FORWARD OSMOSIS WITH AN ALGAL DRAW SOLUTION FOR WASTEWATER CONCENTRATING AND POLISHING

A Thesis presented to the Faculty of the Graduate School of the

University of Missouri-Columbia

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Civil Engineering

By

BRENT J. ROOD

Dr. Zhiqiang Hu, Thesis Advisor

MAY 2018

The undersigned, appointed by the Dean of the Graduate School, have examined the thesis entitled:

FORWARD OSMOSIS WITH AN ALGAL DRAW SOLUTION FOR WASTEWATER CONCENTRATING AND POLISHING

Presented by Brent J. Rood,

A candidate for the degree of Master of Science in Civil Engineering,

And hereby certify that, in their opinion, it is worthy of acceptance.

_____

Dr. Zhiqiang Hu

_____

Dr. Enos Inniss

_____

Dr. Stephen Anderson

ACKNOWLEDGEMENTS

With many to thank during this process, I will begin with my thesis advisor, Dr. Zhiqiang Hu. His vast professional engineering and academic experience helped to provide technical wisdom where mine fell short. This was done with an honest dedication to fostering the improvement of my engineering and research skills, but also while acknowledging the importance of molding strong personal relationships with those you work with.

I must also thank Dr. Inniss and Dr. Stephen Anderson for providing valuable input during the thesis editing process and accepting my invitation to serve as committee members for my thesis defense. It was Dr. Inniss' fluid mechanics course and his evident passion for water and environmental engineering which first sparked my interest in the field.

In addition, my lab-mates, Chiqian Zhang, Yan Li, and Liyuan Hou were consistently present and eager to assist with questions I have had about laboratory methods, research methods, and technical issues.

Throughout my academic career, my family and parents, who through their dedication to scientific careers fostered similar interests in myself, were extremely supportive and available. My girlfriend, SLK, deserves adulation for tolerating my occasional academic frustrations and for serving as an intellectual sparring partner to improve ourselves as engineers and as individuals.

This research was partially supported by the MIZZOU Advantage Program at the University of Missouri.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Forward osmosis (FO) is an emerging wastewater treatment technology capable of high solute rejection by separating water from wastewater across a semi-permeable membrane. However, there is always leaking of ammonium from the feed solution (FS) to the draw solution (DS). Parallel bench-scale FO systems were operated with synthetic municipal wastewater as an FS. Both systems had a synthetic seawater DS with one system also inoculated by an algal species (*Chlorella Vulgaris*) to act as an absorbent (polishing agent). At the completion of three consecutive trials (lasting a total of three days), ammonium removal efficiency in the algae-based FO system improved by 35.4 ± 4.6%. Throughout the fed-batch operation in the DS chamber, the algal biomass concentration was maintained at 606 ± 29 mg/L due to simultaneous algal growth and dilution. The water flux gradually decreased from an average initial flux of 16.5 LMH to an average of 8.2 LMH after each trial operation, with an average water flux of 11.63 ± 0.49 LMH compared to 12.05 ± 0.35 LMH in the system without algae. Meanwhile, organic matter and phosphorus were completely retained in the FS in both systems. At the completion of each trial operation, the concentrations of chemical oxygen demand (COD) and phosphorus in the synthetic wastewater increased by an average of 44%. This work highlights the dual-benefit applications of algae-based FO with improved effluent water quality and concentrated wastewater COD and phosphorus for potential water resource recovery and water reuse.

1.0. INTRODUCTION

1.1. *Water Quality and Resource Challenges*

The scarcity of global water resources has driven the need for creative research solutions. With water quality and quantity being linked very closely, relieving the over-stressing of resources will rely not only on water conservation, but also increased treatment efficiency. Currently, about one-third of the world struggles with clean water scarcity. (Shannon et al. 2008). Though, the human capital and economic benefits of population growth will perhaps be key in providing the prudent engineering solutions that are needed by out-weighing population growth's additional stresses on water resources (Stern et al. 1996). Regardless, the availability of fresh water resources for both drinking and agricultural uses will continue to be a major focal point. Like previous population boom scares, optimists believe that innovative advances in medicine, science, and agriculture will counter-act the phenomenon. Between 1980 and 2015, access to improved water sources has increased from around 50% to greater than 90% of the global population. This is coupled with an increase in access to improved sanitation from around 25% to nearly 70% of the global population (Norberg 2016). This improvement in the usage efficiency of water resources has been led by technological improvements in treatment and agricultural practices and increases in global wealth.

Coastal watersheds inhabit 75% of the world's population, and the rapid development of these areas has led to harmful levels of nutrients being present in water bodies (Paerl 2015). The majority of National Pollutant Discharge Elimination System (NPDES) permitted

facilities are likely to discharge nitrogen or phosphorus while also facing no discharge limits (EPA 2012). By placing total nitrogen (TN) and total phosphorus (TP) discharge limits on many large, coastal wastewater treatment plants (WWTP), one can predict that similar limits will be established in the future for smaller WWTP's. These limits are far too difficult to maintain for many dischargers, so progressive, shrewd engineering action must be taken now in preparation. One of many possible pieces to the solution is a renewed vision for wastewater treatment. This vision includes viewing water reuse, nutrient recycling, and resource recovery as essential elements in future WWTP design philosophy (Ansari et al. 2017, Mo and Zhang 2013).

This connection between water quality and quantity will also be extended to energy, especially in the coming decades. Municipal wastewater treatment is an extremely energy intensive process. According to the Environmental Protection Agency (EPA), the average Energy Star rating of wastewater treatment plants in the United States is just a 48/100 (EPA 2015). Energy use tends to increase with treatment requirements. Therefore, with the trend being that water treatment will continue to increase in complexity, there are few indications that energy demands will decrease. This is, of course, unless alternative treatment methods are investigated.

The complexity and high-fouling nature of wastewater streams from industries such as food and beverage production and hydraulic fracturing hinder the efficiency of many current, traditional treatment technologies. In addition, industrial producers have become subject to increasingly stringent regulations, with some even receiving zero-liquid discharge stipulations. This could include textile producers (Vergili et al. 2012), desalination plants

(Elimelech 2007, Heijman et al. 2009, Martinetti et al. 2009), or a number of other industrial processes (Koppol et al. 2004). To ensure compliance, facility managers will need to focus on water reuse and other emerging management and treatment processes when evaporative processes do not provide the requisite economic efficiency.

1.2. *Introduction to Membrane Technologies*

Population growth will continue to place increased stress on drinking water resources. Options such as seawater desalination and direct wastewater reuse will likely need to be a part of the answer. As resources become scarce, it will become more energy intensive to treat the available sources to an adequate level of quality. This has fostered rapid growth of research in membrane treatment technology. Due to the high-rejection capability of membranes, application in high-complexity waste streams is possible (Coday et al. 2014, Van der Bruggen et al. 2003, Wintgens et al. 2005). The main types of membrane processes in development or in practice are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO). FO has been viewed as a promising technology for some time, but has lacked the developments required to make it feasible in most industrial-scale processes. FO has promising application opportunities in areas such as seawater desalination, municipal wastewater, water reuse, wastewater resource recovery, MBRs (membrane bioreactors), industrial process optimization, and the treatment of highly-complex wastewaters (Linares et al. 2014, Lutchmiah et al. 2014, Nguyen et al. 2013, Wang et al. 2016, Xue et al. 2015). The potential of forward osmosis

(FO) to aid in alleviating global water scarcity and meeting future regulatory permit limits will be thoroughly scrutinized based on current research and practices.

2.0. LITERATURE REVIEW

2.1. *Membrane Processes*

The major membrane treatment processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Despite these all being capable of producing high-quality effluent water, they are prone to a number of efficiency-draining issues such as high-energy demand and high propensity for fouling (Deng et al. 2016, Ghaffour et al. 2013, Kwan et al. 2015, Xie et al. 2015). Reverse osmosis and other membrane processes are reliant on the semi-permeable nature of the polymers used for membranes. The major disadvantage of RO and other processes is that they are pressure-driven processes. In the case of RO, this means that an external pressure must be applied to the incoming (feed) stream to overcome the natural osmotic pressure of the system. The applied pressure has both an energy cost and an efficiency cost in terms of bio-fouling (Altaee et al. 2014, Holloway et al. 2007, Kwan et al. 2015, Lee et al. 2010). In forward osmosis systems, the natural osmotic pressure becomes the driving force which can decrease energy input and bio-fouling potential. Figure 2.1 is a schematic illustrating the driving forces in an FO system.

