Qatar. Qatar is 2nd in terms of per capita water consumption in the world and in 2015 it was 0.7 m^3 per day per person. For the same year, the total consumption for residential and industrial usage was 706 Million m^3 of fresh water (*WATER STATISTICS In The State of Qatar, 2015*, 2017).The demand of water in Qatar comes from residential, industrial, and agricultural sectors. Currently, the water demand is met ~30% by underground water, ~68% by desalination plants, and approximately 2% by treated sewage effluent (*WATER STATISTICS In The State of Qatar, 2015*, 2017). Figure 1 shows the increasing trend of water consumption in Qatar. It can be seen that the ground water consumption level has not changed since 2005. So, extracting more ground water to meet the increasing demand is not possible.

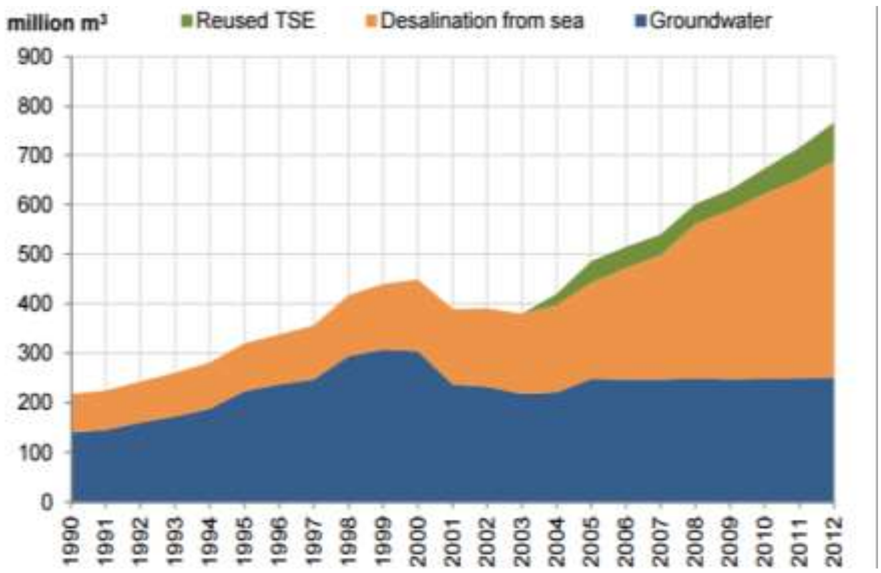

Figure 1:Source of fresh water in Qatar (WATER STATISTICS In The State of Qatar, 2015, 2017)

2.1.1 Ground Water

The ground water from aquifers of Qatar is exclusively used by agricultural sector. In 2013, 250 Million m^3 of water were extracted from the underground aquifers of Qatar (*WATER STATISTICS In The State of Qatar, 2015*, 2017). On the other hand, the total recharge of the aquifers from rainfall and inflow from Kingdom of Saudi Arabia was merely 47.5 Million m^3 (*WATER STATISTICS In The State of Qatar, 2015*, 2017). This imbalance possesses a significant threat to these fresh water aquifers. The influx of seawater to ground water is a direct consequence of this imbalance and the salinity of the water is on rise as indicated by the conductivity of underground water samples. To protect this natural source, desalinated water is being injected in the ground (*WATER STATISTICS In The State of Qatar, 2015*, 2017).

2.1.2 Desalination plant

Desalinated water is used for industrial and residential purposes. The latest available data published in 2018 shows that, total desalination capacity of Qatar is 480 Million Imperial Gallons per Day (MIGD) or 1.69 Million m^3/day("Overview on-KAHRAMAA drinking water quality requirement.," 2014).

There are currently three main desalination technologies used globally: Multi Stage Flash (MSF), Multi Effect Flash (MEF), and Reverse Osmosis (RO) (Burn et al., 2015). In multi stage flash technology, the brine is heated to 95-110^{o}C (Hanshik, Jeong, Jeong, & Choi, 2016). Flash columns are used to evaporate the brine partially. The number of flash columns can vary between 17 and 40. The vapor from each flashing unit is used to heat up the incoming brine (Harandi, Rahnama, Jahanshahi Javaran, & Asadi, 2017). The first 20-30 stages where brine is heated using the vapor from flashing, is known as heat recovery stages. The last 3-10 stages are known as heat rejection stages (Fiorini & Sciubba, 2005). Figure 2 shows a schematic diagram of a MSF desalination plant.

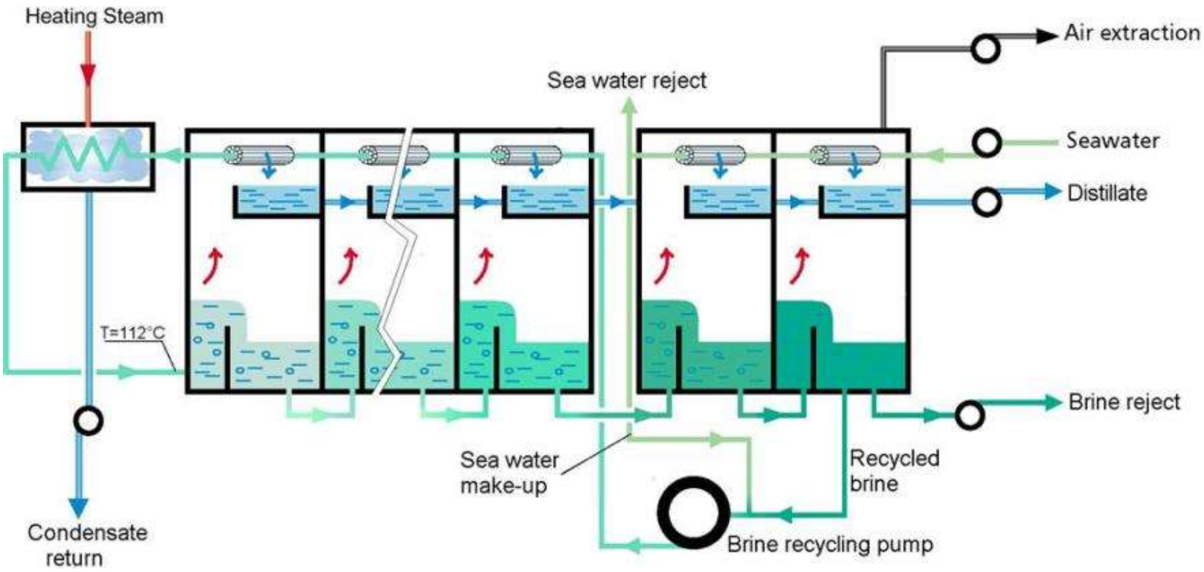

Figure 2 : Schematic of a MSF Desalination plant(Lingkungan, 2012)

In multi effect flash distillation, steam is supplied to the first flashing column (Ullah, Rasul, & Khan, 2013). The brine inside the column gets heated by steam and evaporates. The vapour from first flashing stage enters the second flashing stage and evaporates the brine in second flashing stage. The vapour continues to follow this pattern until the last flashing stage. The vapour from all the stages are finally condensed and collected as fresh water (El-Dessouky, Ettouney, Al-Juwayhel, & Al-Fulaij, 2004). It is to be noted that, the pressure inside the column decreases gradually in the flash drums. This in turn reduces the boiling point of brine inside the flash column (Bromley & Read, 1970). The number of flash columns can be between 20 and 25. A schematic diagram of a MEF desalination process with 3 flash columns can be seen in Figure 3.

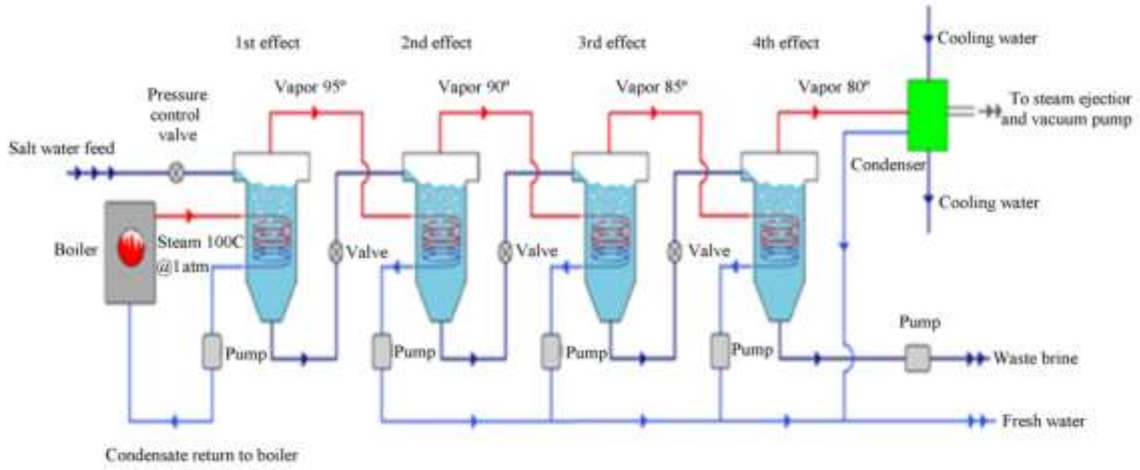

Figure 3: Schematic diagram of a MEF desalination process (Ullah et al., 2013).

Another technology that is widely used for small scale desalination plants is Reverse Osmosis. In reverse osmosis, there are two sides of the filters. Due to osmotic pressure, the natural direction of water is from the side of higher concentration to the side of lower concentration (Malaeb & Ayoub, 2011). In RO, the hydrostatic pressure of the brine is increased above osmotic pressure of the solution. This positive-pressure gradient generates gradient concentration across the membrane against the natural-osmosis direction (Greenlee, Lawler, Freeman, Marrot, & Moulin, 2009).

Almost 98% of the desalinated water comes from MSF and MEF desalination plants ("Overview on- KAHRAMAA drinking water quality requirement.," 2014). Table 1 shows the desalination plants that are currently in operation in Qatar and their corresponding technology.

Table 1: Desalination Plants in Qatar (2018)

Name	Capacity (MIGD)	Technology
Raas Abo Funtas B	33.0	MSF
Raas Abo Funtas B3	29.2	MSF
Raas Abo Funtas A1	45.0	MSF
Raas Abo Funtas A2	36.0	MSF
Raas Abo Funtas A3	36.0	MSF
Dukhan	2.0	RO
Ras Laffan Power	40.0	MED
Qatar Power	60.0	MED
Ras Girtas Power	63.0	MED
Umm Al Houl Power	136.0	RO/MSF
Total	480.2[1]	

1) 2.2 Million m3/day

As seen from Table 1, the main desalination technologies suitable for Qatar are expensive thermal desalination plants. In order to reduce the stress of desalination and ground water, usage of TSE has to be increased.

2.2 Treated sewage Effluent:

The sewage water in Qatar is treated and used mainly for agriculture and landscaping. In 2011, 15.6% of total water demand of the agriculture industry was met by Treated Sewage Effluent (TSE). In 2012, this number increased to 28%. Apart from agriculture, TSE is being used by the district cooling industries (ASHGAL, 2014). It is illegal in Qatar to use potable water for cooling. It is estimated that, 73 Million m^3 of

TSE will be used by cooling industries by the year 2020 (Jasim, Saththasivam, Loganathan, Ogunbiyi, & Sarp, 2016). The other sectors where TSE is being used in Qatar are, fire-fighting training exercises, non-potable use in construction and road works, sanitary flushing and sand washing. Qatar aims to extend their sewage treatment facilities to meet the demand of about 1 Million people by 2020 ("Qatar progresses with wastewater reuse plan," 2016). The wastewater treatment plants in Qatar are listed in Table 2.

Table 2. Wastewater Treatment Plant in Qatar (2019)

Plant	Capacity (m3/d)	Main stages	Tertiary treatment
Doha north sewage treatment works	439,000	Fine Screen – Grit Separator – Bioreactor – Clarifier – Chlorine contact tank – GMF – Ultrafiltration – UV disinfection.	Ultrafiltration + UV disinfection
Doha south sewage treatment works	241,000	Screening - Grit removal - Aeration tanks - Clarifiers - Sand filter- Chlorination	Ultrafiltration
Doha west sewage treatment works	175,500	Screening (6 mm) - Grit traps (VORTEX type) - Aeration tanks – Blowers - Clarifiers (suction type) - Sand filters - Membranes filtration.	Ultrafiltration (Ultrablue™ ZW1000)
Lusail sewage treatment works	60,000	screening (10 mm) – equalization - fine screening - grease removal and cooling - membrane bioreactor – Ultrafiltration – Chlorination.	UltraforTM MBR membrane bioreactor + Ultrafiltration + Chlorination

As seen from Table 2, there are multiple stages used by all the WWTPs to make TSE suitable for discharging to the nature. The stages can be divided in to primary, secondary and tertiary treatment stages.

2.2.1 Preliminary and Primary treatment

Preliminary and primary treatment of wastewater usually contains combination of technologies designed to remove coarse biodegradable material and grit from wastewater and stabilize the stream by chemical additions. In domestic water treatment, preliminary and primary processes can remove up to 25% of the organic matter and approximately the entire nonorganic matter (Salgot & Folch, 2018). In industrial wastewater treatment, primary treatment processes may include pH adjustment and equalization of flow that is extremely important to the treatment plant (Ardley, Arnold, Younker, & Rand, 2019).

A crucial part of the wastewater recycling plant is the facilities and equipment used to eliminate grit, rags, sticks, debris and other undesirable objects (Salgot & Folch, 2018). This may cause severe damage to the facility and reduce the treatment efficiency. A summary of the commonly used unit operations is listed below.

(1) Screening. Screening is a preliminary treatment process used to intercept unwanted solids, to protect mechanical equipment in the treatment plant and prepare the main wastewater stream to enter through the process. Screening shall always be used for different types of wastewater.

(2) Grit removal. Grit is defined as heavyweight inactive particles in the wastewater stream which will not be able to decompose. Grit has a S.G of 2.65, and design

of grit removal chambers is done to remove the particles larger than about 0.011.inch (Hernández-Chover, Bellver-Domingo, & Hernández-Sancho, 2018).

(3) Pre-aeration. This is done by pumping oxygen to the wastewater stream in stage of preliminary treatment. This is conducted by either increasing the detention time in the aerated chamber or separate additional aeration process (Liu et al., 2019).

(4) Equalization. Equalization is usually used for industrial discharges wastewater and some military processes. Equalization process decreases fluctuations of the influent to levels which make it suitable for succeeding processes. A proper facility regulates the wide variations of flow, pH, BOD, and other parameters to make it suitable for downstream systems. Appropriate equalization stage will minimize system problems and provide a higher-quality effluent.

(5) pH control. pH control is used in preliminary treatment of industrial wastewater treatment. Treatment plant equipment can be damaged because of acidic or basic steam (Hernández-Chover et al., 2018). This process is important to meet effluent quality necessary for secondary stage.

(6) Flotation. Is usually used to treat wastewater with high amount of grease and fine suspended particles. This is found in discharges and streams created by industrial application. Domestic wastewater may also contain grease because of food deposits (Ardley et al., 2019). Using aeration to float materials may release scum in a sedimentation tank and reduce the grease concentration to make it suitable for the following treatment processes. Grit removal is usually combined

with the flotation process by introducing sludge-removal facility (Hernández-Chover et al., 2018).

(7) Plain sedimentation. gravity sedimentation is usually done after the preliminary treatment in an inactive tank. In this process, most of the settable solids and suspended solids settle in the basin. Mechanical collectors are used to remove the sludge from the wastewater surface. Skimming is also provided to eliminate floatable particles such as oil, grease and scum that gather at the surface (Brusseau, Famisan, & Artiola, 2004). Wastewater characteristics and the amount of organics present in the solids plays major role in determining the BOD and suspended solids removal efficiency.

(8) Chemical coagulation. Sedimentation using chemical coagulation is applied to remove the phosphate from the domestic wastewater and other elements in industrial wastewater. The removal of BOD and suspended solids is enhanced by chemical coagulating, but it is not usually economical. However, it is used in some specific applications (Hernández-Chover et al., 2018).

2.2.2 Secondary treatment

Secondary wastewater treatment usually contains processes such as coagulation-flocculation, oxidation, precipitation by using biological processes where bacteria are used to remove the pollutant. Biological treatment is used to remove the organic-matter from the wastewater. Hence, biological reactor is usually used in secondary treatment process either in single stage or in multi stage as per the requirements to comply with the discharge standards (J. Tang, Zhang, Shi, Sun, & Cunningham, 2019).

Wastewater biological treatment is done to remove organic substance from the stream which is available in colloidal and soluble form. In addition, it aims to reduce the concentration of nutrients such as phosphorous and nitrogen from wastewater. Cell tissue have high density compared to water, so it can be removed in settling tank. Hence, the cell tissues need to be removed before the process ends.