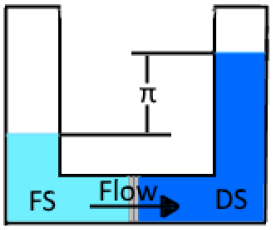


Figure 2.1. Water flow map for FO system.

FO systems consist of two closed-loop systems (feed and draw) separated by a semi-permeable membrane. For the osmotic pressure (π) between the two solutions to move towards equilibrium, water must flow from the feed solution (FS) to the draw solution (DS). This concentrates and increases the osmotic pressure of the FS, while diluting and decreasing the osmotic pressure of the DS. Despite its promise, FO suffers from a number of issues such as inadequate water flux rates for large-scale operation, not having draw solutions capable of maintaining high water flux and being simple to recover, lack of application-specific membrane materials, reverse solute flux, and leaking of ammonium from the FS to the DS (Boo et al. 2012, Lutchmiah et al. 2014, McCutcheon and Elimelech 2006, Wang et al. 2016, Xue et al. 2015). The purpose of this literature review is to evaluate past and current research breakthroughs, identify where FO shows the potential to improved engineering processes, and to provide a review of the factors which dictate the operational efficiency of FO systems.

2.2. ***Forward Osmosis: Processes and Technologies***

2.2.1. FO Theory

Forward osmosis (FO) represents a low-energy demand treatment alternative while remaining capable of producing high-quality effluent. Until recently, FO has not received near the level of consideration as membrane processes, such as RO. Like other membrane processes, FO requires a force or pressure to generate the separation of solutes and water by a semi-permeable membrane. The advantage of FO systems, however, is that this force

does not need to be applied externally. It, instead, relies on a difference in osmotic pressures on each side of the membrane. The osmotic pressure gradient can be related to hydraulic pressure, or water flux by Equation 1.

$$J_w = A\,(\Delta\pi - \Delta P) \quad (1)$$

Where J_w is the water flux in units of L/m^2/hr, A is an intrinsic property of the membrane called the pure water permeability, and $\Delta\pi$ is the osmotic pressure gradient between both sides of the membrane. ΔP is the hydrostatic pressure gradient. The water flux in Equation 1 is a direct result of nature's tendency to reach a point of equilibrium. Solute concentration is directly proportional to osmotic pressure, so as the solute concentration difference between the two membrane sides decreases, so will the rate at which clean water is transported across the membrane. The initial solution of higher concentration, which will be referred to as the draw solution (DS), is responsible for the necessary osmotic pressure imbalance. FO is not only applicable to processes where a high-quality effluent is desired, but potential functions also include those which the desired outcome is a more-highly concentrated feed stream.

2.2.2. Advantages and Disadvantages

Forward osmosis benefits from not requiring external hydraulic pressures to be applied. FO is capable of very high solute rejection rates and is often times less prone to bio-fouling than other membrane processes in most applications (Holloway et al. 2007, Kwan et al. 2015, Lee et al. 2010). Moreover, FO membranes have proven to have very high fouling

reversibility, especially compared to other membrane processes (Mi and Elimelech 2010, Xie et al. 2015). This may be partially due to membrane structures, but is more likely due to the hydraulic nature of how the different membrane systems operate. The lack of applied hydraulic pressure, as well as having a cross-flow system, give FO the advantage in fouling reversibility. Despite the lack of additional hydraulic pressure being a positive in some respects, it also has disadvantages in terms of maintaining water flux.

2.2.3. Concentration Polarization

One of the main reasons forward osmosis has not become proven at large-scale operations is due to its lower permeate flux, in part due to the asymmetric design of FO membranes (Figure 2.2). The difference between FO permeate flux and theoretical permeate flux is largely created by the existence of concentration polarization (McCutcheon and Elimelech 2006). External concentration polarization (ECP) is caused by the consolidation of solute particles in the feed stream on the membrane surface, thus decreasing the effective osmotic pressure difference between FS and DS. Simultaneously, the draw solution is being diluted as it mixes with the incoming permeate stream. These are two of the phenomena responsible for decreasing permeate flux and increasing the osmotic pressure required to transport permeate across the membrane (Elimelech and Bhattacharjee 1998).

Internal concentration polarization (ICP) is an additional cause of lower permeate flux and is related to the asymmetric nature of FO membranes (Zhao and Zou 2011). A possible FO membrane includes a porous support layer and a dense active layer. Therefore, membrane

orientation plays a large role in determining the severity of internal concentration polarization (Gray et al. 2006). When the porous layer is oriented to face the incoming feed stream, a build-up of solute at the active layer boundary can cause concentration polarization. When the membrane is oriented so that the active layer faces the feed stream, the DS is diluted as water permeates from the FS through the support layer. This dilution of the draw solution, relative to the bulk draw solution, causes a decrease in effective DS osmotic pressure. The orientation of the membrane with the active layer facing the DS is not considered for this work. When concentrating a higher fouling FS, such as wastewater in this work, additional irreversible fouling of the porous support layer is possible (Zhao et al. 2011).

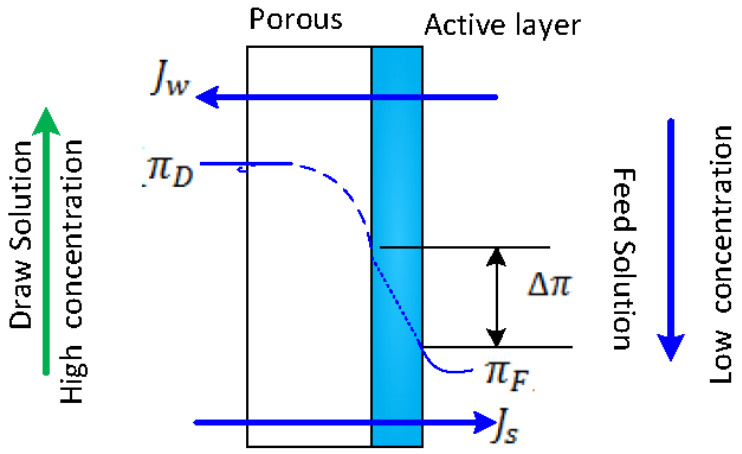


Figure 2.2. Asymmetric FO membrane structure (Mabrouk et al. 2015).

Therefore, water flux is affected in a manner like in external concentration polarization. The principle as to why internal polarization has a greater effect on water flux is that external polarization can be somewhat mitigated by the cross flow of the feed stream (Tang et al. 2010). However, cross-flow is not a factor with internal polarization as its effects are

isolated to within the membrane structure. Efforts in feed and draw solution concentration (McCutcheon et al. 2006) and membrane layer engineering (Emadzadeh et al. 2014, Tiraferri et al. 2011, Zhang et al. 2010, Zhou et al. 2014) are some of the ways that the issue of concentration polarization is being addressed.