Biodegradable organics are biologically removed by multiple steps including mass transfer, adsorption, absorption and biochemical enzymatic reactions. Treatment of organic substances is accomplished by two distinct metabolic processes:

(1) Respiration. organic and inorganic particles are oxidized by the biochemical reactions, which is catalyzed by large protein molecules (enzymes) produced by microorganism. The oxidation process takes place in both aerobic and anaerobic conditions. In aerobic conditions, the final electron is accepted by oxygen. In anaerobic conditions, the final electron is accepted by nitrates, sulphates, carbon dioxide and other organic compounds (Z.-H. Li, Hang, Lu, Zhang, & Yu, 2019). Respiration metabolic products are true inorganics such as carbon dioxide, hydrogen sulfide, water and ammonia. The energy obtained from the respiration is consumed by the microorganisms to create new protoplasm through another group of reactions. The heterotrophic microorganisms originate the energy needed for cell synthesis by oxidation of organic matter (Hernández-Chover et al., 2018). Autotrophic microorganisms derive the energy for synthesis either from the photosynthesis or the inorganic substances. Microorganisms require energy for the maintenance of their life activities.

(2) Catabolism and Anabolism. bacterial metabolism is one of the most important process to remove the organic material from the wastewater. Metabolism is the usage of the organic material as a source of energy for the production of cellular

matter. Catabolism is the process of transferring the organic material into stable end product while using it as source of energy. Anabolism is the process of incorporating the organic material into cell mass. Anabolism process consumes energy and it is only possible if catabolism occurs at parallel time to supply the required energy.

2.2.3 Tertiary treatment

It is the last treatment process that polish the wastewater to make it suitable to being reused, recycled or discharged. This stage treatment eliminates the traces of the nitrogen and phosphorus. Bacteria and viruses are also removed at this stage because it is harmful for the human body.

(1) Physical processes of tertiary treatment. The physical method used for tertiary wastewater treatment depends on passing of the stream through sand-filters or micro screen. The wastewater passes through micro pores which attract fine suspended particles. The retention of the particles is determined by the size of pores. The water enters through the frontal side of the sieve, where suspended solids rest on the sieve surface and water passes to the other side of the sieve. In addition, sand filters can be used in tertiary wastewater treatment which is similar to the sieve. Sand filter is more efficient than micro screens, however it decreases the amount of dissolved oxygen in the wastewater sample (Sharma, Syed, Brighu, Gupta, & Ram, 2019). Micro screen is easier to operate compared to sand filter. Treatment using UV is usually done to prevent the bacterial growth in the treated sample.

(2) Physicochemical processes of tertiary treatment. In tertiary treatment stage more physicochemical methods can be applied such as: chemical coagulation, adsorption, electrodialysis, foaming, distillation, reverse osmosis, solvent extraction, freezing, ionic exchange, chemical and electrochemical oxidation.

The water coming out from the tertiary treatment stage is usually discharged back to the water bodies. However, these treated sewage effluents (TSE) have the potential to be engineered to fertilizing solution after further treatment.

2.3 Fertilizing solution

Phuntsho et al. evaluated the performance of nine different fertilizing DS and seawater as the feed solution (Phuntsho et al., 2016). This was studied in terms of flux and RSF. The study shows that salts with high solubility have high osmotic pressure. DS of KCl and KNO_3 had the highest water flux while $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ had the lowest RSF.

Zhiwei et al evaluated the applicability of using FO process for concentrating of wastewater (Chen et al., 2017). It was done using pilot scale forward osmosis, low strength municipal wastewater as the feed solution and 0.5M NaCl as the draw solution. A spiral-wound membrane module was used to operate the system. 99.8% COD rejection rate, 99.7% total phosphorus rejection rate and 67.8 % of ammonium rejection rate were achieved with flux of 6 LMH.

Hawari et al used dewatering construction water as FS in forward osmosis and seawater used as the draw solution (Hawari, Al-Qahoumi, Ltaief, Zaidi, & Altaee, 2018). It was found that a flow rate of 2.2 LPM has the highest water flux and lowest fouling possibility. Adding spacer behind the membrane support layer was effective at low flow rates. The feed solution was pretreated using multimedia sand filter before applying it to forward osmosis. Results reveled that FO membrane flux was increased by 64.3% when sand multimedia filter was used and 13.5% flux enhancement was achieved when settling was carried out. It was also shown that the membrane flux can by increased by 30% by using PRO mode compared to FO mode.

Zhao et al evaluated the effect of membrane operation mode on FO performance for seawater desalination without foulants and with organic and non-organic foulants (Zhao, Zou, & Mulcahy, 2011). In severe fouling case, FO mode (AL towards feed solution) provides higher flux compared to the PRO mode (AL towards FS). Lower possibility of fouling and higher flux recovery was observed while using the FO mode compared to the PRO mode. Hence, FO mode has better performance while using feed solution with higher fouling tendency.

Chekli et al. evaluated the performance of fertilizer drawn forward osmosis for wastewater reuse and source of nutrients for hydroponic applications (Chekli et al., 2017). Nine different fertilizing draw solution were evaluated according to their FO performance, by measuring different parameters such as membrane flux, recovery rate, RSF and final nutrient concentration. The highest recovery rate of 76% was obtained using ammonium sulfate, the highest flux recovery of 75% was obtained while using KH_2PO_4 and finally ammonium phosphate monobasic had the lowest final nutrient concentration. However, further treatment was required to satisfy the irrigation water standards.

Phuntsho et al evaluated the performance of pilot scale forward osmosis – Nano filtration plant which was operated for six months using saline ground water from the coal mining activities (Phuntsho et al., 2016). Washing with clean water could restore the membrane flux. Fouling in Nano filtration was considered to be low. The study indicate that the hybrid system can produce water quality that meets irrigation standards. The FO feed brine failed to satisfy the discharge effluent standards due to the high concentrations of ammonium and sulfate.

Phuntsho et al. evaluated the performance of fertilizer drawn FO process to generate irrigation water using brackish ground water (Phuntsho et al., 2013). FDFO product water nutrients concentration exceeded the standard limits; further dilution was needed before applying it to crops. NF was assessed in this study as post treatment for FDFO to reduce the nutrients concentration and thereby allow direct use on crops without dilution. NF was found to be efficient while using low salinity brackish water, however when using high salinity brackish water, the product water still needed further dilution before using it as irrigation water.

Li et al showed the effect of DS and FS concentration on the FO process were evaluated (D. Li, Zhang, Simon, & Wang, 2013). Polymer gel that contained carbon filler particles led to the highest water flux because of the improved swelling ratio. The draw solution that contained polymer hydrogels particles of sizes ranging (100 µm - 200 µm) resulted with high water flux compared with larger particles of sizes (500 µm - 700 µm). As the FS concentration increased, the flux decreased due to the decrease in osmotic gradient. The use of CTA membrane resulted in higher flux compared to the use of polyamide-composite RO membrane.

Ortega et al. studied the concentration of sewage effluent using FO (Ortega-Bravo, Ruiz-Filippi, Donoso-Bravo, Reyes-Caniupán, & Jeison, 2016). CTA and TFC membranes were used with sewage and clean water. TFC membranes obtained higher membrane flux compared to CTA, while using clean water as draw and sewage as feed solution. The study shows that concentrating of wastewater using FO would be feasible, and could improve energy recovery from sewage. But the main disadvantage is the low membrane flux which can be solved by increasing the membrane requirement.

Volpin et al. evaluated the performance of FO as pre-treatment process to dilute seawater using wastewater before further dilution using reverse osmosis (Volpin et al., 2018). Membrane fouling is a major issue that was studied through long term experiments carried out in this project. Proper selection of wastewater was needed before applying it to large scale FO-RO setup. Membrane flux and characterization were used to assess the membrane fouling performance. A water flux of 22.5 LMH was obtained while using secondary effluent which caused minimal fouling. Biologically treated wastewater and secondary effluents caused mild to severe fouling (25% - 50% flux decline after 24h). Ammonia leakage to the DS was measured and found to be negligible while using biologically treated wastewater as the FS. Table 3 shows the limit of different nutrients that can be present in TSE to be considered as fertilizing solution.

Table 3. Discharge Limits to the Marine Environment in Qatar. ("Environmental Law No. 30," 2002)

Parameter	Maximum Limit	Unit
Physical characteristics		
Total Dissolvent	1500	ppm
Total Suspended Solids	50	ppm
Hydrogen Base	6-9	
Floating Bodies	Nil	
Temperature	Not more than three degrees above the relevant average	(ΔT) oC
Turbidity	50	ppm
Inorganic material		
NH_4^+	3	ppm
Sediment Chloride	0.05	ppm
Cyanide	0.1	ppm
Fluorides	1	Ppm

Parameter	Maximum Limit	Unit
Inorganic material		
Sulphur	0.1	ppm
Required Vital Oxygen	50	ppm
Required Chemical Oxygen	100	ppm
Urea	2	ppm
Total Nitrogen	100	ppm
Heavy metals		
Aluminium	3	ppm
Arsenic	0.5	ppm
Barium	2	ppm
Boron	1.5	ppm
Cadmium	0.05	ppm
Total Chrome	0.2	ppm
Cobalt	2	ppm
Copper	0.5	ppm
Iron	1	ppm

Parameter	Maximum Limit	Unit
Heavy metals		
Lead	0.1	ppm
Manganese	0.2	ppm
Mercury	0.001	ppm
Nickel	0.5	ppm
Zinc	2	ppm
Silver	0.005	ppm
Selenium	0.02	ppm
Organic material		
Oil and Grease	15	ppm
Total Phenols	0.5	ppm
Halogen Hydrocarbons and Different Kinds of Pesticides	0.1	ppm
Dioxine / Viran	$1.34x10^{-7}$	Ug/L
Tri Halomethane	100	Ug/L

2.4 Forward Osmosis

Osmosis is the property that describes the solvent diffusion through a semipermeable membrane and rejecting solute particle. This property was initially considered by Wilhelm Pfeffer in 1877. Then it was introduced again by Thomas Graham. When solution of high concentration and low concentrated solution are separated by semipermeable membrane, the highly concentrated solution gets diluted and both the solutions become equal in concentration. Osmotic pressure is a natural chemical property generated by the chemical solution and can be calculated using the following equation which is applicable for ideal solutions.

$$\pi = nMRT \tag{1}$$

Here, n is Van't Hoff factor, M is molarity, R is ideal gas constant ($R=0.0821$ $L\cdot atm \cdot mol^{-1} \cdot K^{-1}$) and T is absolute temperature (K).

FO membranes are synthesized using two layers namely active layer (AL) and support layer (SL). The dense AL is attached to a porous SL which allow the forward osmosis membranes to have the nature of asymmetry (Zhao, Zou, Tang, & Mulcahy, 2012). As a result, the FO process can be operated using two different modes forward osmosis and pressure retarded osmosis. In forward osmosis (FO), the AL is placed towards the FS, in (PRO), the AL is placed towards the DS.

FO is a promising desalination technology and is considered as clean energy process. FO is a process which depends on the difference in osmotic pressure between DS and FS. Unlike RO, forward osmosis process does not require a high-pressure pump, because it depends on the osmotic pressure gradient between feed and draw solutions. In FO process, FS is fresh water with low pollutant concentration and draw solution is polluted water with high pollutant concentration. Both solutions are separated by semi-permeable membrane which allows for fresh water extraction through pores with high rejection rate for most of the dissolved salts. There are several advantages for the forward osmosis process such as: low energy consumption compared to RO process as mentioned earlier, low membrane fouling, fouling can be easily reversed using backwashing with clean water and the ability to withstand highly contaminated feed solutions.

The driving force in FO is osmotic pressure, where the driving force in RO is the applied pressure using external pump.

2.4.1 Draw Solution of Forward Osmosis

Draw solution (DS) is a solution which is considered to have high osmotic pressure. The DS must have enough osmotic pressure larger than the FS. As noticed from equation 1 the osmotic pressure depends on solute concentration, number of ions, MW of the solute and the temperature. The performance of the draw solution depends on the draw solutes because it is the source of osmotic pressure. Draw solutes with high solubility tends to have high osmotic pressure. Several DS was evaluated in the previous studies and can be categorized into inorganic DS, organic DS and other types of DS such as, nanoparticles draw solution or Polymer hydrogel particles-based draw solution.

2.4.1.1 Inorganic Draw Solution

Inorganic draw solutions are composed of electrolytic solution. However, non-electrolyte DS are possible in some cases (Achilli, Cath, & Childress, 2010). In Table 4, 14 inorganic based DS are listed for the FO process. The DS compounds were chosen out of 500 inorganic compounds due to the high-water solubility, low cost and osmotic pressure. Several studies have used sodium chloride as draw solute for FO process because saline water is available with large quantities on earth. Also, the thermodynamics of sodium chloride have been widely studied making it easier to be used.

Table 4. Physical - Chemical Properties and Experimental Water Flux of Inorganic Draw Solutions

Draw Solute	MW	Osmotic pressure (2.0 M)	Max solubility (g/mol)	Experimental water flux (µm/s)
KCl	74.60	89.30	4.6	6.337
$Ca(NO_3)_2$	164.10	108.50	7.9	5.022
NH_4Cl	53.50	87.70	7.4	5.348
$(NH_4)_2SO_4$	132.10	92.10	5.7	5.391
NH_4HCO_3	79.10	66.40	2.9	2.04
Na_2SO_4	142.00	95.20	1.8	2.14
$NaHCO_3$	84.00	46.70	1.2	2.47
NaCl	58.40	100.40	5.4	2.68
$MgSO_4$	120.40	54.80	2.8	1.54
$MgCl_2$	95.20	256.50	4.9	2.33
K_2SO_4	174.20	32.40	0.6	2.52
$KHCO_3$	100.10	79.30	2.0	2.25
KBr	119.00	89.70	4.5	2.84
$CaCl_2$	111.00	217.60	7.4	2.64

2.4.1.2 Organic draw solution

Many organic compounds have been tested as draw solution for forward osmosis. Fructose and glucose solutions are common draw solutions because it can be consumed by the human body (Stache, 1989). Although organic solution consists of non-electrolyte compounds, they tend to have high osmotic pressure because of high solubility. Glucose was the first organic compound to be used as DS in FO for emergency water supply in boats. In addition, glucose was tested as DS for concentration of tomato juice to extract water from saline feed water. Fructose was tested for production of nutrients rich draw solution using saline feed solution.

Table 5. Physical - Chemical Properties and Experimental Water Flux of Organic Draw Solutions

Draw Solution	MW	Osmotic pressure (2.0 M)	Max solubility (g/mol)	Experimental water flux (μm/s)	References
Fructose	180.2	55.02	22.4	7.5	(Stache, 1989)
Glucose	180.2	55.02	800.0	7.5	(Stache, 1989)
Sucrose	342.3	56.81	6.1	0.35	(Stache, 1989)
Ethanol	46.1	43.93	N/A	N/A	(Stache, 1989)

2.4.1.3 Magnetic nanoparticles draw solutions

Nanoparticles is an area of extensive research due to the different applications in different industries. In water treatment, nanoparticles has been used as DS in FO for desalination (Ling, Wang, & Chung, 2010). Hydrophilic magnetic nanoparticles (MNPs) has been used as DS. The magnetic nanoparticles have been tested as DS for forward osmosis: polyacrylic acid magnetic nanoparticles, 2-Pyrrolidonemagnetic nanoparticles and triethyleneglycol magnetic nanoparticles. Even though they are non-electrolyte, they generate high osmotic pressure and can be recovered easily compared to organic and inorganic draw solutions due to high surface area / volume ratio.

2.4.1.4 Polymer hydrogel particles-based draw solution

A new class consisting of polymer hydrogel has been used as DS in forward osmosis. Hydrogels are defined as 3D web of polymer chain linked together using chemical or physical bonds. The particle size is ranged between (50 - 150 µm). Hydrogels with ionic based particles can attract water, which increase the osmotic pressure. The polymer hydrogels have reversible volume change property in response to light, pressure and pH. It can change from hydrophilic to hydrophobic. This characteristic makes the recovery of this DS very easy compared to thermal or membrane process.

The main challenge of membrane based osmotic processes is membrane fouling and the main reasons for reduced flux through fouling are concentration polarization and reverse solute flux.

2.4.2 Concentration polarization

Generally, the experimental flux is less than the theoretical one calculated using Equation 1, this is attributed to an inevitable phenomenon known as Concentration polarization (CP) (Cath, Childress, & Elimelech, 2006; Jeffrey R. McCutcheon & Elimelech, 2006; Zhang, Ning, Wang, & Diniz da Costa, 2014; Zhao et al., 2012). The structure of the FO membranes leads to elevation or drop of the concentration of solution at the interface between the solution and membrane. As a result, the concentration of both solutions is different than the bulk solutions as the water is being depleted from the boundary layer (Klaysom, Hermans, Gahlaut, Van Craenenbroeck, & Vankelecom, 2013; J. R. McCutcheon, McGinnis, & Elimelech, 2005). CP phenomenon also reduces water flux of the permeate (Sablani, Goosen, Al-Belushi, & Wilf, 2001). CP is categorized into external concentration polarization and internal concentration polarization. External concentration polarization is developed in the membrane-solution interface. Internal concentration polarization is developed within the support layer. (Klaysom et al., 2013; J. R. McCutcheon et al., 2005). CP is one of the major challenges in FO membrane processes therefore, Equation 1 has been modified in a way to consider the effect of CP in water flux (C. Y. Tang, She, Lay, Wang, & Fane, 2010; Zhang et al., 2014) Equation 2.

$$J_w = A\sigma\Delta\pi_{EFFECTIVE} = A\sigma(\pi_{DS_A} - \pi_{FS_A}) \quad (2)$$

Where $\Delta\pi_{EFFECTIVE}$ is the effective osmotic pressure difference (net driving force) and it is less than $\Delta\pi_b$ as a result of CP effects, π_{DS_A} is DS osmotic pressure at active layer and π_{FS_A} is FS osmotic pressure at active layer.

2.4.2.1 External concentration polarization (ECP)

The ECP occurs on the interface between the AL and bulk FS or active layer (AL) and DS. In FO mode, the feed solution’s concentration increases at FS-AL interaction point. As a result of the concentrative ECP (CECP), solutes build up at the AL surface. Thus, the osmotic pressure gradient ($\Delta\pi$) will be reduced to the effective osmotic pressure gradient ($\Delta\pi_{EFFECTIVE}$), which is less than the bulk osmotic pressure gradient $\Delta\pi_b$ as illustrated in Figure 4. ECP appears at the AL of the membrane and can be dilutive (DECP) or concentrative (CECP) based on the operation mode. In FO mode, concentrative external concentration polarization is more likely to occur. On the contrary, dilutive external concentration polarization occur in PRO mode. As mentioned earlier, ECP occurs due to the increase in the FS concentration at the AL. Hence, the FS osmotic pressure increases π_{FS_A} at the AL and the net driving force decreases as shown in Equation 3. Since FO process is low energy process, the solute build-up is relatively low compared to other membrane processes, this reduces the effects of ECP on water flux. The boundary layer film theory has been used by McCutcheon and Elimelech to create a model to estimate the water flux in presence of CECP in FO mode and is described as(Jeffrey R. McCutcheon & Elimelech, 2006; McGinnis & Elimelech, 2007):

$$\frac{\pi_{FS_m}}{\pi_{FS_b}} = \exp(\frac{J_w}{K_F}) \tag{3}$$

Where $\pi_{FS_m}$and π_{FS_b} are the osmotic pressures of the FS at the membrane surface and in the bulk, and K_F is the mass transfer coefficient on the FS of the membrane.

As the flow rate increase, the turbulence can minimize the influence of CECP.

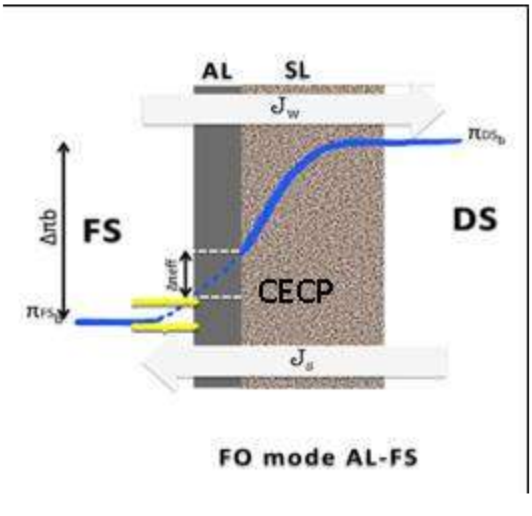

Figure 4. CECP in FO mode.

Dilutive external concentration polarization (DECP) is developed due to the decrease of draw solution concentration at the AL-DS interaction point which is a result of DS dilution as the water diffused from FS to DS. This reduce $\Delta\pi$ to be less than the $\Delta\pi_b$ as in the FO mode; however, the $\Delta\pi_{EFFECTIVE}$ in this mode is greater than that in FO mode that is depicted in Figure 4Figure 5. The flux is modeled according to the following equation.

$$\frac{\pi_{DS_m}}{\pi_{DS_b}} = \exp(-\frac{J_w}{K_D}) \tag{4}$$

Where $\pi_{DS_m}$and π_{DS_b} are the osmotic pressures of the DS at the membrane surface and bulk, and K_D is the mass transfer coefficient on the DS of the membrane. The mass transfer coefficient in both models is related to Sherwood-number which is expressed as:

$$K = \frac{Sh\, D}{d_h} \tag{5}$$

Where D is the solute diffusion coefficient and $d_h$is the hydraulic diameter of the flow channel in other words the pipe diameter (Jeffrey R. McCutcheon & Elimelech, 2006).

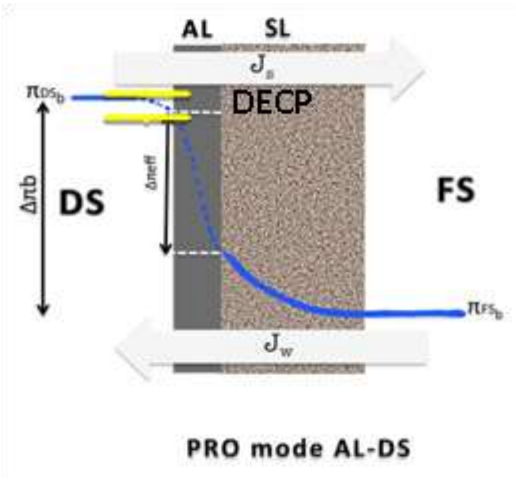

Figure 5. DEC in PRO mode

Generally, the ECP phenomenon in both types decreases the effective osmotic driving force in other words reduces the water flux. This unfavorable impact of the ECP can be reduced by increasing circulating flow rate or mixing that minimize the thickness of the boundary layer.

2.4.2.2 Internal concentration polarization

Internal concentration polarization (ICP) is developed within the SL due to asymmetrical nature of the FO membranes. Internal concentration polarization is divided into two types dilutive internal concentration polarization (DICP) which occurs in forward osmosis mode and concentrative internal concentration polarization (CICP) which occurs in PRO mode. DICP is considered as a challenging issue which negatively affects the water flux and reduces the driving force for the FO process (Cornelissen et al., 2008; Jeffrey R. McCutcheon & Elimelech, 2006; J. R. McCutcheon et al., 2005; Tan & Ng, 2008). DICP occurs in FO mode where AL is facing the FS, passage of water from the FS to the DS results in dilution of DS solute within the SL as in Figure 6. As a result, the water flux might be reduced by 80% in some cases (Ge et al., 2013). The water flux can be estimated in the presence of DICP combined with CECP in FO mode as (Jeffrey R. McCutcheon & Elimelech, 2006):

$$J_w = A\left[\pi_{DS_b}\exp(-J_w K) - \pi_{FS_b}\exp\left(\frac{J_w}{k_d}\right)\right] \tag{6}$$

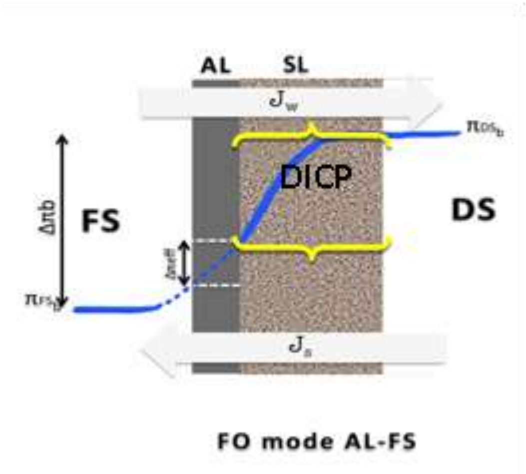

Figure 6. DICP in FO mode

On the other hand, while using PRO mode the concentration of the FS increased within the SL and form a polarized layer called concentrative ICP (CICP) (J. R. McCutcheon et al., 2005). The CICP phenomenon has the same concept of the CECP but different point of occurrence (J. R. McCutcheon et al., 2005). In PRO mode, the FS solutes enters the support layer due to convection phenomenon. Moreover, DS solutes diffuse through the AL due to the diffusion phenomenon into the SL. The effective driving force is reduced due to increased concentration around support layer and leads to severe flux reduction as shown in Figure 7 (Cath et al., 2006; Jeffrey R. McCutcheon & Elimelech, 2006). CICP combined with DECP occurs as the membrane is operating under PRO mode. A model was developed for the PRO mode by Loeb et al. (Loeb, Van Hessen and Shahaf, 1976) and is expressed as:

$$J_w = A\left[\pi_{DS_b}\exp\left(\frac{J_w}{k_D}\right) - \pi_{FS_b}\exp(J_w K)\right] \tag{7}$$

Where K measures the easiness of solute diffusion in and out of SL and measures the ICP severity (Zhang et al., 2014) and it is given:

$$K = \frac{t\tau}{D\varepsilon} \tag{8}$$

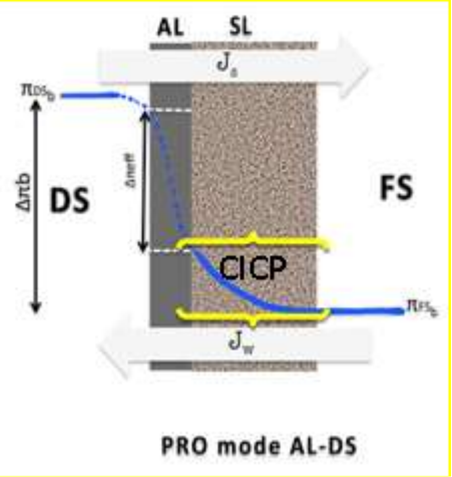

Figure 7. CICP in PRO mode

Equation 6 and Equation 7 are valid for specific conditions such as low concentrations of DS using membrane parameters only and measurable experimental conditions. Hence, recent study done by Bui et al. created a model that estimates the flux considering both DECP and CICP for asymmetric and TFC membranes in PRO mode that considers hydraulic pressure gradient across the SL and is expressed as(Bui, Arena, & McCutcheon, 2015):

$$J_w = A\left[\frac{\pi_{DS_b}\exp\left(\left(\frac{-J_w}{k_D}\right)\right) - \pi_{FS_b}\exp\left(J_w\left(\frac{1}{K_F}+\frac{S}{D_F}\right)\right)}{1+\frac{B}{J_w}\left[exp\left(\frac{1}{K_F}+\frac{S}{D_F}\right) - exp\left[-\left(\frac{J_w}{k_D}\right)\right]\right]} - \Delta P\right] \tag{9}$$

A similar study was done by Bui et al, where they developed a model that estimates the water flux which accounts for both CECP and DICP for asymmetric and TFC membranes in FO mode (Bui et al., 2015). The most recent tool used to estimate the flux of asymmetric and TFC membranes is:

$$J_w = A\left[\frac{\pi_{DS_b}\exp\left(-J_w\left(\frac{1}{k_D}+\frac{S}{D_D}\right)\right)-\pi_{FS_b}\exp\left(\frac{J_w}{K_F}\right)}{1+\frac{B}{J_w}\left[exp\left(\frac{J_w}{K_F}\right)-exp\left[-J_w\left(\frac{1}{k_D}+\frac{S}{D_D}\right)\right]\right]}\right] \quad (10)$$

Where B is the intrinsic solute permeability coefficient of the membrane, and D_D is the solute diffusivity in the DS.

As discussed in the ICP section, the ICP is considered as a challenging issue in FO processes. In order to mitigate the ICP phenomena, the FO membranes should have a high permeability and hydrophilicity with a small structure parameter and with thin SL (Gray, McCutcheon, & Elimelech, 2006; Jeffrey R. McCutcheon & Elimelech, 2006; Tan & Ng, 2008; C. Y. Tang et al., 2010). In addition, a draw solution with a high Van’t Hoff factor, diffusion coefficient and low viscosity is required to minimize the ICP impacts (Cath et al., 2006; Gray et al., 2006; Tan & Ng, 2008). A promising way to inhibit ICP impacts is by preparing a double-skinned FO membrane with thin porous SL facing the FS that look like an ultrafiltration or nanofiltration membrane and inhibit foulants from entering into the SL and a dense AL facing the DS. This design of membrane is not commercially available yet (Tan & Ng, 2008).

2.4.3 Reverse solute flux (RSF)

Reverse solute Flux (RSF) is one of the main challenges to FO processes (Cath et al., 2006; M. J. Hancock, Maher, Latimer, Herbert, & McAuley, 2009; Zhao et al., 2012). RSF is considered as a reason for ICP in FO mode. The presence of RSF can affect the operating cost of the FO desalination processes in case of solutes permeation from DS side into the FS side owing to the additional treatment needed for the concentrated FS preceding discharge to the environment. The RSF can be reduced to an extent that can decrease the operating cost by utilizing a DS that contains multivalent ions solutes as they have lower diffusion coefficients (Cath et al., 2006; Zhao et al., 2012). However, a severe ICP occurs due to using multivalent ions that have large ions(C. Y. Tang et al., 2010; Zhao et al., 2012). In addition, the tendency of fouling can increase once being in contact with foulants in FS (Zhao et al., 2011). Some models have been studied to define the RSF:

$$J_s = B\Delta c \tag{11}$$

Where J_s is the RSF, B is the membrane solute permeability coefficient, and Δc is the difference in concentration across the semipermeable membrane.

A model was developed by Philip et al. for the purpose of RSF determination in FO process without considering the impacts of ECP on FS and DS sides (Phillip, Yong and Elimelech, 2010). Using cellulose triacetate membrane (CTA) and NaCl DS where the experimental results revealed an agreement with the model expectations (Phillip, Yong and Elimelech, 2010) And is expressed as:

$$J_s = \frac{J_w C_{DS_b}}{1 - \left(1 + \frac{J_w}{B^*}\right) \exp\left(\frac{J_w S^*}{D}\right)} \tag{12}$$

Where C_{DS_b} is DS concentration in the bulk, S^* is the membrane structural parameter, and $B^*$is the AL permeability coefficient of salt defined as:

$$B^* = \frac{D^A\, H}{t_A} \tag{13}$$

$$B^* = \frac{D^A\, H}{t_A} \tag{14}$$

Where t_s is the membrane SL thickness and t_A is the membrane AL thickness, H is the partition coefficient, and $D^A$is the DS diffusion coefficient in the AL.

Moreover, Suh and Lee established a model that is more accurate than Equation 12 as it highlighted all the main physical processes that happens in FO process involving the RSF, ECP, and ICP as (D. Li et al., 2013).:

$$J_s = B\left[\frac{C_{DS_b} + \left(\frac{Js}{J_w}\right)}{\exp(J_w K)\exp\left(\frac{J_w}{k_D}\right)} - \left(C_{FS_b} + \left(\frac{J_s}{J_w}\right)\right)\exp\left(\frac{J_w}{K_F}\right)\right] \tag{15}$$

A model was developed to calculate the RSF and J_s in FO mode process. The difference is that use of $B_{DS}$and B_{FS} draw and feed solute permeability, respectively instead of single solute permeability (B) as in the models as in Equation 17 and Equation 18 and both models considered the CECP and DICP:

$$J_{Ds_S} = RSF = B_{DS}\left[\frac{C_{DS_b} exp\left(-\frac{J_w S}{D}\right)}{1 + \frac{B_{DS}}{J_w}\left(1 - \exp\left(-\frac{J_w}{D}\right)\right)}\right] \tag{16}$$

$$J_{FS_S} = J_s = B_{FS}\left[\frac{C_{FS_b} exp\left(\frac{J_w}{K_F}\right)}{1+\frac{B_{FS}}{J_w}\left(1-\exp\left(\frac{J_w}{K_F}\right)\right)}\right] \tag{17}$$

Yong at al. used three neutral draw solutes to investigate the reverse flux: urea, ethylene glycol, and glucose (Yong, Phillip, & Elimelech, 2012). The study concluded that for rapid permeating draw solutes, ECP on the FS side of the membrane will result in additional resistance of mass transfer:

$$J_s = \frac{J_w B^*(C_{FS_b} \exp\left(Pe^s + Pe^\delta\right) - C_{DS_b})}{(B^* \exp(Pe^\delta) + J_w) \exp(Pe^s) - B^*} \tag{18}$$

Where Pe^s is the Peclet number in the SL and Pe^δ is the Peclet number in the boundary layer. In order to carry out FO, suitable membrane has to be selected.