2.2.4. Reverse Solute Flux

Current FO membranes have struggled with DS solute retention, so it is worth discussing the potential impacts of salt diffusion on potential downstream treatment processes (Boo et al. 2012, Phillip et al. 2010, Wong et al. 2012). One of these processes is anaerobic digestion and biogas harvesting. Salt concentrations exceeding certain levels (e.g., > 8 g/L) may have inhibitory impacts on anaerobic digestion (Anwar et al. 2016, Chen et al. 2008, Ozalp et al. 2004). Therefore, continued efforts to minimize reverse salt flux through draw solution and membrane engineering are needed (Achilli et al. 2010). Sodium chloride, which is the main constituent in seawater, has higher diffusivity than some other FO draw solutes (Ansari et al. 2015). Despite this, the positives of seawater as a DS may outweigh the negatives, as the potential to eliminate draw solution regeneration by directly discharging into saline water bodies may be a practical approach. Although other draw solutes such as sodium acetate and EDTA-2Na have lower reverse solute flux rates (Ansari et al. 2016, Nguyen et al. 2015), further research remains necessary with an emphasis on FO membrane properties. The mass transfer properties of an FO membrane can be partially described by two factors. These are the pure water permeability coefficient, A, and the

reverse solute permeability coefficient, B. Similar to Equation 1 which describes the relationship of A with the water flux and osmotic pressure difference, Equation 2 relates B to the flux rate of solute, J_s, which has units of g/(m^2 hr), from the DS into the FS and the difference in concentration across the membrane, ΔC.

$$J_s = B\ (\Delta C) \tag{2}$$

2.2.5. Fouling by organic particles

Understanding of membrane fouling processes in FO systems is limited, especially compared to the amount of research that has been dedicated to pressure-driven membrane processes. It has been observed that total organic fouling is affected by adhesive forces between the clean membrane surface and foulant particles, as well as foulant-foulant attraction (Mi and Elimelech 2008). Stronger organic fouling is noted with greater adhesion forces. Moreover, the rate of cake buildup depends strongly on the type of foulant and membrane orientation.

In addition to molecular forces, hydrodynamics, including cross-flow velocity, provide some understanding for FO biofouling being less detrimental than for RO (Kwan et al. 2015, Sun et al. 2016, Xie et al. 2015). Additionally, efforts in membrane surface engineering and nanocomposites have been made to alleviate biofouling issues (Faria et al. 2017, Li et al. 2016). The understanding of these fouling principles is fundamental to future membrane design and decision-making about hydrodynamic conditions.

2.2.6. Draw solutions

The product of FO is a combination of purified water and draw solution. For most, but not all, applications the water must be recovered from the draw solution by an external process. Therefore, it is imperative that the draw solution be engineered to maximize water flux, decrease reverse salt flux, minimize fouling, and be as simple as possible to recover, or regenerate.

Since osmotic pressure is dependent on differences in solution concentrations and compositions only, it is accurate to predict that differences in water flux between the draw solutions are mostly caused by differences in internal concentration polarization. The performance of many inorganic draw solutions including $CaCl_2$, $Ca(NO_3)_2$, KBr, KCl, $KHCO_3$, K_2SO_4, $MgCl_2$, $MgSO_4$, NaCl, $NaHCO_3$, Na_2SO_4, NH_4Cl, NH_4HCO_3, and $(NH_4)_2SO_4$ was evaluated (Achilli et al. 2010). Several factors must be considered when selecting a draw solution for FO including cost, water flux, and reverse salt diffusion. Achilli found that $KHCO_3$, $MgSO_4$, and $NaHCO_3$ were superior to the other solutions based on water flux, reverse salt flux, and cost analysis. Seawater is also a common draw solution in part due to the possibility of eliminating the DS regeneration step by discharging directly into a saline water body (Xue et al. 2015).

In addition to the inorganic draw solutions discussed, some novel draw solutions have been tested. One interesting idea is the use of magnetic particles in the draw solution to provide the necessary osmotic pressure (Ling et al. 2011). This is intriguing as once the draw solution is to be recycled, a magnetic field can be used to separate the magnetic solute

particles from the permeate solution. It is unclear, however, if this idea has the potential to be energy efficient enough due to the potential of draw solutes to aggregate, thus decreasing their reusability.

2.2.7. Membrane design and technology

At present, forward osmosis membrane technology is mostly centered around cellulose triacetate (CTA) and thin-film composite membranes. Recently, many studies have attempted to improve water flux, reduce reverse solute flux, and reduce the effects of concentration polarization and fouling (Emadzadeh et al. 2014, Faria et al. 2017, Lu et al. 2016, Ong et al. 2015, Shaffer et al. 2015, Xie et al. 2013). This is expected to be a continued area of development in forward osmosis research. Besides material, orientation also is a major factor in membrane performance due to their asymmetric nature (Gray et al. 2006). CTA membranes have positive qualities such as high flux potential, low fouling potential, and normally sufficient degradation (Geise et al. 2010, Zhang et al. 2010). The main drawbacks of these membranes are their struggle with hydrolysis, biological attachment, and only being functional in a small pH range (Geise et al. 2010). TFC membranes are also made from CTA material, but are normally about half the thickness (Zhao et al. 2012).

Under typical test conditions, TFC FO membranes have higher water flux, better DS salt rejection, and higher resistance to hydrolysis or degradation (Geise et al. 2010, Wei et al. 2011, Yip et al. 2010). The support layer thickness is a main component in mitigating

internal concentration polarization. An effectively thinner support layer allows more efficient diffusion between the diluted draw solution at the active layer boundary and the bulk draw solution. This fact was demonstrated by varying the casting conditions during the fabrication of the support layer of TFC membranes (Tiraferri et al. 2011). Future membrane development and research will be targeted at mitigating ICP, maximizing water flux, and minimizing reverse salt flux.

2.2.8. Algae as a tool for wastewater polishing

Algae have been used extensively in wastewater treatment for pollution control and nutrient removal (Hoffmann 1998, Ruiz-Marin et al. 2010, Tang and Hu 2016, Xu et al. 2015). They are a leading candidate for large-scale biofuel production, animal feedstock, and value-added products (Chen et al. 2015, Dahiya 2015, Lundquist et al. 2010, Mehrabadi et al. 2015, Quinn and Davis 2015). Assimilatory algal uptake of inorganic nitrogen (e.g., NH_4^+ and NO_3^-) plays an important role in nitrogen removal (Arango et al. 2008, Green et al. 1996). A typical formula for rapidly growing algae is $C_{106}H_{181}O_{45}N_{16}P$ (Green et al. 1996). The nitrogen percent of algae is 9.2%, slightly less than that of bacteria ($C_5H_7O_2N$, 12.4%) (Grady Jr et al. 2011). In algae systems for secondary wastewater polishing, nitrogen is predominantly removed by cell uptake followed by biomass wasting (Shen et al. 2016a, Xu et al. 2015).

3.0. EXPERIMENTAL WORK

3.1. *Introduction*

Membrane-based water and wastewater treatment processes have continued to improve and grow in research interest. The major membrane treatment processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Despite these all being capable of producing high-quality effluent water, they are prone to issues such as high-energy demand and high propensity for fouling (Deng et al. 2016, Ghaffour et al. 2013, Kwan et al. 2015, Xie et al. 2015). A major disadvantage of these processes is that they are pressure-driven processes. In the case of RO, this means that a high external pressure must be applied to the incoming (feed) stream to overcome the natural osmotic pressure of the system, often resulting in high energy costs and bio-fouling. By comparison, forward osmosis (FO), employs osmotic pressure as the driving force which can decrease energy input and bio-fouling potential while maintaining high solute recovery (Altaee et al. 2014, Holloway et al. 2007, Kwan et al. 2015, Lee et al. 2010). Due, in part, to a lack of applied external pressure, FO membranes have high fouling reversibility, when compared to other membrane processes (Mi and Elimelech 2010, Xie et al. 2015). Hence, FO has promising application opportunities in areas such as seawater desalination, water reuse, wastewater resource recovery, and the treatment of highly-complex industrial wastewaters (Doyle and Smith 1997, Lutchmiah et al. 2014, Nguyen et al. 2013, Wang et al. 2016). Additionally, the simultaneous dilution of the DS and concentration of the FS have potential water resource recovery applications, as higher chemical concentrations in

the FS can improve resource recovery efficiency (e.g., in anaerobic digestion) (Chen et al. 2014, Linares et al. 2014, Xie et al. 2014).

An FO system consists of two solutions with an osmotic pressure gradient separated by a semi-permeable membrane. The solution of initial higher osmotic pressure is referred to as the draw solution (DS), and the initially lower osmotic pressure solution as the feed solution (FS). Like other membrane process, FO requires a force or pressure to achieve the separation of solutes and water by the membrane. The advantage of FO systems, however, is that this force does not need to be applied externally. It, instead, relies on a difference in osmotic pressures on each side of the membrane. The osmotic pressure gradient can be related to hydraulic pressure, and water flux in the following equation:

$$J_w = A\ (\Delta\pi - \ \Delta P)$$

(1)

Where J_w is the water flux in units of L/(m^2 hr), A is an intrinsic property of the membrane called the pure water permeability coefficient, and $\Delta\pi$ is the osmotic pressure gradient between both sides of the membrane. ΔP is the hydrostatic pressure gradient.