2.5 FO membrane

2.5.1 Cellulose Tri-Acetate (CTA) membrane

Hydration Technologies, Inc. (HTI) developed a FO membrane that was made of Cellulose Tri-Acetate (CTA) and supported by a polyester mesh (Cath et al., 2006; Qiu, Setiawan, Wang, Tang, & Fane, 2012). This type of membranes is made by submerging rolled polymer dope into coagulants in which phase-inversion occurs and produces an asymmetric-membrane that has an AL supported by a SL (Ong & Chung, 2012; Yen, Mehnas Haja N, Su, Wang, & Chung, 2010). Preparation of the polymer dope must be using a volatile solution in the presence of added acetone to ease the evaporation process of the solution and confirm the AL formation. When Cellulose Acetate (CA) and CTA membranes are compared to other membrane such as Thin Film Composite (TFC), the fouling propensity in CA/CTA membrane was less than TFC membrane owing to its hydrophilicity nature and the strong resistance to chlorine (Ong & Chung, 2012). The water flux when CA/CTA membranes were used was observed to be below 20 LMH during FO mode with a highly concentrated DS as shown in Table 6. In addition, the RSF values were quite high compared to the RSF values when TFC membrane was used.

Table 6: Types of CTA Membranes

FO membrane	DS/FS	Water flux (LMH)	Reference
CA flat sheet membrane	DS: 2 M Glucose/ FS: 0.1 M NaCl	FO mode: 11.6–12.7	(Xu et al., 2016)
HTI FO membrane	DS: 1 M NaCl/ FS: DIW	PRO mode: 15.5/ FO mode: 10	(Gray et al., 2006; Ling & Chung, 2011)
CA flat sheet	DS: 2 M $MgCl_2$/ FS: DIW	PRO mode: 26/ FO mode: 17	(Yen et al., 2010)
CA-hollow fiber	DS: 2 M $MgCl_2$/ FS: DIW	PRO mode: 36/ FO mode: 8	(Su and Chung, 2011)

2.5.2 Thin Film Composite (TFC) membrane

In year 2010, TFC FO membrane was developed into two configurations, flat sheet and hollow fiber. Similar to CTA membranes, Hydration Technologies, Inc. (HTI) provided the first commercial TFC FO membrane. Other companies has also provided TFC FO membranes, Porifera Inc. and Oasys Water Inc. (Hickenbottom, Vanneste, Elimelech, & Cath, 2016) . Some types of TFC membrane is shown in table 7.

Table 7: Types of TFC Membranes

FO membrane	DS/FS	Water flux (LMH)	References
TFC/ Phase Inversion substrate	DS: 1.5 M NaCl / FS: DIW	FO mode: 18.16	(Yip et al.., 2010)
TFC/ PI	DS: 0.5 M NaCl/ FS: 10mM	PRO mode: 20/ FO mode: 13.5	(Wei et al., 2011)
TFC/ Nanofiber substrate	DS: 0.5 M NaCl/ FS: DIW	FO mode: 37.8	(Yang et al., 2011)
	DS: 1.5 M NaCl / FS: DIW	PRO mode: 50/ FO mode: 29	(Tian et al., 2013)
TFC/ Nanoparticles in substrate	DS: 0.5 M NaCl/ FS: DIW	PRO mode: 42.5/ FO mode: 21	(Ma et al., 2013)
	DS: 0.5 M NaCl/ FS: 10mM	PRO mode: 31.2/ FO mode: 17.1	(Emadzadeh et al., 2014)

2.5.3 Chemically modified membranes

Newly, FO membranes have been chemically modified using different chemical modification methods to prepare new FO membranes with improved performance (Zhao et al., 2012). Arena et al. utilized a new hydrophilic polymer known as Poly-Dop-Amine (PDA) to adjust TFC RO support layer (SL) to be used in engineering applications (Arena, McCloskey, Freeman, & McCutcheon, 2011). They showed reduction in ICP and enhancement of water. Other study done by Setiawan et al. on modified hollow fiber FO membrane with active layer (AL) that is positively charged through polyelectrolyte post treatment using Poly-Ethylene-Imine (PEI) for Poly-Amide-Imide (PAI) substrate (Setiawan, Wang, Li, & Fane, 2011). The positively charged AL allows the membrane to be used to remove heavy metals. The same group also improved a flat sheet membrane with AL that is positively charged on a substrate made of a woven fabric.

2.6 Reverse Osmosis

2.6.1 Reverse osmosis process

Reverse osmosis (RO) is a separation technique suitable for multiple applications such as wastewater treatment, desalination and treatment of brackish water. RO technology is generally used to remove salts or dissolved solids. RO is considered as one of the most economic solid/liquid separation technologies which is currently used in different applications. It is used to treat solutions with TDS of 100-50000 ppm to produce clean water. Cross flow configuration is used for RO process, the feed water is applied under a pressure of (55-68) bars on the membrane surface. Fraction of the feed solution passes through the pores of the membrane and majority of the feed solution travel on the membrane surface back to the feed solution. The permeate solution is considered as pure water with low concentration of salts, and the reject solution is concentrated solution having high concentration of salts and solids. The feed solution is constantly applied to the membrane with constant pressure, while operating the foulants accumulates on the membrane surface and cause fouling.

As mentioned earlier, osmosis is a natural property defined as the separation of pure water from a solution of low to high concentration through semipermeable membrane. Reverse osmosis occurs when a pressure higher than the osmotic pressure is applied to the feed solution. Water is forced to separate from dissolved solids and pass through semipermeable membrane to the diluted solution side. The process is illustrated in Figure 8.

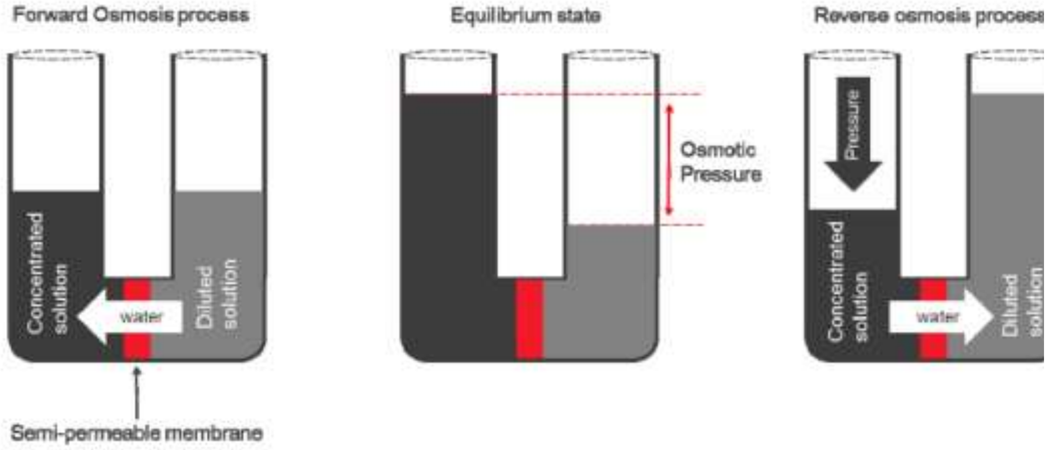

Figure 8. Natural osmosis, forward osmosis and reverse osmosis

Reverse Osmosis is facing three major constraints to extract fresh water namely; i) extensive energy required to operate the system. ii) high possibility of membrane fouling which decrease the water flux during operation. iii) The need for feed water pretreatment which is essential for extending membrane lifecycle and reduce operational cost.

Reverse osmosis membranes are categorized into hollow fine fiber and flat sheet. Generally, the RO membrane is composed of three layers, polyester support layer, polysulfone layer and polyamide barrier layer on the top surface. The performance of RO process is measured using membrane flux, salt rejection and recovery rate. Membrane flux describes the amount of permeate water which passes through membrane pores during RO process. The flux is calculated as:

$$J_v = \frac{Q_p}{S} \tag{19}$$

In which: J_v is membrane flux (LMH), S is area of the membrane(m^2), Q_p is flow rate of permeate (L/h).

The salt rejection is a percentage which represents the amount of solute retained on the membrane surface. The salt rejection is calculated using the following equations:

$$R = \left(1 - \frac{C_p}{C_{ave}}\right) x\ 100 \tag{20}$$

$$C_{ave} = \frac{C_f + C_c}{2} \tag{21}$$

Here, R is rejection, Cp is permeate concentration(ppm), Cf is feed concentration (ppm), Cc is concentrate concentration (ppm) and C_{ave} is average feed concentration (ppm).

The recovery rate is defined as the fraction of the feed flow which passes through the membrane. The recovery rate is calculated as:

$$Y = \frac{Q_p}{Q_f} \tag{22}$$

Here, Y is recovery rate, Q_p is permeate flow rate (LPH) and Q_f isfeed flow rate (LPH).

2.7 Hybrid FO for DS recovery

A hybrid system comprised of FO and heating process for DS recovery was developed by McCutcheon et al. and McGinnis et al. using a new thermolytic DS known as Ammonium Bicarbonate (NH4HCO3) (Jeffrey R. McCutcheon &

Elimelech, 2006) (J. R. McCutcheon et al., 2005). Modeling this system using a chemical modeling software resulted in an average water recovery of about 64% for the hybrid system and power consumption to be less than 0.25 kWh/m^3 for FO system (McGinnis & Elimelech, 2007). On the other hand, the power consumption for DS recovery, which is mainly heating required more than 75kWh/m^3 including single distillation that is impractical process unless waste heat is used to power the regeneration process. Another issue in this hybrid desalination system is the high Reverse Salt Flux (RSF) that reached 18.2 GMH compared to the low water flux value (7.2 LMH). In this study, after permeation and dilution of the thermolytic DS to be fed into the distillation unit, it was found that the produced water did not meet the drinking water standard provided by the World Health Organization (WHO) for ammonia to be less than 1.5 mg/L (Chekli et al., 2016). Hence, other DSs were used for the aim of seawater desalination. Forward Osmosis process (FO) was integrated with Membrane Distillation (MD) unit to form a hybrid system called FO/MD and investigated by Yen et al. using an organic compound known as 2-Methylimidazole as the DS (Yen et al., 2010). A high-water flux was achieved approaching 8 LMH, however, the solutes in the DS were moving to the FS side and causing the RSF. Another study examined the performance of FO/MD hybrid system using Na-functionalized carbon quantum dots (Na-CQD) **(ref)**. The presence of the MD process was for reconcentration of the Na- CQDs at 45 °C. The outcomes of the integration of both systems resulted in small water flux with a value of 3.5 LMH and no significant RSF was observed during the experimental work.

2.7.1 Hybrid FO–RO systems

Technically, implementing FO integrated with RO aimed to remove the dissolved salts from the FS so that the diluted draw solution is the inlet into RO system. Consequently, the quality of the RO product will get enhanced as fouling is less and reversible when FO is used as pretreatment to the RO (Mi & Elimelech, 2008). The reason for the widespread usage of FO in several applications is the requirement of less energy, the slight propensity of fouling, and the higher recovery of water. These advantages are not achieved without selecting the appropriate draw solutes that has high osmotic gradient and competent recovery at lower energy requirement (Chekli et al., 2016). Several studies reported the higher rejection of trace contaminants, dissolved ions and salts using FO combined with RO process (Coday et al., 2014; Shaffer et al., 2012). Forward Osmosis integrated with Reverse Osmosis (FO/RO) pilot scale system was implemented by Hancock et al. to examine the capability of the FO/RO system in rejecting dissolved ions (Hancock et al., 2013). The FS was deionized water or 2000mg/L NaCl solution. On the other hand, the DS was prepared by using synthetic sea salt with 54.8% of Cl^-, 3.54% of Mg^{2+}, and 1.26% of Ca^{2+}. The FO system was operating in FO mode at flow rate of 1.2 L/min. The membranes employed were (SW30 2540, DOW Filmtec, Edina, MN) used in the RO pilot system and (Albany, OR) FO membrane provided from HTI. The hybrid system experiments were running for 1300 hours producing 10,000 L of permeate from 900,000L of the FS. The results of the study indicated that the hybrid process rejection percentage approached 99.99% for orthophosphate and this high rejection was in agreement with the previous studies (Holloway, Childress, Dennett, & Cath, 2007). Moreover, the rejection percentage of nitrate was 95.8% that means the produced water has a high quality that is below the EPA contaminant level for the nitrate (10mg/L) (USEPA, 2009). The percentage of organic and inorganic salts rejection was performed by FO/RO system by (Xie & Gray, 2016) using an anaerobically digested sludge as FS and 0.6 M NaCl DS. The used membrane was flat sheet TFC from HTI for the FO process and RO membrane supplied by Dow FilmTec that composed of a AL and porous SL. The FO membrane was operating in FO mode considering a flow velocity of 9 cm/s at 25oC. The results approved the high percentage of rejection of organic matter and inorganic salts up to 95%. The double membrane barriers against this several contaminants lead to this extreme rejection and that was already agreed with previous studies (D. Li et al., 2013). Beside the high rejection achieved by the FO-RO system, a noticeable increase in the nutrient and dissolved organic matter in the DS due to the accumulation of contaminants. The performance of FO/RO hybrid system was studied by integrating a bench-scale FO subsystem with RO using CTA membranes (HTI, Albany, OR) and circulating FS and DS at 1.5LPM. The FS and DS concentrations were kept constant where the DS is concentrated NaCl (50g/L) and the FS was filtered contrate at the same temperature of 23oC and operating the FO subsystem under FO mode. The process was maintained for 50hours, and the permeate volume was 4L for each 10hours. The results of the contrate concentration of the integrated FO/RO system outperformed the RO subsystem (Holloway et al., 2007) utilized a hybrid FO/RO system for landfill leachate treatment that can be considered as the contrate in the previous study (Holloway et al., 2007). The landfill leachate has a wide range of pollutants such as TDS, suspended solids, organic compounds, heavy metals, and organic and inorganic nitrogen. The water recovery percentage that has been achieved was up to 95%. In addition, high quality permeate water that met the allowable limits of freshwater quality standards was produced. Furthermore, a study examined the performance of FO/RO hybrid system at different feed salinities between 35000ppm and 45000ppm to be compared with the conventional RO. The model calculations revealed that when no Energy Recovery Device (ERD) was utilized, the FO/RO performance was more energy efficient than RO. On the other hand, the hybrid system was not highly efficient in power consumption when a high efficient ERD was employed (Altaee, Zaragoza, Drioli, & Zhou, 2017). In addition, FO/RO hybrid desalination system was developed by a modeling study. The used DS was 1.2 M NaCl and FS was seawater. As permeate is moving across the FO membrane, the diluted DS is fed into the RO membrane system to extract the fresh water and recycle the concentrated FS. The simulation results represented a higher efficiency of FO/RO than the conventional RO at higher seawater salinities that lead to highly competitive behavior of FO/RO at high FS salinities. The flux in FO/RO hybrid system was lower than that in RO process (Altaee, Zaragoza, & van Tonningen, 2014). Lastly, a study done by Bamaga et al. illustrated the capability of hybrid FO/RO system to be a suitable system for desalination as the generated water flux using the available FO membranes is low. Hence, further researches on FO/RO system are needed in developing a new membranes with high water flux, low fouling possibility and reversibility to allow the FO processes to be one of the pretreatment processes (Bamaga, Yokochi, Zabara, & Babaqi, 2011).

CHAPTER 3: EXPERIMENTAL MATERIALS AND METHODS

3.1 Feed and Draw Solution (Forward osmosis)

The feed solution (FS) in the FO system was treated sewage effluent (TSE). Treated sewage effluent samples were collected after the treatment with membrane bioreactor (MBR) unit from Lusail wastewater treatment plant located in Doha, Qatar. The characteristics of the collected TSE samples are summarized in Table 8. Two types of draw solutions (DS) were studied in the FO system. The first draw solution was made of 0.5M NaCl solution (i.e. seawater). The second draw solution was the engineered fertilizing solutions (EFS). The EFS was composed of 0.5M NaCl and 0.01M diammonium phosphate ((NH4)2HPO4). The diammonium phosphate was added to the draw solution as a nutrient source in the product water while NaCl is the source of osmotic pressure across the FO membrane. The product water from the hybrid system is supposed to be used directly on crops for irrigation purposes.

Table 8: Characteristics of the Treated Sewage Effluent (TSE) Collected Form a Wastewater Treatment Plant in Doha, Qatar.

Parameter (unit)	Value	Standard Method
pH	6.9	APHA 4500-H+ B. Electrometric Method
Temperature I	22.2	APHA 2550 TEMPERATURE
Turbidity (NTU)	0.84	APHA 2130 B. Nephelometric Method
COD (mg/L)	206.3	APHA 5220 D. Closed Reflux, Colorimetric Method
Conductivity (mS/cm)	5.12	APHA 2510 B. Conductivity
TDS (mg/L)	2816	APHA 2540 C. Total Dissolved Solids Dried at 180°C
TSS (g)	0	APHA 2540 D. Total Suspended Solids Dried at 103–105°C
TP(mg/L)	7.583	1. APHA 4500-P C. Vanadomolybdophosphoric Acid Colorimetric Method 2. APHA 4500-P E. Ascorbic Acid Method
NH_4(mg/L)	0.492	ASTM D 1426 – 03 Standard Test Methods for Ammonia Nitrogen In Water.

3.2 Forward Osmosis Setup

A schematic diagram for the FO-RO hybrid system is shown in Figure 9. In the FO system, a Sterlitech CF042 Delrin membrane cell was used. The cell dimensions are 12.7 x 8.3 x 10 cm with an active inner dimension of 4.6 x 9.2 cm and a slot depth of 0.23 cm. The membrane was positioned in the membrane cell so that the feed and the draw solutions would flow from each side separately. Two tanks with a capacity of 6 L were used for the FS and DS. Two Cole-Parmer gear pumps (0.91 ml/rev) were used to circulate the FS and DS through the membrane cell. Two flow meters (Sterlitech Site Read Panel Mount Flow Meter) have been used to measure the flow rate of the feed and the draw solutions. A digital balance (EW-11017-04 Ohaus Ranger™ Scale) was used to measure the mass variation of the DS in order to calculate the water flux in the FO system. The volume of the FS and DS was 4 L each at the beginning of each experiment. The solutions going out from the FO cell were recycled back into the same tanks with an operating time of 180 min for each experiment. A new membrane was used for each trial. Porifera FO membrane with a structural parameter value of 215 microns was used in these experiments. The used FO membrane has a high rejection rate for dissolved solids, bacteria and viruses. The membrane was cut to be placed inside the cell with dimensions of 5.75 x 11.5 cm. The membrane was washed for 20 minutes with distilled water for pre-conditioning and removal of any chemicals from its surface. A 1 mm Sepa CF high fouling spacer (8 x 3.5 cm) was always placed on the SL of the membrane.

3.3 Reverse Osmosis Setup

A diagram for the experimental setup is shown in Figure 9. The diluted DS produced from the FO system was used as the FS in the RO system. The reject from the RO system was sent back to the FO system as the regenerated draw solution and the permeate was the produced fertilizing solution. A CF042D crossflow cell assembly, natural acetal copolymer (Delrin) produced by Sterlitech was used for the RO setup. The cell dimensions are 12.7 x 8.3 x 10 cm with active inner dimensions of 4.6 x 9.2 cm and 0.23 cm slot depth. Two tanks were used to store feed and permeate solutions and a M-03S HYDRACELL pump (230V, 50HZ, 3PH, 6.7 LPM) was used to pressurize the feed solution through the RO membrane. The RO system has a pressure relief valve (1000 PSI/69 bar) in order to ensure a maximum pressure of 69 bar. Concentrate/Back pressure control valve assembly was used to control water flow through the system and to regulate pressure inside the system. Flow meters (Sterlitech Site Read Panel Mount Flow Meter) were used to measure the flow rate at specific points in the RO system. A digital balance (Mettler Toledo – ICS 241) was connected to a computer in order to measure the permeate flux in the RO system. Two types of RO membranes were used, SW30HR and BW30LE membranes produced by DOW Company. Both membranes have a high rejection rate, which can reach up to 99.6% and flux of 29-41 LMH. The SW30HR membrane is used for the treatment of seawater with a pore size of 100 Da. The BW30LE membrane is used for brackish water treatment with a flux of 44 LMH and rejection rate of 99% and pore size of 100 Da. Both membranes were washed for 30 minutes with distilled water before use for pre conditioning and removal of any impurities from their surface. BW30LE and SW30HR were operated with pressure of 40 and 50 bars respectively.

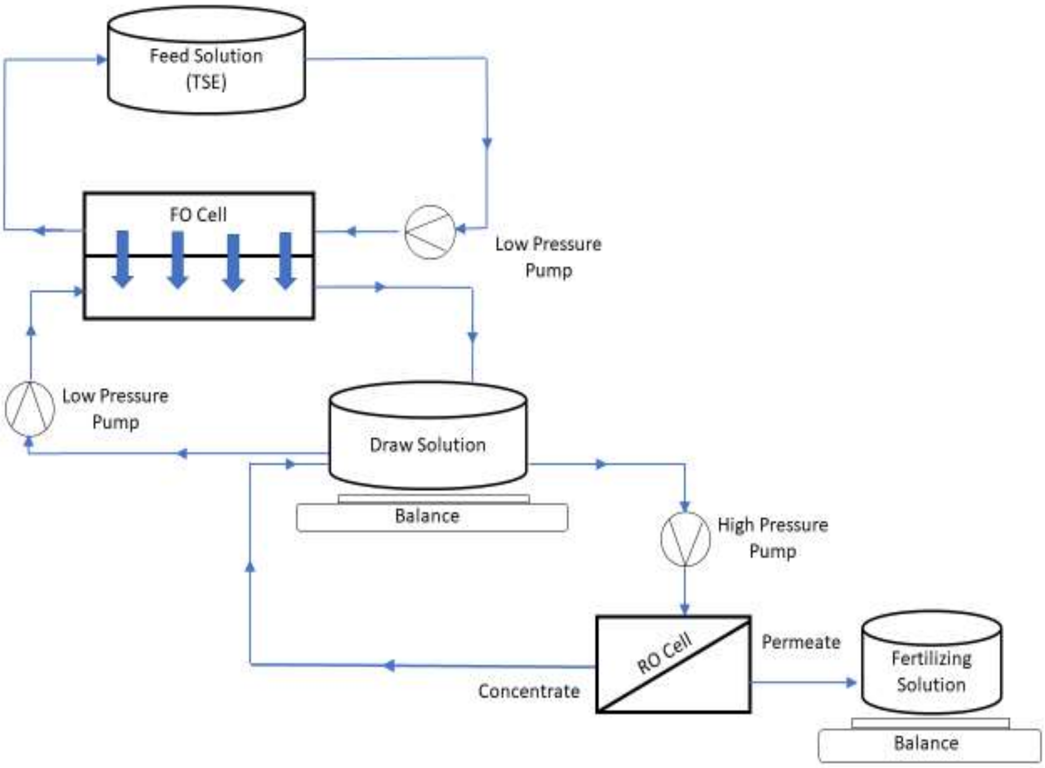

Figure 9: The hybrid FO-RO system used for the production of the engineered fertilizing solution.

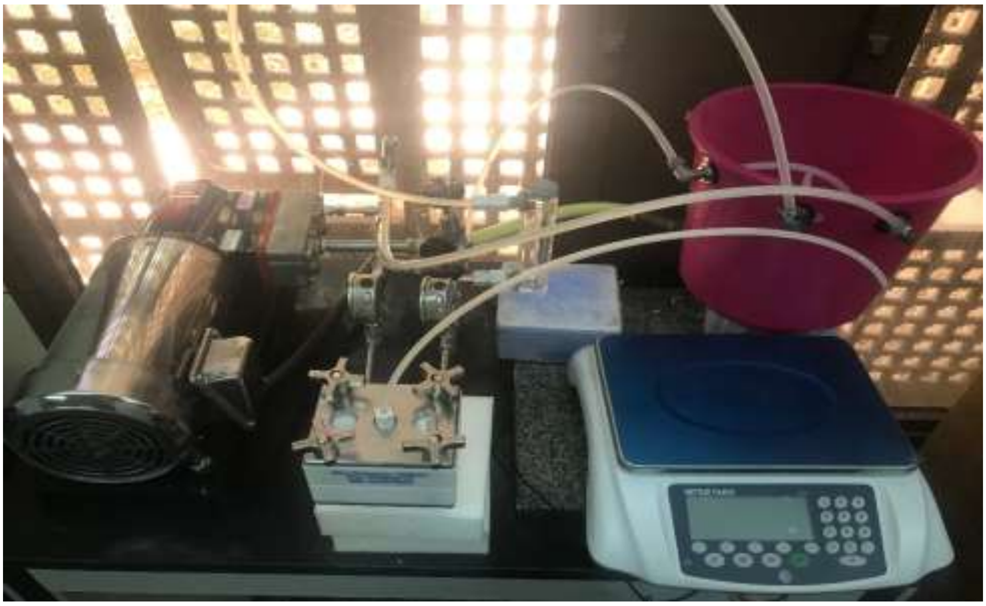

Figure 10: Reverse osmosis setup

Figure 11: Forward osmosis setup

3.4 Measured parameters

3.4.1 Conductivity and TDS

Conductivity and total dissolved solids (TDS) measurements were determined using Hach – sensION5 conductivity meter. Series standard method (ASTM D5907).

3.4.2 pH

pH measurements were determined using Hanna HI 2211 pH meter.

CHAPTER 4: RESULTS & DISCUSSION

4.1 Forward osmosis

4.1.1 Membrane flux

The study investigated the impact of the flow rates of the draw and feed solutions and the mode of operation of FO process on the membrane flux. The FS was TSE and two types of draw solutions were examined (i.e. 0.5M NaCl and EFS (0.5M NaCl and 0.01M diammonium phosphate ((NH4)2HPO4)). It can be seen from Figure 12(A) and (B) that when the two different draw solutions were used the membrane flux decreased with time in both membrane orientations. The reduction of the flux was due to the dilution of the DS and FO membrane fouling. In fact, TSE contains trace concentration of organic matters, which are source of contamination and FO membrane fouling when they accumulate on the membrane surface (Ansari et al., 2016; Ortega-Bravo et al., 2016; Valladares Linares et al., 2013; Zhao et al., 2011). It can be also seen from Figure 12 (A) and (B) that the average membrane flux increased as the flow rates of the draw and FS increased in both membrane orientations. As shown in Figure 12(A) in the forward osmosis mode and when 0.5M NaCl was used as DS, the average flux increased from 9.0 L/m2.h to 11.8 L/m2.h as the flow rates increased from 1.2 L/min to 2 L/min, respectively. In the PRO mode the average membrane flux increased from 5.5 L/m2.h to 10.0 L/m2.h as the flow rates increased from 1.2 to L/min 2 L/min, respectively. As shown in Figure 12 (b) a similar trend was obtained for the EFS where in the FO mode the flux increased from 11.0 L/m2.h to 13.2 L/m2.h as the flow rates of the draw and the feed solutions increased from 1.2 L/min to 2 L/min, respectively (Figure 12 (b)). In the PRO mode the average membrane flux increased from 8.0 L/m2.h to 10.5 L/m2.h as the flow rates of the DS and FS increased from 1.2 L/min to 2 L/min, respectively. The increase of the membrane flux with the increase of the flow rates of the draw and the feed solutions is due to the minimized concentration polarization effect at higher flow rates (Jeffrey R. McCutcheon & Elimelech, 2006). Concentration polarization plays a major role in decreasing the osmotic effect across the FO membrane which would decrease the membrane flux (Devia et al., 2015; Hawari et al., 2018). Increasing the flow rates of the DS and FS would increase the turbulence around the membrane surface, which in turn decrease the effect of CP and increases the mass transfer coefficient (Jung et al., 2011).

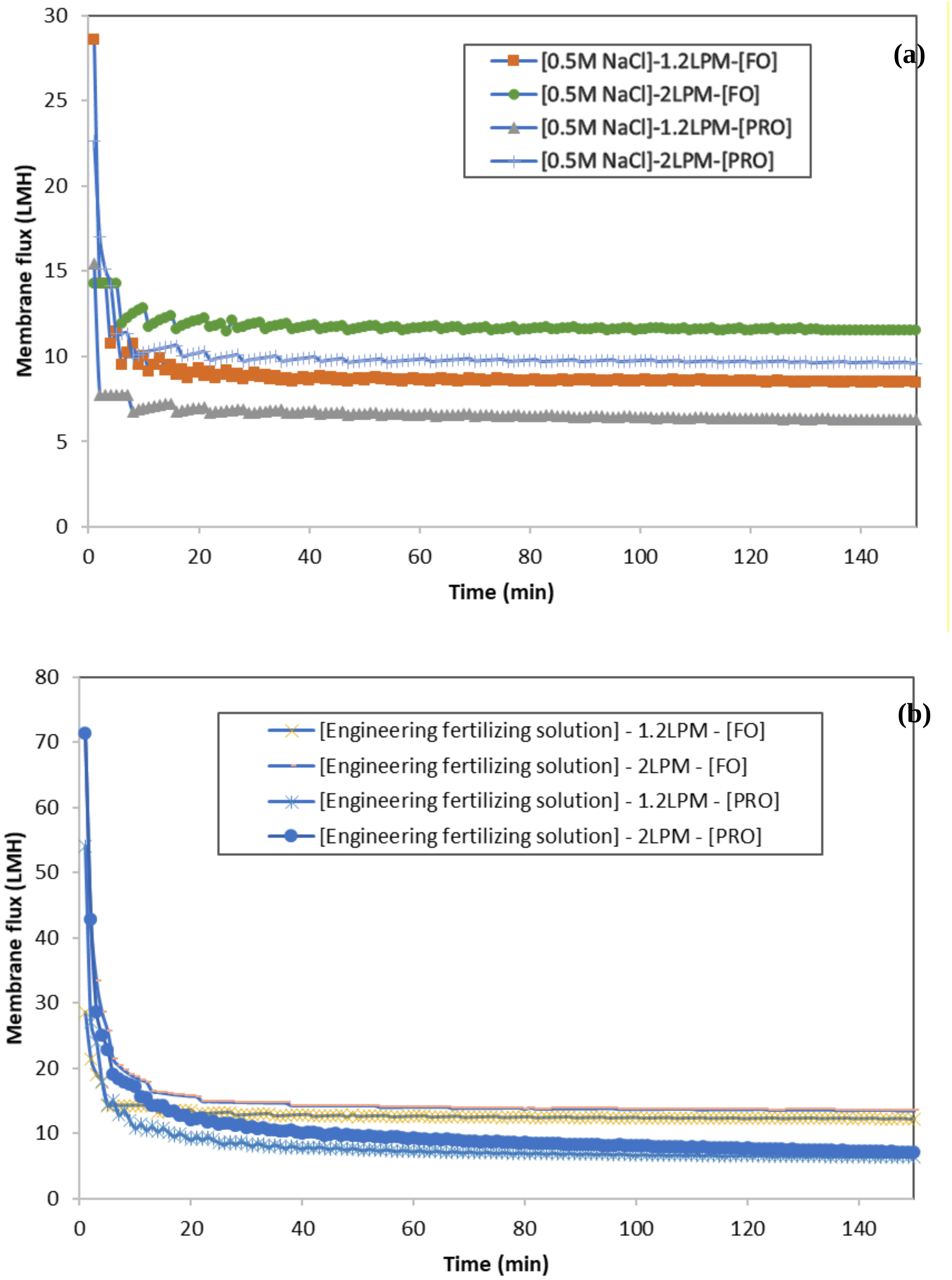

Figure 12: Membrane flux using different draw solutions in FO mode and PRO mode at different DS and FS flow rates (a) 0.5M NaCl draw solution (b) EFS draw solution.

Figure 13 shows that using EFS as the draw solution has higher average membrane flux compared to when using 0.5M NaCl as the draw solution. This is due to the fact that the osmotic pressure of 0.5M NaCl and 0.01M diammonium phosphate (DAP) mixture (i.e. EFS) is higher than that of 0.5M NaCl. The osmotic pressure for the 0.5M NaCl solution was 23 bar while it was 58 bar for the EFS. The osmotic pressure was calculated using the Van't Hoff's equation (A. Altaee, G. Millar, A. Sharif, & G. Zaragoza, 2016). Therefore, it is expected that the driving force of the EFS draw solution would be higher than that of the 0.5M NaCl draw solution. Figure 13 also shows that the average membrane flux in the FO mode was always higher than that in the PRO mode for both the 0.5M NaCl and EFS draw solutions. In the PRO mode, the support layer faces the feed solution, which in this case was the TSE. Using such a feed solution with a high concentration of organic matter could promote membrane fouling due to the accumulation of foulants on the rough support layer (Parida & Ng, 2013). The rough surface of the support layer would provide more surface area for the foulants to reside on (Honda et al., 2015). The SEM images show that high concentration of foulants accumulated on the surface of the support layer when it is facing the TSE feed solution (PRO mode) compared to when the support layer was facing the EFS (i.e. FO mode) (Figure 14). Similar findings were reported in the literature where the FO mode resulted in a higher membrane flux compared to the PRO mode (C. Y. Tang et al., 2010; Zhao et al., 2011). In general, the FO mode is recommended when the feed solution contains high concentration of fouling materials such as TSE. While the PRO mode is recommended when using a feed solution with low concentration of fouling materials (Zhao et al., 2011).