Solute concentration is directly proportional to osmotic pressure. As the solute concentration difference between the two sides of the membrane decreases, so will the rate at which water is transported across the membrane from the FS to the DS. Previous studies using forward osmosis membranes included thin-film composite FO membranes achieving initial water flux rates of 18 L/(m^2 hr) or higher (Kwan et al. 2015, Lutchmiah et al. 2014, Yip et al. 2010). The relatively low FO water flux rates compared to other membrane

processes, however, is a main factor in preventing widespread FO adoption. The difference between observable FO permeate flux and theoretical permeate flux is largely caused by internal and external concentration polarization (IECP) which decreases the effective osmotic pressure difference (McCutcheon and Elimelech 2006). Efforts in draw solution innovation (McCutcheon et al. 2006) and membrane engineering (Emadzadeh et al. 2014, Tiraferri et al. 2011, Zhang et al. 2010, Zhou et al. 2014) are some of the ways to address the issue of concentration polarization. Additionally, FO suffers from a number of issues, including not having draw solutions capable of simple DS recovery, reverse solute flux (DS to FS), and leaking of ammonium from the FS to the DS (Boo et al. 2012, Lutchmiah et al. 2014, McCutcheon and Elimelech 2006, Wang et al. 2016, Xue et al. 2015).

Algae have been used extensively in wastewater treatment for pollution control and nutrient removal (Hoffmann 1998, Ruiz-Marin et al. 2010, Tang and Hu 2016, Xu et al. 2015). In algae systems for secondary wastewater polishing, nitrogen is predominantly removed by cell uptake followed by biomass wasting (Shen et al. 2016a, Xu et al. 2015). Hence, algae is a good candidate to remove un-rejected ammonium in the DS. The performance of algae-based FO systems is, however, largely unknown. The main objective of this study was to determine the ammonium removal efficiency in the FO system using an algal draw solution and evaluate the overall performance of the FO system in terms of feed solute (substrate) concentration, water flux, salt rejection, and algal biomass growth.

3.2. *Material and Methods*

3.2.1. Algal species

For the preparation of algae-based draw solution, *Chlorella Vulgaris* was selected because it is abundant in both freshwater and marine environments (Bayat Tork et al. 2017, Nie et al. 2008). The marine species (Florida Aqua Farms, Dade City, FL), received on an agar disk, was cultured in 1,000 mL, followed by 2,000 mL, Erlenmeyer flasks in a seawater, f/2 medium (provided by the vendor) at 23 ± 1˚C while receiving about 60 µmol/(m^2 s) of light for 16 hr/day without air bubbling. Three growth periods were completed to ensure adequate acclimation of the algal species. The algal specific growth rate, µ, was determined to be approximately 0.2 day^{-1} in this lab condition. Before each trial for FO operation, the biomass from the flask was separated with an Eppendorf centrifuge (5702, Eppendorf, Hamburg, Germany) and re-suspended in the new DS.

3.2.2. FO bench scale systems

Figure 3.1 shows the schematic of a bench-scale FO system using a flat-sheet thin-film composite (TFC) membrane manufactured by Aquaporin, and purchased from Sterlitech Corporation (Kent, WA). The Aquaporin-TFC membranes were housed inside custom-fabricated (acrylic plastic) FO reactor cells. Each FO reactor cell had an effective membrane surface area of 12.25 cm^2. The symmetrical channels on each side of the membrane were approximately 7 cm length and 1.75 cm width. The depth on each side was 0.32 cm, and no spacers were installed in the cells.

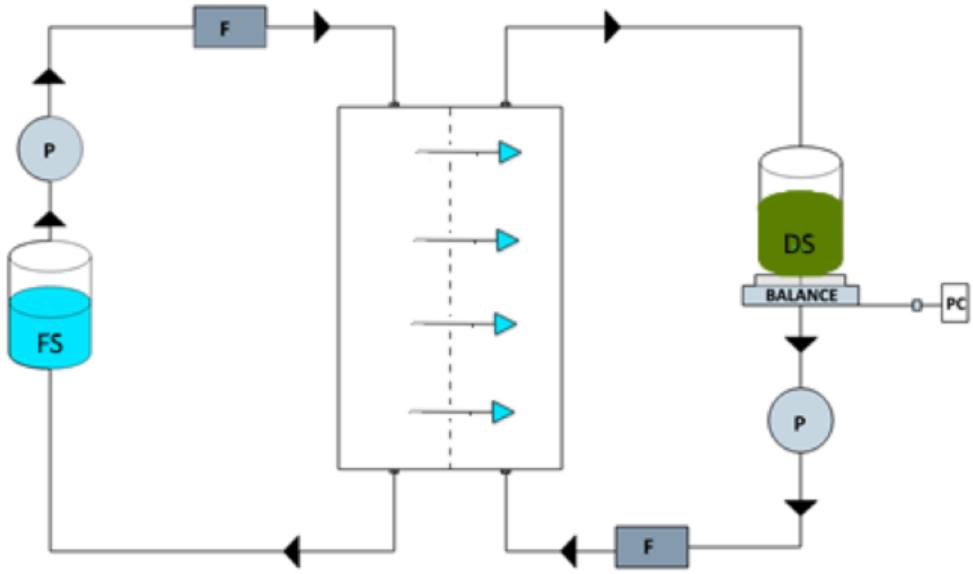


Figure 3.1. A schematic of FO system using an algal draw solution (DS). "F" indicates flow meter and "P" indicates pump.

For FO system operation, the experiment was carried out in batch mode, resulting in a decreasing-volume (increasing substrate concentration) FS and an increasing-volume (decreasing solute concentration) DS. Both the FS and DS began as 1-L in their respective flasks. Variable-speed peristaltic pumps (Cole Parmer, Vernon Hills, IL) were operated at a flow rate of 300 mL/min, as measured by in-line water flow meters (Dakota Instruments, Orangeburg, NY). This corresponds to a cross-flow velocity (CFV) of 9.0 cm/s. An analytical balance (Scout Ohaus SPX6201, Parsippany, NJ), interfaced with a computer, was used to record mass change in the DS at one-hour intervals. This, when converted from mass to volume, allows the calculation of water flux using an active membrane area of 12.25 cm^2. Additionally, in the FO system using algae in the draw solution, fluorescent

light was provided for 16 hr per day at an irradiation intensity of about 60 µmol/(m^2 s). The system set-up is pictured in Figure 3.2.

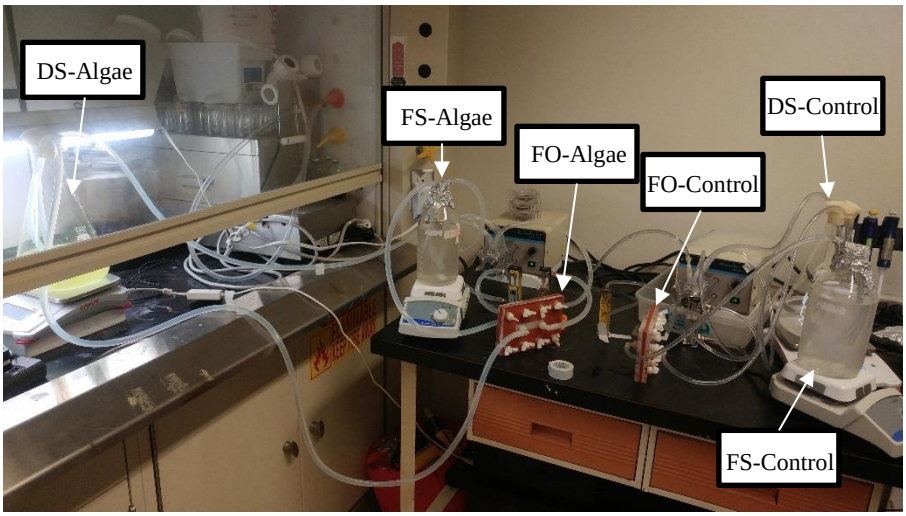


Figure 3.2. Parallel bench-scale FO system set-up during operation.