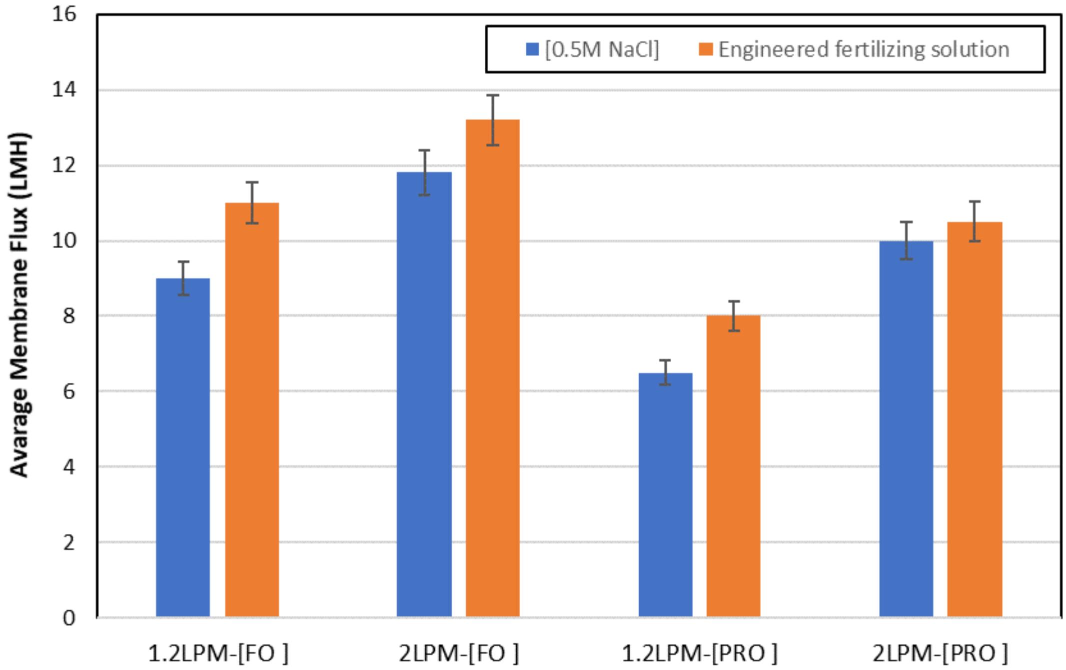

Figure 13: Average membrane flux using different draw solutions in FO mode and PRO mode at different DS and FS flow rates.

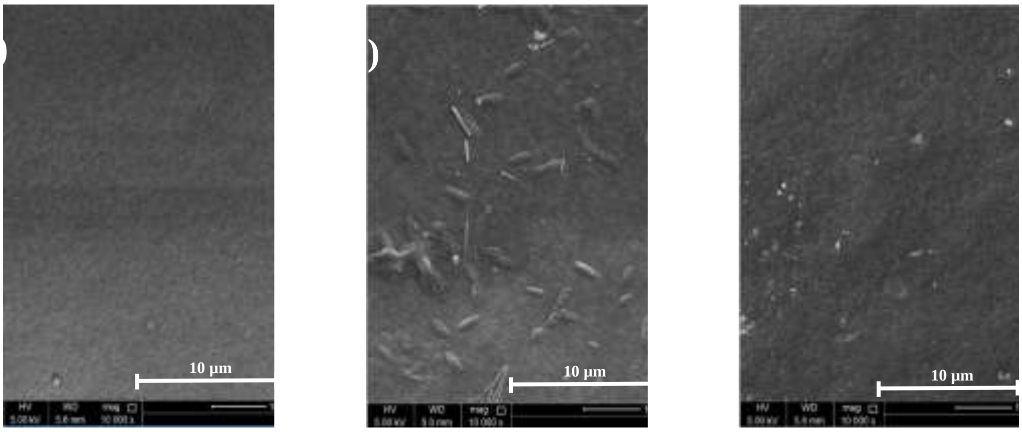

Figure 14: Scanning Electron Microscopy (SEM) images of the FO membrane at FS and DS flow rates of 1.2LPM, using EFS as draw solution and TSE as the feed solution (a) Clean Support layer, (b) Support layer facing the feed solution (PRO

mode), (c) Support Layer facing the draw solution (FO mode). The SEM images are at 10,000x magnification.

4.1.2 Reverse solute flux (RSF)

Reverse solute flux (RSF) is the back diffusion of the DS across the FO membrane to the FS. RSF must be considered in the FO studies because it might contaminate the FS. Figure 15 shows that the RSF decreased as the flow rates of the FS and DS increased for 0.5M NaCl and EFS draw solutions in both membrane orientations. In the FO mode and when EFS was used as the draw solution the RSF was 74.3 g/m2.h and 70.3 g/m2.h at 1.2 LPM and 2.0 LPM flow rates of the DS and FS, respectively. When 0.5M NaCl solution was used as the draw solution, the RSF was 48.3 g/m2.h and 44.9 g/m2.h at 1.2 LPM and 2.0 LPM flow rates of the FS and DS, respectively. In the PRO mode and when EFS was used as the DS the RSF was 66.7 g/m2.h and 65.1 g/m2.h at 1.2 LPM and 2.0 LPM flow rates of the DS and FS, respectively. When 0.5M NaCl solution was used as the DS, the RSF was 43.7 g/m2.h and 38.6 g/m2.h at 1.2 LPM and 2.0 LPM flow rates of the draw and the feed solution, respectively. Using EFS as the draw solution had lower reverse solute flux compared to when using 0.5M NaCl solution was used as the DS. In general, NaCl has high RSF due to its small ion size (Achilli et al., 2010; Bowden, Achilli, & Childress, 2012; N. T. Hancock & Cath, 2009). The addition of 0.01M of diammonium phosphate (DAP) in the draw solution has lowered the RSF by an average of 36% in all operating conditions. DAP is a large molecule with a high molecular weight and high chelating ability which could be the reason behind the high reduction in the RSF (Achilli et al., 2010). In addition, the RSF decreases with the increase of the flow rates of the FS and DS due to the increase of the membrane flux which would increase the dilution of the draw solution.

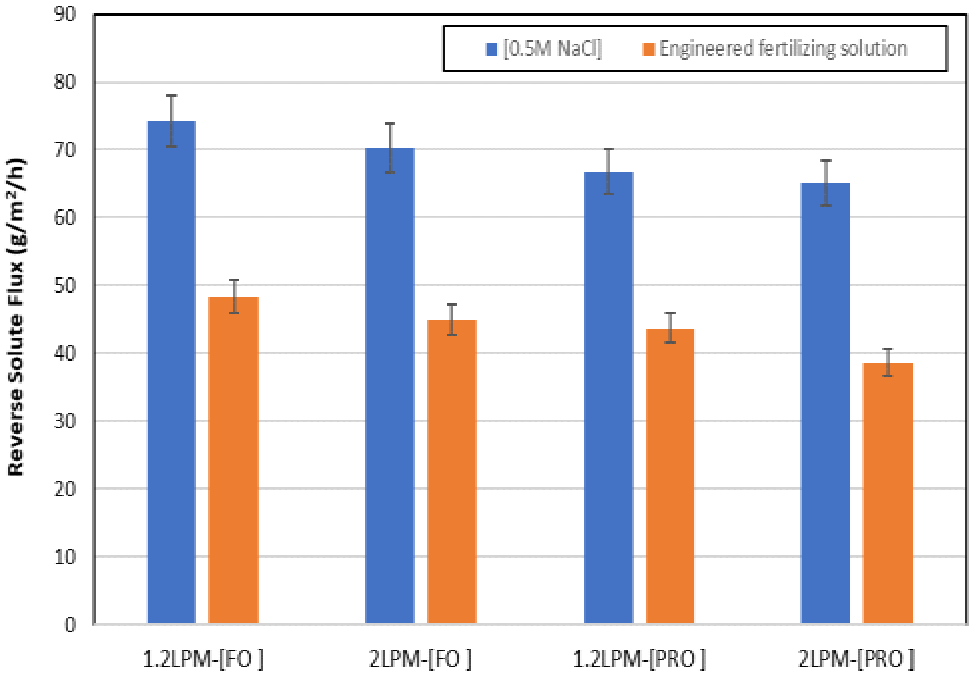

Figure 15: RSF in the FO using TSE as a feed solution and 0.5M NaCl or engineered fertilizing solution as draw solution

As mentioned earlier the 0.01M of DAP was added to the draw solution for two purposes: 1) to enhance the membrane flux by increasing the osmotic pressure and 2) to add the required nutrients to the final product water. The concentration of DAP in the DS should be carefully selected in order not to cause high fouling of the membrane. When 0.5M DAP alone was used as the DS the flux decreased rapidly with time where the membrane flux reached zero in the first few minutes of the experimental run (Figure 16).

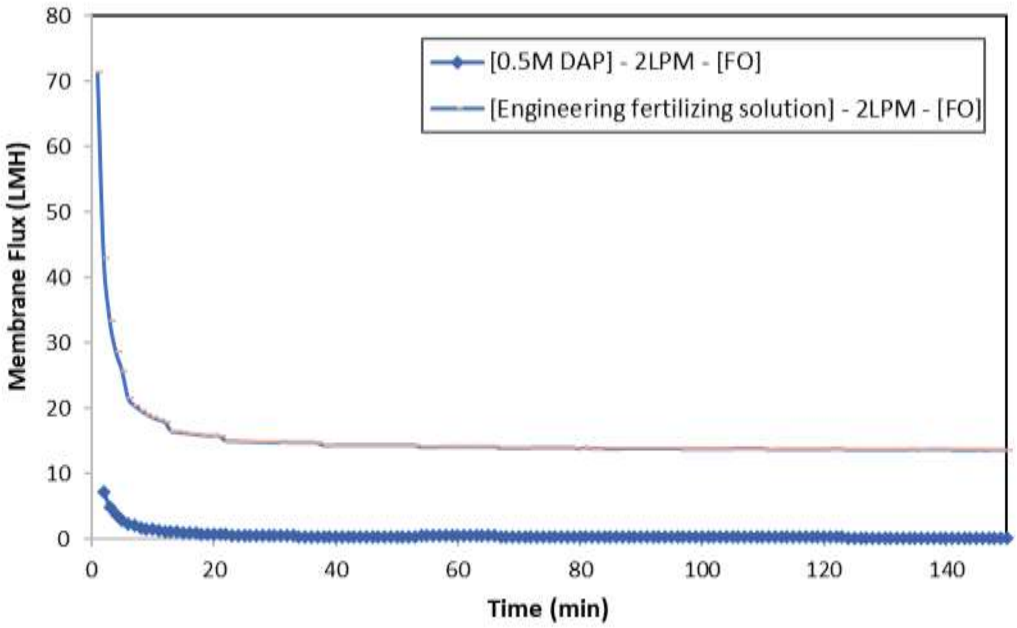

Figure 16: Membrane flux using different draw solutions in FO mode at 2 LPM DS and FS flow rates.

In general, using 0.5M DAP DS resulted in a sharp decline in flux comparing to 0.5M NaCl and 0.01M DAP draw solution, indicating to fouling development on the FO membrane (Figure 16). This shows the advantage of using engineering fertilizing solution to reduce membrane fouling. Figure 17 shows SEM images for the FO membrane when 0.5M DAP alone was used as the draw solution. The images show the active and support layer when AL was facing the FS and when the AL was facing the DS. The SEM images show that the layer facing the draw solution (i.e. 0.5M DAP) always faced severe fouling compared to the other layer facing the feed solution (i.e TSE). Therefore, a 0.01M DAP concentration was selected to be used in the engineered fertilizing solution.

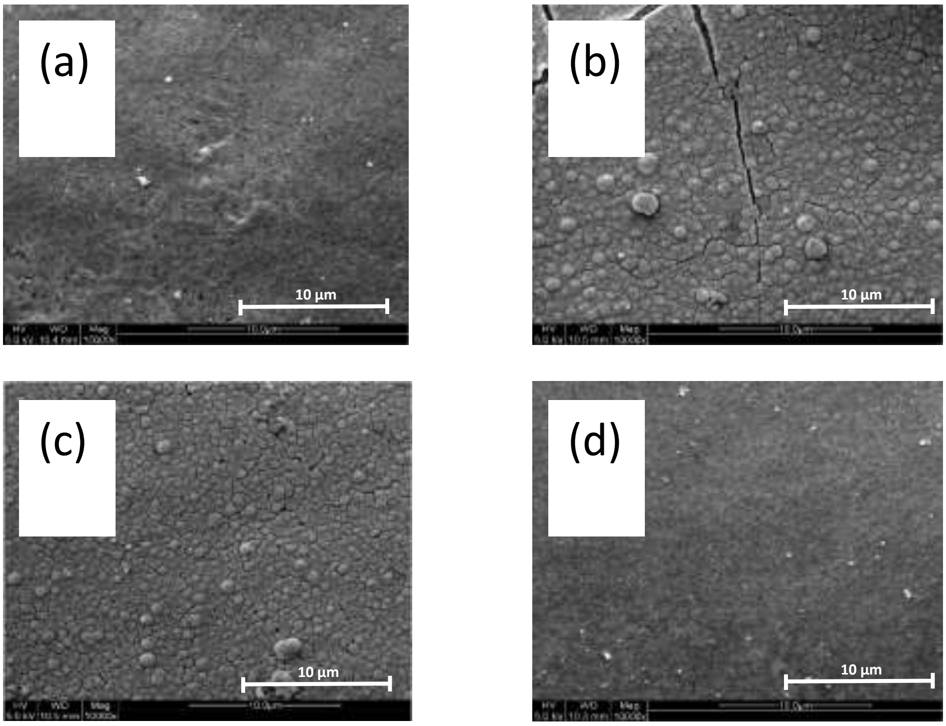

Figure 17: Scanning Electron Microscopy (SEM) images of active layer and support layer with 0.5M DAP draw solution and TSE feed solution at a flow rate of 2 LPM in FO mode and PRO mode. (a) Active layer in FO mode (b) Support layer in FO mode (c) Active layer in PRO mode (d) Support layer in PRO mode. The SEM images are at 10,000x magnification.

4.1.3 Rejection rate

High rejection rate of the FO membrane is required to reduce contaminants diffusion from the feed to the draw solution or reverse salt diffusion (RSD) to the feed side. The rejection rate of total phosphorous (TP) and ammonium (NH4+) were measured at the different studied flow rates and the different membrane orientations when the engineered fertilizing solution was used as the DS. It was found that the used FO membrane had high rejection for total phosphorous (TP) and ammonium (NH4+) as shown in Figure 18. It can be seen from Figure 18 (A) that the total phosphorus (TP) rejection rate exceeded 99% in the FO mode and in the PRO mode at 1.2 LPM and 2 LPM flowrates of DS and FS. Phosphorous rejection rate is expected to be high due to its high molecular weight and large hydrated ion diameter (Devia et al., 2015). It can be seen from Figure 18(B) that ammonium (NH4+) rejection rate was lower than the TP rejection rate in PRO mode. The ammonium rejection rate was 92.5% and 95% at 1.2 LPM and 2 LPM DS-FS flowrates, respectively. In the FO mode the ammonium rejection rate was 95% and 97% at 1.2 LPM and 2 LPM DS and FS flowrates, respectively. The NH4+ rejection rate is lower than the total phosphorus rejection rate because of ammonium lower molecular weight and smaller hydrated ion diameter (Devia et al., 2015). It can also be noticed that ammonium rejection rate was generally higher in the PRO mode compared to the FO mode due to the fact that the used TFC FO membrane is expected to attract positively charged ions (i.e. NH4+) (Lu, Boo, Ma, & Elimelech, 2014). High rejection rates for TP and NH4+ was reported by other previous studies.

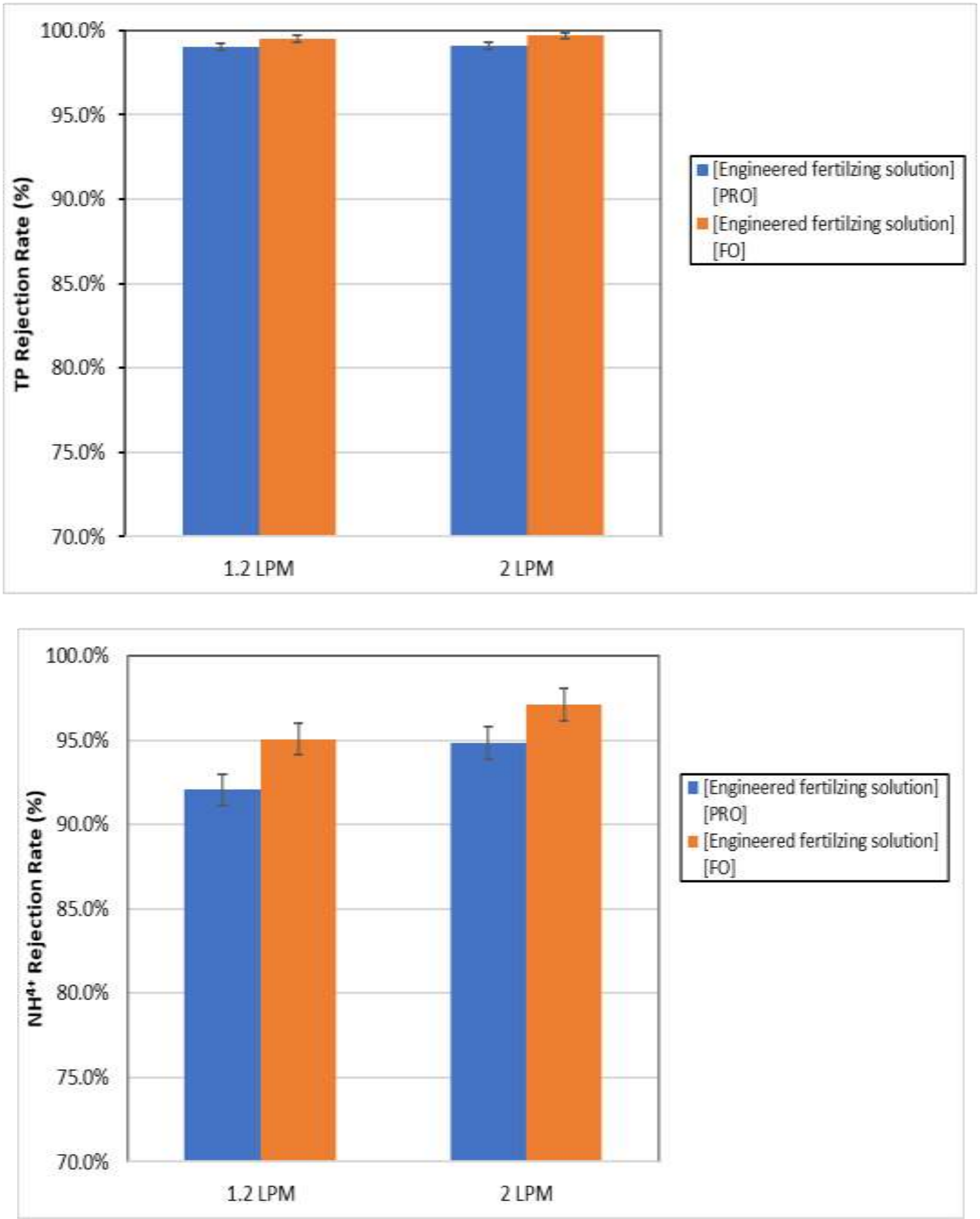

Figure 18: Rejection rate at different DS and FS flow rates and different membrane orientations with TSE as feed solution and Engineered fertilizing solution as draw solution (a) Total phosphorus (TP) rejection rate (b) Ammonium (NH4+) rejection rate.

4.2 Regeneration of draw solution using reverse osmosis process

The DS from the FO process was regenerated by reverse osmosis. The diluted engineered fertilizing draw solution (EFS) produced form the FO process is sent to a RO system as a feed solution where the reject from the RO system is the regenerated draw solution and the permeate is the product fertilizing water. Two types of RO membranes were used namely, SW30HR DOW and BW30LE DOW. The two different membranes were tested in order to compared energy requirements and product water quality. A single stage RO separation process was used in this study. According to the membrane manufacturer (DOW), a total salt rejection rate of 99.7% can be achieved by SW30HR DOW membrane and 99.0% by BW30LE DOW membrane. The calculated total salts rejection rate was found to be 99% and 98% for SW30HR DOW and BW30LE DOW, respectively. Table 9 summarizes the conductivity of the feed and permeate solutions in the RO system using the two different RO membranes. The permeate conductivity was 0.410 mS/cm and 0.767 mS/cm for SW30HR and BW30LE membrane, respectively. According to the Food and Agriculture Organization of the United Nation, an irrigation water with conductivity between 0.25 – 0.75 mS/cm is classified as good quality irrigation water (Ayres & Westcot, 1985). The concentration of other ions in the permeate solution were furtherly checked in order to ensure that the product fertilizing solution contains the right concentrations. According to the Food and agriculture organization of the united nations (FAO), the max concentration of sulfate in irrigation water is 321 mg/l (Ayres & Westcot, 1985). Table 9 shows that the sulfate concentration in the product fertilizing solution was 2.5 mg/l and 22.0 mg/l using SW30HR and BW30LE membranes, respectively. According to the Food and agriculture organization of the united nations (FAO) (Ayres & Westcot, 1985), the max concentration of chloride in irrigation water is 350 mg/l taking into consideration that sensitive crops may show some injuries with a concentration above 140 mg/l. The chloride concentration in the product fertilizing solution was 117.9 mg/l and 176.7 mg/l using SW30HR and BW30LE membranes, respectively. According to FAO the max concentration of sodium in irrigation water is 46-230 mg/l. A Sodium concentration of 170.2 mg/l and 246.4 mg/l was obtained in the product water using SW30HR and BW30LE membranes, respectively. According to FAO the maximum concentration of phosphate in irrigation water is 2 mg/l. The Phosphate concentration in the product fertilizing solution was 6.6 mg/l and 27.8 mg/l using SW30HR and BW30LE membranes, respectively. The phosphate concentration in the product water using SW30HR was 75% lower than BW30LE. The phosphate concentration in the product water did not comply with FAO. The concentration of phosphate was still almost 3 times higher than what is recommended by FAO. A RO system with two passes could resolve this issue or a lower concentration of DAP in the draw solution could also lower the phosphate concentration in the product water. In general, regenerating the EFS with SW30HR membrane yielded a better-quality fertilizing solution in terms of compliance with the FAO guidelines for irrigation water (Table 9). Therefore, SW30HR membrane is recommended for the regeneration of EFS in this study. Simulation software produced by DOW Co. named ROSA was used to calculate the energy consumed by the RO process using the two different membranes. A single unit with eight vessels was used in the model. As shown in Table 9 the energy consumption in the RO process for the SW30HR and BW30LE membranes were 2.58 Kwh/m3 and 2.18 Kwh/m3, respectively. Even though, the use of SW30HR membrane in the RO process consumed 15% more energy still it would be recommended to use the SW30HR membrane as it gave better quality of product water especially for phosphate where the concentration of phosphate was 77% lower than the phosphate concentration in the permeate solution when using the BW30LE membrane.

Table 9: Feed Solution and Permeate Solution Characteristics in the RO System.

	SW30HR DOW	BW30LE	Max Limit (Irrigation water)(Ayres & Westcot, 1985)
Chloride (ppm)	117.9	176.7	350
Nitrate (ppm)	0.230	0.280	5
Phosphate (ppm)	6.6	27.8	2
Sulfate (ppm)	2.5	22.0	321
Sodium (ppm)	170.3	246.5	230
Feed solution conductivity (mS)	33.4	33.4	-
Permeate solution conductivity(mS)	0.410	0.767	0.75
Energy consumption (Kwh/m^3)	2.58	2.18	-

CHAPTER 5: CONCLUSIONS & RECOMMENDATIONS

This thesis evaluated the performance of an integrated FO-RO process to produce a fertilizing solution applicable for irrigation purposes. In the FO process real treated sewage effluent (TSE) was used as the FS and two types of DS were tested namely, 0.5M NaCl solution and a mixture of 0.5M NaCl and 0.01M Diammonium phosphate ($(NH_4)_2HPO_4$). Seawater RO membrane (SW30HR) and brackish water RO membrane (BW30LE) were tested for the regeneration process of the DS. In the FO process the impact of the flow rate of the feed solution and the draw solution, the membrane orientation (i.e. FO mode and PRO mode) on the flux were tested. The following conclusions were drawn:

- Using a mixture of 0.5M NaCl and 0.01M Diammonium phosphate ($(NH_4)_2HPO_4$) as the draw solution resulted in a higher average membrane flux compared to when using 0.5M NaCl alone as the draw solution. This is due to the fact that the osmotic pressure of 0.5M NaCl and 0.01M diammonium phosphate (DAP) mixture is higher than that of 0.5M NaCl alone. Therefore, it is expected that the driving force of the mixed draw solution would be higher than that of the 0.5M NaCl DS.
- The average membrane flux in the FO mode was always higher than that in the PRO mode for both the 0.5M NaCl solution and the 0.5M NaCl and 0.01M diammonium phosphate mixture. In the PRO mode, the support layer faces the feed solution, which in this case was the TSE. Using such a FS with a high concentration of organic matter could promote membrane fouling due to the accumulation of foulants on the rough SL. It is recommended that the FO mode should be used when

the FS contains high concentration of fouling materials. While the PRO mode is recommended when using a feed solution with low concentrations of fouling materials.

- The addition of 0.01M of diammonium phosphate (DAP) in the draw solution has lowered the RSF by an average of 36% in all operating conditions. DAP is a large molecule with a high molecular weight and high chelating ability which could be the reason behind the high reduction in the RSF. When 0.5M DAP alone was used as the DS the membrane flux decreased rapidly with time where the membrane flux reached zero in the first few minutes of the experimental run and the membrane faced severe fouling problems.
- It was found that the used FO membrane had high rejection rate for total phosphorous (TP) and ammonium (NH^{4+}). The total phosphorus (TP) rejection rate exceeded 99% in the FO mode and in the PRO mode at 1.2 LPM and 2 LPM flowrates of DS and FS. The ammonium (NH^{4+}) rejection rate was lower than the TP rejection rate. Where in the PRO mode the ammonium rejection rate was 92.5% and 95% at 1.2 LPM and 2 LPM DS and FS flowrates, respectively. In the FO mode the ammonium rejection rate was 95% and 97% at 1.2 LPM and 2 LPM DS and FS flowrates, respectively. The NH^{4+} rejection rate is lower than the total phosphorus rejection rate because of ammonium lower molecular weight and smaller hydrated ion diameter.
- It would be highly recommended to use SW30HR membrane in the RO system for the regeneration of the draw solution since this membrane had lower energy consumption and better quality of product water especially for phosphate where the

concentration of phosphate was 77% lower than the phosphate concentration in the permeate solution when using the BW30LE membrane.

REFERENCES

Achilli, A., Cath, T. Y., & Childress, A. E. (2010). Selection of inorganic-based draw solutions for forward osmosis applications. *Journal of Membrane Science, 364*(1), 233-241. doi:https://doi.org/10.1016/j.memsci.2010.08.010

Altaee, A., Millar, G., Sharif, A., & Zaragoza, G. (2016). *Forward osmosis process for supply of fertilizer solutions from seawater using a mixture of draw solutions* (Vol. 57).

Altaee, A., Millar, G. J., Sharif, A. O., & Zaragoza, G. (2016). Forward osmosis process for supply of fertilizer solutions from seawater using a mixture of draw solutions. *Desalination and Water Treatment, 57*(58), 28025-28041. doi:10.1080/19443994.2016.1180642

Altaee, A., Zaragoza, G., Drioli, E., & Zhou, J. (2017). Evaluation the potential and energy efficiency of dual stage pressure retarded osmosis process. *Applied Energy, 199*, 359-369. doi:https://doi.org/10.1016/j.apenergy.2017.05.031

Altaee, A., Zaragoza, G., & van Tonningen, H. R. (2014). Comparison between Forward Osmosis-Reverse Osmosis and Reverse Osmosis processes for seawater desalination. *Desalination, 336*, 50-57. doi:https://doi.org/10.1016/j.desal.2014.01.002

Ansari, A. J., Hai, F. I., Guo, W., Ngo, H. H., Price, W. E., & Nghiem, L. D. (2016). Factors governing the pre-concentration of wastewater using forward osmosis for subsequent resource recovery. *Science of The Total Environment, 566-567*, 559-566. doi:https://doi.org/10.1016/j.scitotenv.2016.05.139

Ardley, S., Arnold, P., Younker, J., & Rand, J. (2019). Wastewater characterization and treatment at a blueberry and carrot processing plant. *Water*

Resources and Industry, 21, 100107. doi:https://doi.org/10.1016/j.wri.2019.100107

Arena, J. T., McCloskey, B., Freeman, B. D., & McCutcheon, J. R. (2011). Surface modification of thin film composite membrane support layers with polydopamine: Enabling use of reverse osmosis membranes in pressure retarded osmosis. *Journal of Membrane Science, 375*(1), 55-62. doi:https://doi.org/10.1016/j.memsci.2011.01.060

ASHGAL. (2014). Treated Sewage Effluent Networks in Qatar. In: KAHRAMAA.

Ayres, R. S., & Westcot, D. W. (1985). FAO IRRIGATION AND DRAINAGE PAPER. *Food and Agriculture Organization of the United Nations*.

Bamaga, O. A., Yokochi, A., Zabara, B., & Babaqi, A. S. (2011). Hybrid FO/RO desalination system: Preliminary assessment of osmotic energy recovery and designs of new FO membrane module configurations. *Desalination, 268*(1), 163-169. doi:https://doi.org/10.1016/j.desal.2010.10.013

Bowden, K. S., Achilli, A., & Childress, A. E. (2012). Organic ionic salt draw solutions for osmotic membrane bioreactors. *Bioresource Technology, 122*, 207-216. doi:https://doi.org/10.1016/j.biortech.2012.06.026

Bromley, L. A., & Read, S. M. (1970). Multiple effect flash (MEF) evaporator. *Desalination, 7*(3), 343-391. doi:https://doi.org/10.1016/S0011-9164(00)80206-4

Brusseau, M. L., Famisan, G. B., & Artiola, J. F. (2004). 16 - CHEMICAL CONTAMINANTS. In J. F. Artiola, I. L. Pepper, & M. L. Brusseau (Eds.), *Environmental Monitoring and Characterization* (pp. 299-312). Burlington: Academic Press.

Bui, N.-N., Arena, J. T., & McCutcheon, J. R. (2015). Proper accounting of mass transfer resistances in forward osmosis: Improving the accuracy of model predictions of structural parameter. *Journal of Membrane Science, 492*, 289-302. doi:https://doi.org/10.1016/j.memsci.2015.02.001

Burn, S., Hoang, M., Zarzo, D., Olewniak, F., Campos, E., Bolto, B., & Barron, O. (2015). Desalination techniques — A review of the opportunities for desalination in agriculture. *Desalination, 364*, 2-16. doi:https://doi.org/10.1016/j.desal.2015.01.041

Cath, T. Y., Childress, A. E., & Elimelech, M. (2006). Forward osmosis: Principles, applications, and recent developments. *Journal of Membrane Science, 281*(1), 70-87. doi:https://doi.org/10.1016/j.memsci.2006.05.048

Chekli, L., Kim, Y., Phuntsho, S., Li, S., Ghaffour, N., Leiknes, T., & Shon, H. K. (2017). Evaluation of fertilizer-drawn forward osmosis for sustainable agriculture and water reuse in arid regions. *Journal of Environmental Management, 187*, 137-145. doi:https://doi.org/10.1016/j.jenvman.2016.11.021

Chekli, L., Phuntsho, S., Kim, J. E., Kim, J., Choi, J. Y., Choi, J.-S., . . . Shon, H. K. (2016). A comprehensive review of hybrid forward osmosis systems: Performance, applications and future prospects. *Journal of Membrane Science, 497*, 430-449. doi:https://doi.org/10.1016/j.memsci.2015.09.041

Chen, Z., Luo, J., Wang, Y., Cao, W., Qi, B., & Wan, Y. (2017). A novel membrane-based integrated process for fractionation and reclamation of dairy wastewater. *Chemical Engineering Journal, 313*, 1061-1070. doi:https://doi.org/10.1016/j.cej.2016.10.134

Coday, B. D., Xu, P., Beaudry, E. G., Herron, J., Lampi, K., Hancock, N. T., & Cath, T. Y. (2014). The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. *Desalination, 333*(1), 23-35. doi:https://doi.org/10.1016/j.desal.2013.11.014

Cornelissen, E. R., Harmsen, D., de Korte, K. F., Ruiken, C. J., Qin, J.-J., Oo, H., & Wessels, L. P. (2008). Membrane fouling and process performance of forward osmosis membranes on activated sludge. *Journal of Membrane Science, 319*(1), 158-168. doi:https://doi.org/10.1016/j.memsci.2008.03.048

Devia, Y. P., Imai, T., higuchi, T., Kanno, A., Yamamoto, K., & Sekine, M. (2015). *Effect of Operating Conditions on Forward Osmosis for Nutrient Rejection Using Magnesium Chloride as a Draw Solution.* Paper presented at the International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering.