3.2.3. Experimental FO experiments using synthetic wastewater and algae

This experiment was completed over 3 consecutive trials (cycles) with two identical FO systems only varying in DS composition. Briefly, the FS and DS were replaced with fresh synthetic wastewater and synthetic seawater (each with a theoretical osmotic pressure of 26.44 bar according to an online calculator (Lenntech), respectively. The major components of the synthetic raw wastewater were as follows: glucose and sodium acetate as the carbon source with each having a concentration of 250 mg/L COD; 16 mg/L NH_4^+-N; 4.5 mg/L PO_4^3-P; 350 mg/L $NaHCO_3$; 50 mg/L $CaCl_2$; 12 mg/L $MgCl_2$; 12 mg/L $FeCl_2$; 10 mg/L NaCl according to the literature (Sun et al. 2016). The system was operated in fed-batch mode to the FS chamber at a flow rate of 300 mL/min (Figure 3.1). The draw

solution was made of synthetic seawater with the major components as follows: 24.53 g/L NaCl; 5.2 g/L $MgCl_2$; 4.09 g/L Na_2SO_4; 1.16 g/L $CaCl_2$; 0.695 g/L KCl; 0.201 g/L $NaHCO_3$; 0.101 g/L KBr; 0.027 g/L H_3BO_3; 0.003 g/L NaF. The draw solution was also recirculated around the draw solution chamber at a flow rate of 300 mL/min (Figure 3.1). Each cycle ended after approximately 22 h and was followed by membrane cleaning and FS/DS solution regeneration. Cleaning was completed by first cycling 4-L DI water through the feed side. Then, osmotic backwashing was employed for 10 min with the same flow rate and CFV (9.0 cm/s) (Sagiv and Semiat 2005), using 0.7 M NaCl on the feed side and DI water on the draw side. Once this cycle was complete, DI water was pumped through both sides of the reactor to prepare for the next cycle.

3.2.4. Salt rejection and FO membrane intrinsic properties

The mass transfer properties of an FO membrane can be partially described by two factors. These are the pure water permeability coefficient, A, and the reverse solute permeability coefficient, B. Similar to Equation 1 which describes the relationship of A with the water flux and osmotic pressure difference, Equation 2 relates B to the flux rate of solute, J_s, which has units of g/(m^2 hr), from the DS into the FS and the difference in concentration across the membrane, ΔC.

$$J_s = B\ (\Delta C) \tag{2}$$

To determine these values, additional tests were conducted in the bench-scale FO system operating with a 1-L DI water as an FS and a 1-L, 1 M NaCl DS following published

procedures (Cath et al. 2013, Wang et al. 2016). Hydraulic conditions were identical to those described in section 2.2. Once steady state flux was established (after approximately 10 min), water flux and conductivity values were recorded for 30 min of operation time at 5-min intervals. Due to the relatively large FS and DS volumes, factors such as the concentration of the FS and dilution of the DS due to water flux within 30 min of operation may be ignored.

3.2.5. Chemical and statistical analysis

Samples of the FS and DS were gathered at the beginning, 12-hr mark, and end of each of the three trials (cycles). Algal biomass concentration in the DS was measured in COD units, with the ratio of COD and VSS (volatile suspended solids) for biomass measured at 1.64 g COD/g VSS (Tang and Hu 2016). The concentrations of COD, PO_4^{-3}-P, and NH_4^{+}-N were determined with a Hach spectrophotometer (DR/2400, Hach Company, Loveland, CO) according to the standard methods (APHA 2012). One-way analysis of variance (ANOVA) was applied to determine the difference in flux and effluent water quality between the algae-based FO and control at a significance level (α) of 0.05.

3.3. *Results and discussion*

3.3.1. Water flux in the FO systems in the presence or absence of algae

Through three consecutive cycles of FO operation with each lasting for about 22 h, the water flux across the FO membrane decreased with time, resulting in about 50% reduction at the end of each cycle (Figure 3.3). Regardless of the use of algae in DS, there appeared little difference in trend of the flux between the two types of FO systems. The average water flux in the algae-based system and control were 11.63 ± 0.49 and 12.05 ± 0.35 L/(m^2 hr), respectively. There was no statistical difference of average water flux between the two FO systems in the presence of algae or in the absence of algae.

Despite the flux decrease over time, the fouling appeared to be very reversible when the membrane cleaning process was implemented after each FO run. Initial water flux was recovered at more than 91% for both systems over three trials (cycles). Compared to other membrane processes such as MF and NF, the lack of additional hydraulic pressure, along with hydraulic shear forces, is possibly a reason for increased fouling reversibility in FO systems (Kwan et al. 2015, Xie et al. 2015). The relative contributions of internal concentration polarization (ICP), membrane fouling, and DS dilution to total flux decrease during this experiment were not determined. Though, it is suspected that the dilution of the draw solution (ECP) was the foremost cause of decreased water flux during each trial. Overall, this study shows that the bench-scale FO systems were capable of achieving the same initial water flux rates as those in the literature (Kwan et al. 2015, Lutchmiah et al.

2014, Yip et al. 2010) with minimal irreversible fouling when concentrating synthetic wastewater with a synthetic seawater DS.

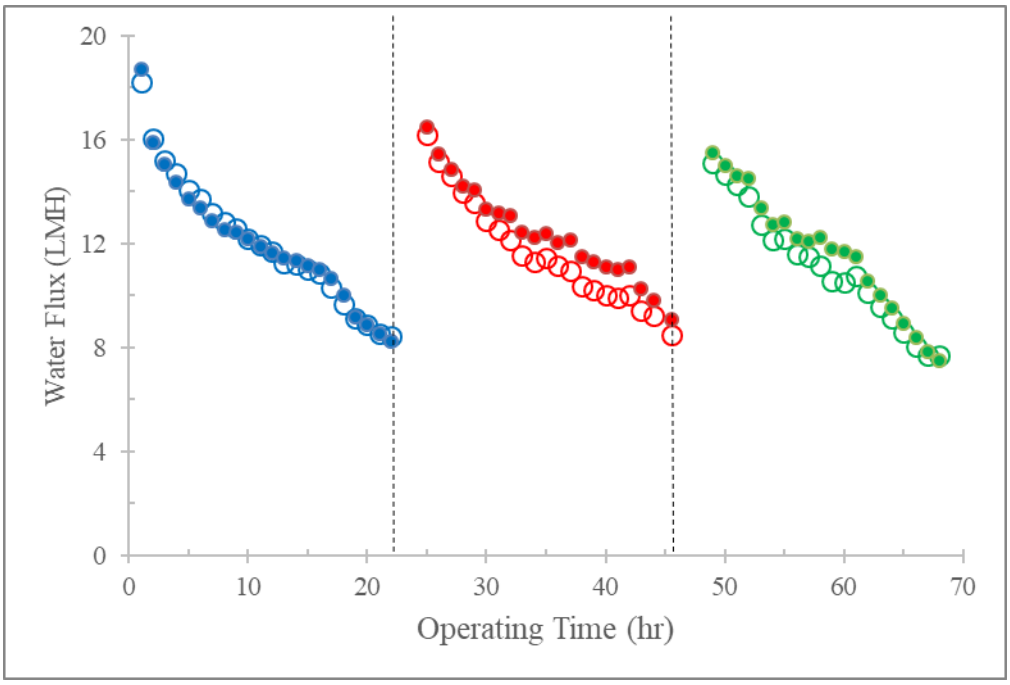


Figure 3.3. Change in water flux across the membrane in the FO systems through three consecutive trials (cycles) over 3 days of operation. Open circles indicate the algae-based FO system and closed circles indicate the control FO system. Dash lines indicate the end of each trial.