El-Dessouky, H., Ettouney, H., Al-Juwayhel, F., & Al-Fulaij, H. (2004). Analysis of Multistage Flash Desalination Flashing Chambers. *Chemical Engineering Research and Design, 82*(8), 967-978. doi:https://doi.org/10.1205/0263876041580668

Environmental Law No. 30, (2002).

Fiorini, P., & Sciubba, E. (2005). Thermoeconomic analysis of a MSF desalination plant. *Desalination, 182*(1), 39-51. doi:http://dx.doi.org/10.1016/j.desal.2005.03.008

Ge, Q., Ling, M., & Chung, T.-S. (2013). Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future. *Journal of Membrane Science, 442*, 225-237. doi:https://doi.org/10.1016/j.memsci.2013.03.046

Gray, G. T., McCutcheon, J. R., & Elimelech, M. (2006). Internal concentration polarization in forward osmosis: role of membrane orientation. *Desalination, 197*(1), 1-8. doi:https://doi.org/10.1016/j.desal.2006.02.003

Greenlee, L. F., Lawler, D. F., Freeman, B. D., Marrot, B., & Moulin, P. (2009). Reverse osmosis desalination: Water sources, technology, and today's challenges. *Water Research, 43*(9), 2317-2348. doi:https://doi.org/10.1016/j.watres.2009.03.010

Hancock, M. J., Maher, C. G., Latimer, J., Herbert, R. D., & McAuley, J. H. (2009). Can rate of recovery be predicted in patients with acute low back pain? Development of a clinical prediction rule. *European Journal of Pain, 13*(1), 51-55. doi:https://doi.org/10.1016/j.ejpain.2008.03.007

Hancock, N. T., & Cath, T. Y. (2009). Solute Coupled Diffusion in Osmotically Driven Membrane Processes. *Environmental Science & Technology, 43*(17), 6769-6775. doi:10.1021/es901132x

Hanshik, C., Jeong, H., Jeong, K.-W., & Choi, S.-H. (2016). Improved productivity of the MSF (multi-stage flashing) desalination plant by increasing the TBT (top brine temperature). *Energy, 107*, 683-692. doi:https://doi.org/10.1016/j.energy.2016.04.028

Harandi, H. B., Rahnama, M., Jahanshahi Javaran, E., & Asadi, A. (2017). Performance optimization of a multi stage flash desalination unit with thermal vapor compression using genetic algorithm. *Applied Thermal Engineering, 123*, 1106-1119. doi:https://doi.org/10.1016/j.applthermaleng.2017.05.170

Hawari, A. H., Al-Qahoumi, A., Ltaief, A., Zaidi, S., & Altaee, A. (2018). Dilution of seawater using dewatered construction water in a hybrid forward osmosis system. *Journal of Cleaner Production, 195*, 365-373. doi:https://doi.org/10.1016/j.jclepro.2018.05.211

Hernández-Chover, V., Bellver-Domingo, Á., & Hernández-Sancho, F. (2018).

Efficiency of wastewater treatment facilities: The influence of scale economies. *Journal of Environmental Management, 228,* 77-84. doi:https://doi.org/10.1016/j.jenvman.2018.09.014

Hickenbottom, K. L., Vanneste, J., Elimelech, M., & Cath, T. Y. (2016). Assessing the current state of commercially available membranes and spacers for energy production with pressure retarded osmosis. *Desalination, 389,* 108-118. doi:https://doi.org/10.1016/j.desal.2015.09.029

Holloway, R. W., Childress, A. E., Dennett, K. E., & Cath, T. Y. (2007). Forward osmosis for concentration of anaerobic digester centrate. *Water Research, 41*(17), 4005-4014. doi:https://doi.org/10.1016/j.watres.2007.05.054

Honda, R., Rukapan, W., Komura, H., Teraoka, Y., Noguchi, M., & Hoek, E. M. V. (2015). Effects of membrane orientation on fouling characteristics of forward osmosis membrane in concentration of microalgae culture. *Bioresource Technology, 197,* 429-433. doi:https://doi.org/10.1016/j.biortech.2015.08.096

Jasim, S. Y., Saththasivam, J., Loganathan, K., Ogunbiyi, O. O., & Sarp, S. (2016). Reuse of Treated Sewage Effluent (TSE) in Qatar. *Journal of Water Process Engineering, 11,* 174-182. doi:https://doi.org/10.1016/j.jwpe.2016.05.003

Jung, D. H., Lee, J., Kim, D. Y., Lee, Y. G., Park, M., Lee, S., . . . Kim, J. H. (2011). Simulation of forward osmosis membrane process: Effect of membrane orientation and flow direction of feed and draw solutions. *Desalination, 277*(1), 83-91. doi:https://doi.org/10.1016/j.desal.2011.04.001

Klaysom, C., Hermans, S., Gahlaut, A., Van Craenenbroeck, S., & Vankelecom, I. F. J. (2013). Polyamide/Polyacrylonitrile (PA/PAN) thin film composite osmosis membranes: Film optimization, characterization and performance evaluation.

Journal of Membrane Science, 445, 25-33. doi:https://doi.org/10.1016/j.memsci.2013.05.037

Li, D., Zhang, X., Simon, G. P., & Wang, H. (2013). Forward osmosis desalination using polymer hydrogels as a draw agent: Influence of draw agent, feed solution and membrane on process performance. *Water Research, 47*(1), 209-215. doi:https://doi.org/10.1016/j.watres.2012.09.049

Li, Z.-H., Hang, Z.-Y., Lu, M., Zhang, T.-Y., & Yu, H.-Q. (2019). Difference of respiration-based approaches for quantifying heterotrophic biomass in activated sludge of biological wastewater treatment plants. *Science of The Total Environment, 664*, 45-52. doi:https://doi.org/10.1016/j.scitotenv.2019.02.007

Ling, M. M., & Chung, T.-S. (2011). Desalination process using super hydrophilic nanoparticles via forward osmosis integrated with ultrafiltration regeneration. *Desalination, 278*(1), 194-202. doi:https://doi.org/10.1016/j.desal.2011.05.019

Ling, M. M., Wang, K. Y., & Chung, T.-S. (2010). Highly Water-Soluble Magnetic Nanoparticles as Novel Draw Solutes in Forward Osmosis for Water Reuse. *Industrial & Engineering Chemistry Research, 49*(12), 5869-5876. doi:10.1021/ie100438x

Lingkungan, A. (2012). Get to know Multi Stage Flash Distillation. In.

Liu, Y., Ngo, H. H., Guo, W., Peng, L., Wang, D., & Ni, B. (2019). The roles of free ammonia (FA) in biological wastewater treatment processes: A review. *Environment International, 123*, 10-19. doi:https://doi.org/10.1016/j.envint.2018.11.039

Lu, X., Boo, C., Ma, J., & Elimelech, M. (2014). Bidirectional Diffusion of

Ammonium and Sodium Cations in Forward Osmosis: Role of Membrane Active Layer Surface Chemistry and Charge. *Environmental Science & Technology, 48*(24), 14369-14376. doi:10.1021/es504162v

Malaeb, L., & Ayoub, G. M. (2011). Reverse osmosis technology for water treatment: State of the art review. *Desalination, 267*(1), 1-8. doi:https://doi.org/10.1016/j.desal.2010.09.001

McCutcheon, J. R., & Elimelech, M. (2006). Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. *Journal of Membrane Science, 284*(1), 237-247. doi:https://doi.org/10.1016/j.memsci.2006.07.049

McCutcheon, J. R., McGinnis, R. L., & Elimelech, M. (2005). A novel ammonia-carbon dioxide forward (direct) osmosis desalination process. *Desalination, 174*, 1.

McGinnis, R. L., & Elimelech, M. (2007). Energy requirements of ammonia–carbon dioxide forward osmosis desalination. *Desalination, 207*(1), 370-382. doi:https://doi.org/10.1016/j.desal.2006.08.012

Mi, B., & Elimelech, M. (2008). Chemical and physical aspects of organic fouling of forward osmosis membranes. *Journal of Membrane Science, 320*(1), 292-302. doi:https://doi.org/10.1016/j.memsci.2008.04.036

Ong, R. C., & Chung, T.-S. (2012). Fabrication and positron annihilation spectroscopy (PAS) characterization of cellulose triacetate membranes for forward osmosis. *Journal of Membrane Science, 394-395*, 230-240. doi:https://doi.org/10.1016/j.memsci.2011.12.046

Ortega-Bravo, J. C., Ruiz-Filippi, G., Donoso-Bravo, A., Reyes-Caniupán, I. E.,

& Jeison, D. (2016). Forward osmosis: Evaluation thin-film-composite membrane for municipal sewage concentration. *Chemical Engineering Journal, 306*, 531-537. doi:https://doi.org/10.1016/j.cej.2016.07.085

. Overview on- KAHRAMAA drinking water quality requirement. (2014). Retrieved from www.km.com.qa

Parida, V., & Ng, H. Y. (2013). Forward osmosis organic fouling: Effects of organic loading, calcium and membrane orientation. *Desalination, 312*, 88-98. doi:https://doi.org/10.1016/j.desal.2012.04.029

Peñate, B., & García-Rodríguez, L. (2012). Current trends and future prospects in the design of seawater reverse osmosis desalination technology. *Desalination, 284*, 1-8. doi:https://doi.org/10.1016/j.desal.2011.09.010

Phuntsho, S., Hong, S., Elimelech, M., & Shon, H. K. (2013). Forward osmosis desalination of brackish groundwater: Meeting water quality requirements for fertigation by integrating nanofiltration. *Journal of Membrane Science, 436*, 1-15. doi:https://doi.org/10.1016/j.memsci.2013.02.022

Phuntsho, S., Kim, J. E., Johir, M. A. H., Hong, S., Li, Z., Ghaffour, N., . . . Shon, H. K. (2016). Fertiliser drawn forward osmosis process: Pilot-scale desalination of mine impaired water for fertigation. *Journal of Membrane Science, 508*, 22-31. doi:https://doi.org/10.1016/j.memsci.2016.02.024

Phuntsho, S., Shon, H. K., Hong, S., Lee, S., & Vigneswaran, S. (2011). A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions. *Journal of Membrane Science, 375*(1), 172-181. doi:https://doi.org/10.1016/j.memsci.2011.03.038

. Qatar progresses with wastewater reuse plan. (2016). *Water and wastewater*

International. Retrieved from http://www.waterworld.com/articles/wwi/2016/02/qatar-progresses-with-wastewater-reuse-plan.html

Qiu, C., Setiawan, L., Wang, R., Tang, C. Y., & Fane, A. G. (2012). High performance flat sheet forward osmosis membrane with an NF-like selective layer on a woven fabric embedded substrate. *Desalination, 287*, 266-270. doi:https://doi.org/10.1016/j.desal.2011.06.047

Sablani, S. S., Goosen, M. F. A., Al-Belushi, R., & Wilf, M. (2001). Concentration polarization in ultrafiltration and reverse osmosis: a critical review. *Desalination, 141*(3), 269-289. doi:https://doi.org/10.1016/S0011-9164(01)85005-0

Salgot, M., & Folch, M. (2018). Wastewater treatment and water reuse. *Current Opinion in Environmental Science & Health, 2*, 64-74. doi:https://doi.org/10.1016/j.coesh.2018.03.005

Setiawan, L., Wang, R., Li, K., & Fane, A. G. (2011). Fabrication of novel poly(amide–imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer. *Journal of Membrane Science, 369*(1), 196-205. doi:https://doi.org/10.1016/j.memsci.2010.11.067

Shaffer, D. L., Yip, N. Y., Gilron, J., & Elimelech, M. (2012). Seawater desalination for agriculture by integrated forward and reverse osmosis: Improved product water quality for potentially less energy. *Journal of Membrane Science, 415-416*, 1-8. doi:https://doi.org/10.1016/j.memsci.2012.05.016

Sharma, A., Syed, Z., Brighu, U., Gupta, A. B., & Ram, C. (2019). Adsorption of textile wastewater on alkali-activated sand. *Journal of Cleaner Production, 220*, 23-32. doi:https://doi.org/10.1016/j.jclepro.2019.01.236

Stache, K. (1989).

Tan, C. H., & Ng, H. Y. (2008). Modified models to predict flux behavior in forward osmosis in consideration of external and internal concentration polarizations. *Journal of Membrane Science, 324*(1), 209-219. doi:https://doi.org/10.1016/j.memsci.2008.07.020

Tang, C. Y., She, Q., Lay, W. C. L., Wang, R., & Fane, A. G. (2010). Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration. *Journal of Membrane Science, 354*(1), 123-133. doi:https://doi.org/10.1016/j.memsci.2010.02.059

Tang, J., Zhang, C., Shi, X., Sun, J., & Cunningham, J. A. (2019). Municipal wastewater treatment plants coupled with electrochemical, biological and bio-electrochemical technologies: Opportunities and challenge toward energy self-sufficiency. *Journal of Environmental Management, 234*, 396-403. doi:https://doi.org/10.1016/j.jenvman.2018.12.097

Ullah, I., Rasul, M., & Khan, M. M. (2013). *An overview of solar thermal desalination technologies*.

Valladares Linares, R., Li, Z., Abu-Ghdaib, M., Wei, C.-H., Amy, G., & Vrouwenvelder, J. S. (2013). Water harvesting from municipal wastewater via osmotic gradient: An evaluation of process performance. *Journal of Membrane Science, 447*, 50-56. doi:https://doi.org/10.1016/j.memsci.2013.07.018

Volpin, F., Fons, E., Chekli, L., Kim, J. E., Jang, A., & Shon, H. K. (2018). Hybrid forward osmosis-reverse osmosis for wastewater reuse and seawater desalination: Understanding the optimal feed solution to minimise fouling. *Process Safety and Environmental Protection, 117*, 523-532.

doi:https://doi.org/10.1016/j.psep.2018.05.006

WATER STATISTICS In The State of Qatar, 2015. (2017). Retrieved from http://www.mdps.gov.qa/en/knowledge/ReportsandStudies/WaterStats2016En.pdf

Wei, Y., Shen, L., Wang, Z., Yang, W.-D., Zhu, H., & Liu, H. (2011). A novel membrane for DMFC - Na2Ti3O7 nanotubes/Nafion® composite membrane. *International Journal of Hydrogen Energy, 36*(8), 5088-5095. doi:https://doi.org/10.1016/j.ijhydene.2010.12.096

Xie, M., & Gray, S. R. (2016). Gypsum scaling in forward osmosis: Role of membrane surface chemistry. *Journal of Membrane Science, 513*, 250-259. doi:https://doi.org/10.1016/j.memsci.2016.04.022

Yang, S., Gu, J.-S., Yu, H.-Y., Zhou, J., Li, S.-F., Wu, X.-M., & Wang, L. (2011). Polypropylene membrane surface modification by RAFT grafting polymerization and TiO2 photocatalysts immobilization for phenol decomposition in a photocatalytic membrane reactor. *Separation and Purification Technology, 83*, 157-165. doi:https://doi.org/10.1016/j.seppur.2011.09.030

Yen, S. K., Mehnas Haja N, F., Su, M., Wang, K. Y., & Chung, T.-S. (2010). Study of draw solutes using 2-methylimidazole-based compounds in forward osmosis. *Journal of Membrane Science, 364*(1), 242-252. doi:https://doi.org/10.1016/j.memsci.2010.08.021

Yong, J. S., Phillip, W. A., & Elimelech, M. (2012). Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes. *Journal of Membrane Science, 392-393*, 9-17. doi:https://doi.org/10.1016/j.memsci.2011.11.020

Zhang, X., Ning, Z., Wang, D. K., & Diniz da Costa, J. C. (2014). Processing municipal wastewaters by forward osmosis using CTA membrane. *Journal of Membrane Science, 468*, 269-275. doi:https://doi.org/10.1016/j.memsci.2014.06.016

Zhao, S., Zou, L., & Mulcahy, D. (2011). Effects of membrane orientation on process performance in forward osmosis applications. *Journal of Membrane Science, 382*(1), 308-315. doi:https://doi.org/10.1016/j.memsci.2011.08.020

Zhao, S., Zou, L., Tang, C. Y., & Mulcahy, D. (2012). Recent developments in forward osmosis: Opportunities and challenges. *Journal of Membrane Science, 396*, 1-21. doi:https://doi.org/10.1016/j.memsci.2011.12.023