3.3.2. Pollutant concentration in the FS and ammonium leaking to the DS

Figure 3.4 shows the changes in COD and ammonium concentrations in the FS and DS through three consecutive FO operation trials. There was no COD or phosphate detected in the DS in either FO system. PO_4^{3-}-P and COD were recovered in the FS at approximately 99.5% and 98.7%, respectively. Both PO_4^{3-}-P and COD were concentrated in the FS as

water from the FS solution diffused across the FO membrane. At the end of each FO operation trial (cycle), the COD and phosphorus concentrations in the FS increased by an average of 44%.

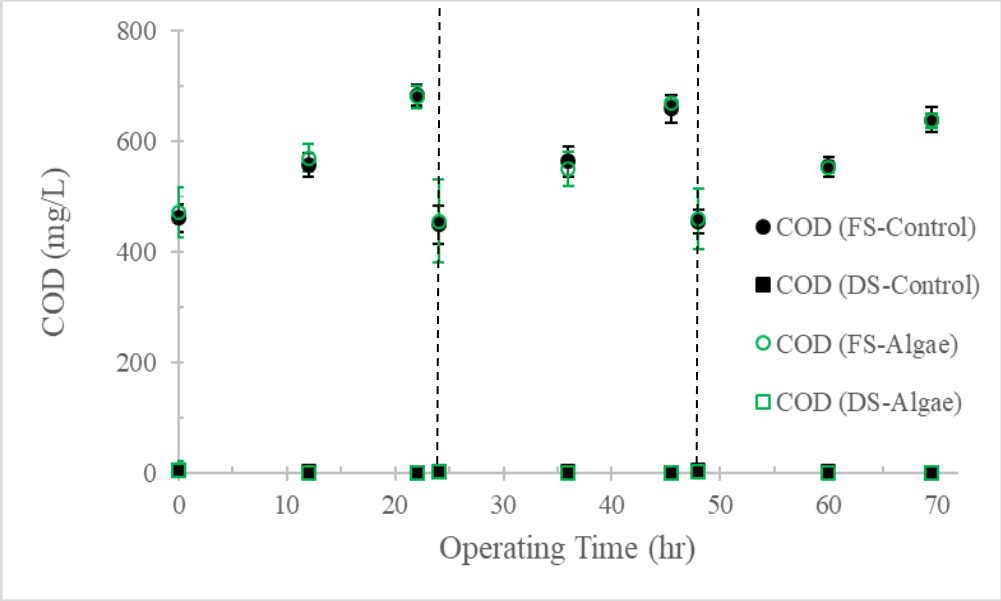
However, NH_4^+-N was not completely retained in the FS. At the end of each algae-based FO operation cycle, the NH_4^+-N concentration in the FS decreased from 15.03 ± 2.06 mg/L to 10.03 ± 1.59 mg/L while its concentrations in the DS increased to 3.73 ± 0.32 mg/L. For comparison, in the control (FO system in the absence of algae), the NH_4^+-N concentration in the FS decreased from 15.27 ± 2.14 mg/L to 10.27 ± 1.72 mg/L while its concentrations in the DS increased to 5.93 ± 0.76 mg/L. Figure 3.4b shows that the ammonium concentration in the algal DS was lower than in DS of the control for each dilution cycle due to ammonium uptake by algae.

The algal biomass was inoculated in the DS at between 570 and 651 mg/L for the experiment. Throughout the fed-batch operation in the DS chamber, the algal biomass concentration was maintained at 606 ± 29 mg/L due to simultaneous algal growth and dilution. A mass balance analysis (Tab) concludes that ammonium removal efficiency was improved by 28.1 ± 3.7%, 40.4 ± 4.5%, and 37.8 ± 5.5% in the algae-based FO (FO-Algae) for each of the operation cycles, respectively. Overall, the presence of algae in the draw solution improved ammonia removal by 35.4 ± 4.6%.

Table 3.1 displays the concentration and mass of pollutant calculated for both systems at the sampling intervals. A mass balance analysis was conducted for the pollutants present

in FO and DS for both FO systems, indicating the overall accuracy of chemical and data analysis throughout this study.

(a)



(b)

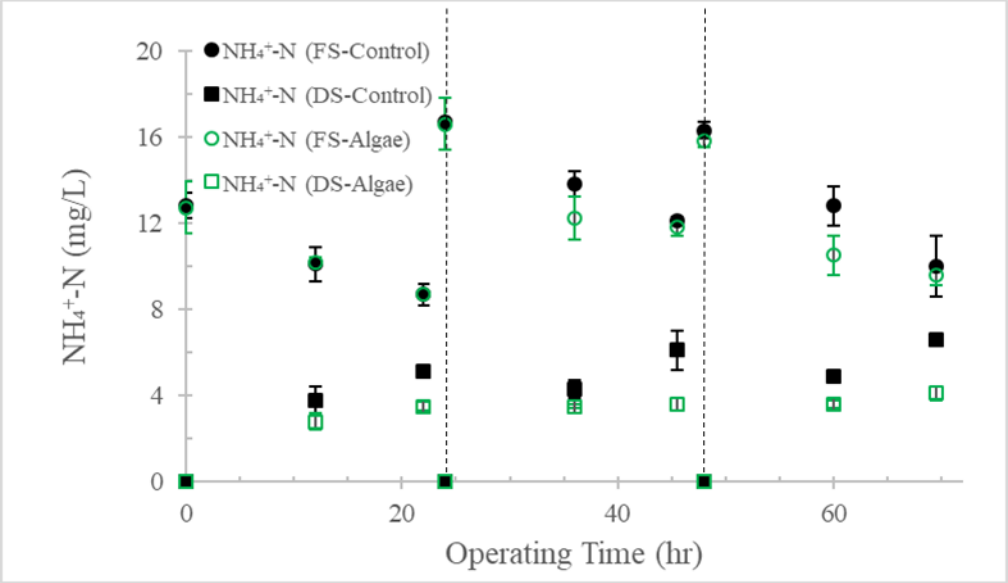


Figure 3.4. Changes in concentrations of COD (a) and NH_4^+-N (b) in FS and DS over time in the algae-based FO system and control.

Table 3.1. A mass balance analysis conducted based on the mass of chemical in FS and DS at the start and during the FO operation: (a) COD, (b) NH_4^+-N (in FO-Control), and (c) NH_4^+-N (in algae-based FO or FO-Algae).

(a)

	FO-Control			FO-Algae		
Trial	**FS Volume (L)**	**COD (mg/L)**	**COD (mg)**	**FS Volume (L)**	**COD (mg/L)**	**COD (mg)**
Start	1.003*	461	462	1.003	471	472
1	0.801$^+$	557	446	0.799	570	455
End	0.678√	683	463	0.69	680	469
Start	1.003	449	450	1.003	455	456
2	0.802	563	452	0.811	549	445
End	0.678	659	447	0.686	669	459
Start	1.003	455	456	1.003	459	460
3	0.808	554	448	0.819	553	453
End	0.717	639	458	0.723	637	461

(b)

	FO-Control					
Trial	**FS Volume (L)**	**NH_4^+-N (mg/L)**	**NH_4^+-N (mg)**	**DS Volume (L)**	**NH_4^+-N (mg/L)**	**NH_4^+-N (mg)**
Start	1.003	12.8	12.9	0.984	0.0	0.0
1	0.801	10.1	8.1Σ	1.186	3.8	4.5Σ
End	0.678	8.7	5.9	1.327	5.1	6.8
Start	1.003	16.7	16.7	1.026	0.0	0.0
2	0.802	13.8	11.1	1.227	4.3	5.3
End	0.678	12.1	8.2	1.382	6.1	8.4
Start	1.003	16.3	16.4	1.052	0.0	0.0
3	0.808	12.8	10.4	1.247	4.9	6.1
End	0.717	10.0	7.2	1.363	6.6	8.9

(c)

	Algae-based FO System					
Trial	**FS Volume (L)**	**NH_4^+-N (mg/L)**	**NH_4^+-N (mg)**	**DS Volume (L)**	**NH_4^+-N (mg/L)**	**NH_4^+-N (mg)**
Start	1.003	12.7	12.7	1.054	0.0	0.0
1	0.799	10.2	8.2Σ	1.258	2.8	3.5Σ
End	0.690	8.7	6.0	1.367	3.5	4.8
Start	1.003	16.6	16.7	1.086	0.0	0.0
2	0.811	12.2	9.8	1.278	3.5	4.5
End	0.686	11.8	8.1	1.403	3.6	5.1
Start	1.003	15.8	15.8	1.106	0.0	0.0
3	0.819	10.5	8.4	1.29	3.6	4.7
End	0.723	9.6	6.6	1.386	4.1	5.7

* samples taken at time zero; + samples taken after 12 h of operation; √ samples taken at the end of FO operation trial. Σ The total amount of NH_4^+-N in the FS and DS should equal original mass.

3.3.3. Salt rejection and membrane performance properties

Preliminary tests were also completed to determine the overall membrane and system performance (without algae). Using NaCl as a draw solution and pure DI water as a feed solution, we determined the initial reverse solute flux rates to be 14.44, 18.48, and 31.15 g/(m^2/hr) at NaCl concentrations of 0.67, 1.0, and 1.67 M, respectively, based on the volume change of pure water and mass change of NaCl over 30 min in the FS.

By using 1-L of DI water as FS and 1-L, 1M NaCl as DS and equations 1 and 2, the intrinsic membrane coefficients were determined to be 0.464 L/(m^2 hr bar) and 0.418 L/(m^2 hr) for the values of A and B, respectively. Selected examples of FO membrane performance analysis from the literature are included in Table 3.2 for comparison.

Table 3.2. Performance of cellulose triacetate and thin-film composite membranes: pure water permeability, A and reverse solute permeability, B.

Membrane manufacturer and type	A L/(m^2 hr bar)	B L/(m^2 hr)	FS	DS	Reference
Aquaporin (TFC)	0.46	0.32	DI	1 M NaCl	This study
HTI (CTA)	0.70	0.53	DI	0.5-4 M NaCl	(Wang et al. 2016)
HTI (CTA)	0.94	1.88	DI	RO mode	(Wong et al. 2012)
HTI (CTA)	0.65	0.25	DI	RO mode	(Xie et al. 2013b)
Oasys (TFC)	4.72	0.16	DI	RO mode	(Xie et al. 2013b)
TFC (fabricated, treated)	2.85	0.35	DI	1 M NaCl	(Ong et al. 2015)

3.4. *Conclusions*

This study has demonstrated the potential of algae-based FO system to treat synthetic municipal wastewater using synthetic seawater as a DS and maintain adequate water flux at an average of 11.63 L/(m^2 hr). It also confirmed that that most of the flux decrease was recoverable after membrane cleaning. There was no leaking of PO_4^{3-}-P or COD from the FS into the DS, but ammonium rejection averaged 66.8 ± 5.6%. The incorporation of *C. Vulgaris* in the DS increased ammonium rejection efficiency by 35.4 ± 4.6%. This study has proposed a new strategy of combining forward osmosis wastewater concentrating with an algae-based draw solution for wastewater polishing.

4.0. IMPLICATIONS/FUTURE RESEARCH DIRECTION

This work emphasizes the idea of combining low-energy wastewater treatment by FO with biological nutrient removal by microalgae to improve water quality and resource recovery. A major issue with the performance of FO systems is the poor ammonium rejection ability of current membrane technology. Although there was no leaking of PO_4^{3-}-P or COD from the FS into the DS, ammonium rejection averaged 66.8 ± 5.6% during each operation cycle. Typical ammonium-nitrogen recovery rates are between 40-60%, though this depends on many other factors such as ammonium concentration, FS chemistry, and operation cycle time (Boo et al. 2012, Lutchmiah et al. 2014, McCutcheon and Elimelech 2006, Wang et al. 2016, Xue et al. 2015). Rather than focusing on improved membrane properties to improve ammonium rejection, the aim of this study was to accept this deficiency and examine the feasibility of employing marine algae as a polishing agent. Algae was chosen due to its capability of nutrient uptake and valuable uses such as for biofuel production, animal feedstock, and value-added products (Chen et al. 2015, Dahiya 2015, Lundquist et al. 2010). The algae-based FO system was proven successful in improving overall ammonium removal of the FO system and to not be accompanied by any deleterious impacts due to the incorporation of algal species. The algae-based FO system improved ammonium removal efficiency by 35.4 ± 4.6% in the algal draw solution. The use of algal species in the DS is not expected to pose unique solution regeneration complications. It is worth noting that the algae biofuel applications of this study may be somewhat limited. Many algae species produce the highest concentration of lipids in nitrogen limited-

conditions, not in phosphorus limited-conditions such as in this study (Converti et al. 2009, Shen et al. 2016b). Theoretical calculations conclude that ammonium uptake by algal species in the algal DS was low compared to their maximum potential in a lab growth culture setting (with a specific growth rate of 0.2 d^{-1}), but was clearly present and could likely be improved with system optimization. Further improvement is possible by optimizing the algal growth conditions such as light exposure, the use of higher biomass concentration, and selection of algal species capable of improved growth under phosphorus limited conditions.

With water resource recovery rapidly becoming a focal point within wastewater treatment, forward osmosis has been identified as a potentially impactful technology (Ansari et al. 2017, Xie et al. 2014). Simultaneous concentration of COD and phosphorus in the FS can improve the efficiency of subsequent water resource recovery processes such as nutrient recovery in anaerobic digestion and biogas harvesting (Shen et al. 2015). For instance, ammonia and phosphate concentrations could be increased up to 10-times using a seawater-driven FO system, thus improving the efficiency of processes such as struvite precipitation and anaerobic digestion/biogas harvesting (Ansari et al. 2017, Holm-Nielsen et al. 2009). Through a short-term 22 h) fed batch operation, this study demonstrated that phosphate and COD concentrations in the FS increased by 44%. A more highly concentrated FS may have the potential to increase biogas production during anaerobic digestion, for example (Ozgun et al. 2013).

At present, forward osmosis membrane technology is mostly centered around cellulose triacetate (CTA) and thin-film composite membranes. Recently, many studies have

attempted to improve water flux, reduce reverse solute flux, and reduce the effects of concentration polarization and fouling (Emadzadeh et al. 2014, Faria et al. 2017, Lu et al. 2016, Ong et al. 2015, Shaffer et al. 2015, Xie et al. 2013). This is expected to be a continued area of development in forward osmosis research. Current FO membranes have struggled with DS solute retention, so it is worth discussing the potential impacts of salt diffusion on potential downstream treatment processes (Boo et al. 2012, Phillip et al. 2010, Wong et al. 2012). One of these processes is anaerobic digestion and biogas harvesting. Salt concentrations exceeding certain levels (e.g., > 8 g/L) may have inhibitory impacts on anaerobic digestion (Anwar et al. 2016, Chen et al. 2008, Ozalp et al. 2004). Therefore, continued efforts to minimize reverse salt flux through draw solution and membrane engineering are needed (Achilli et al. 2010). Sodium chloride, which is the main constituent in seawater, has higher diffusivity than some other FO draw solutes (Ansari et al. 2015). Despite this, the positives of seawater as a DS may outweigh the negatives, as the potential to eliminate draw solution regeneration by directly discharging into saline water bodies may be practical approach. Although other draw solutes such as sodium acetate and EDTA-2Na have lower reverse solute flux rates (Ansari et al. 2016, Nguyen et al. 2015), further research remains necessary with an emphasis on FO membrane properties.

5.0.REFERENCES

Achilli, A., Cath, T.Y. and Childress, A.E. (2010) Selection of inorganic-based draw solutions for forward osmosis applications. Journal of Membrane Science 364(1–2), 233-241.

Altaee, A., Zaragoza, G. and van Tonningen, H.R. (2014) Comparison between Forward Osmosis-Reverse Osmosis and Reverse Osmosis processes for seawater desalination. Desalination 336, 50-57.

Ansari, A.J., Hai, F.I., Guo, W., Ngo, H.H., Price, W.E. and Nghiem, L.D. (2015) Selection of forward osmosis draw solutes for subsequent integration with anaerobic treatment to facilitate resource recovery from wastewater. Bioresource technology 191, 30-36.

Ansari, A.J., Hai, F.I., Guo, W., Ngo, H.H., Price, W.E. and 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.

Ansari, A.J., Hai, F.I., Price, W.E., Drewes, J.E. and Nghiem, L.D. (2017) Forward osmosis as a platform for resource recovery from municipal wastewater - A critical assessment of the literature. Journal of Membrane Science 529, 195-206.

Anwar, N., Wang, W., Zhang, J., Li, Y., Chen, C., Liu, G. and Zhang, R. (2016) Effect of sodium salt on anaerobic digestion of kitchen waste. Water Science and Technology 73(8), 1865-1871.

APHA, W.A. (2012) Standard Methods for the Examination of Water and Wastewater. 22nd ed. American Public Health Association: Washington, DC, USA.

Arango, C., Tank, J., Johnson, L. and Hamilton, S. (2008) Assimilatory uptake rather than nitrification and denitrification determines nitrogen removal patterns in streams of varying land use. Limnology and Oceanography 53(6), 2558-2572.

Bayat Tork, M., Khalilzadeh, R. and Kouchakzadeh, H. (2017) Efficient harvesting of marine Chlorella vulgaris microalgae utilizing cationic starch nanoparticles by response surface methodology. Bioresource technology 243, 583-588.

Boo, C., Lee, S., Elimelech, M., Meng, Z. and Hong, S. (2012) Colloidal fouling in forward osmosis: Role of reverse salt diffusion. Journal of Membrane Science 390-391, 277-284.

Cath, T.Y., Elimelech, M., McCutcheon, J.R., McGinnis, R.L., Achilli, A., Anastasio, D., Brady, A.R., Childress, A.E., Farr, I.V., Hancock, N.T., Lampi, J., Nghiem, L.D., Xie, M. and Yip, N.Y. (2013) Standard Methodology for Evaluating Membrane Performance in Osmotically Driven Membrane Processes. Desalination 312, 31-38.

Chen, G., Zhao, L. and Qi, Y. (2015) Enhancing the productivity of microalgae cultivated in wastewater toward biofuel production: A critical review. Applied Energy 137, 282-291.

Chen, L., Gu, Y., Cao, C., Zhang, J., Ng, J.-W. and Tang, C. (2014) Performance of a submerged anaerobic membrane bioreactor with forward osmosis membrane for low-strength wastewater treatment. Water research 50, 114-123.

Chen, Y., Cheng, J.J. and Creamer, K.S. (2008) Inhibition of anaerobic digestion process: a review. Bioresource technology 99(10), 4044-4064.

Coday, B.D., Xu, P., Beaudry, E.G., Herron, J., Lampi, K., Hancock, N.T. and 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.

Converti, A., Casazza, A.A., Ortiz, E.Y., Perego, P. and Del Borghi, M. (2009) Effect of temperature and nitrogen concentration on the growth and lipid content of Nannochloropsis oculata and Chlorella vulgaris for biodiesel production. Chemical Engineering and Processing: Process Intensification 48(6), 1146-1151.
Dahiya, A. (2015) Algae biomass cultivation for advanced biofuel production, pp. 219-238, Elsevier.
Deng, L., Guo, W., Ngo, H.H., Zhang, H., Wang, J., Li, J., Xia, S. and Wu, Y. (2016) Biofouling and control approaches in membrane bioreactors. Bioresource technology 221, 656-665.
Doyle, S.J. and Smith, R. (1997) Targeting Water Reuse with Multiple Contaminants. Process Safety and Environmental Protection 75(3), 181-189.
Elimelech, M. (2007) Yale constructs forward osmosis desalination pilot plant. Membrane Technology 2007(1), 7-8.
Elimelech, M. and Bhattacharjee, S. (1998) A novel approach for modeling concentration polarization in crossflow membrane filtration based on the equivalence of osmotic pressure model and filtration theory. Journal of Membrane Science 145(2), 223-241.
Emadzadeh, D., Lau, W.J., Matsuura, T., Ismail, A.F. and Rahbari-Sisakht, M. (2014) Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization. Journal of Membrane Science 449, 74-85.
EPA (2012) Action towards Limiting Total Nitrogen, Total Phosphorus, and Total Inorganic Nitrogen Loads from NPDES-Permitted Facilities, EPA.
EPA (2015) Energy Use in Wastewater Treatment Plants. EPA (ed), EnergyStar.gov.
Faria, A.F., Liu, C., Xie, M., Perreault, F., Nghiem, L.D., Ma, J. and Elimelech, M. (2017) Thin-film composite forward osmosis membranes functionalized with graphene oxide–silver nanocomposites for biofouling control. Journal of Membrane Science 525, 146-156.
Geise, G.M., Lee, H.-S., Miller, D.J., Freeman, B.D., McGrath, J.E. and Paul, D.R. (2010) Water purification by membranes: The role of polymer science. Journal of Polymer Science Part B: Polymer Physics 48(15), 1685-1718.
Ghaffour, N., Missimer, T.M. and Amy, G.L. (2013) Technical review and evaluation of the economics of water desalination: Current and future challenges for better water supply sustainability. Desalination 309, 197-207.
Grady Jr, C.L., Daigger, G.T., Love, N.G. and Filipe, C.D. (2011) Biological wastewater treatment, CRC press.
Gray, G.T., McCutcheon, J.R. and Elimelech, M. (2006) Internal concentration polarization in forward osmosis: role of membrane orientation. Desalination 197(1), 1-8.
Green, F.B., Bernstone, L., Lundquist, T. and Oswald, W. (1996) Advanced integrated wastewater pond systems for nitrogen removal. Water Science and Technology 33(7), 207-217.
Heijman, S.G.J., Guo, H., Li, S., van Dijk, J.C. and Wessels, L.P. (2009) Zero liquid discharge: Heading for 99% recovery in nanofiltration and reverse osmosis. Desalination 236(1), 357-362.
Hoffmann, J.P. (1998) Wastewater treatment with suspended and nonsuspended algae. Journal of Phycology 34(5), 757-763.

Holloway, R.W., Childress, A.E., Dennett, K.E. and Cath, T.Y. (2007) Forward osmosis for concentration of anaerobic digester centrate. Water research 41(17), 4005-4014.
Holm-Nielsen, J.B., Al Seadi, T. and Oleskowicz-Popiel, P. (2009) The future of anaerobic digestion and biogas utilization. Bioresource technology 100(22), 5478-5484.
Koppol, A.P.R., Bagajewicz, M.J., Dericks, B.J. and Savelski, M.J. (2004) On zero water discharge solutions in the process industry. Advances in Environmental Research 8(2), 151-171.
Kwan, S.E., Bar-Zeev, E. and Elimelech, M. (2015) Biofouling in forward osmosis and reverse osmosis: Measurements and mechanisms. Journal of Membrane Science 493, 703-708.
Lee, S., Boo, C., Elimelech, M. and Hong, S. (2010) Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO). Journal of Membrane Science 365(1–2), 34-39.
Lenntech Osmotic pressure calculator, www.Lenntech.com.
Li, F., Cheng, Q., Tian, Q., Yang, B. and Chen, Q. (2016) Biofouling behavior and performance of forward osmosis membranes with bioinspired surface modification in osmotic membrane bioreactor. Bioresource technology 211, 751-758.
Linares, R.V., Li, Z., Sarp, S., Bucs, S.S., Amy, G. and Vrouwenvelder, J.S. (2014) Forward osmosis niches in seawater desalination and wastewater reuse. Water research 66, 122-139.
Ling, M.M., Chung, T.-S. and Lu, X. (2011) Facile synthesis of thermosensitive magnetic nanoparticles as "smart" draw solutes in forward osmosis. Chemical Communications 47(38), 10788-10790.
Lu, P., Liang, S., Qiu, L., Gao, Y. and Wang, Q. (2016) Thin film nanocomposite forward osmosis membranes based on layered double hydroxide nanoparticles blended substrates. Journal of Membrane Science 504, 196-205.
Lundquist, T.J., Woertz, I.C., Quinn, N. and Benemann, J.R. (2010) A realistic technology and engineering assessment of algae biofuel production. Energy Biosciences Institute, 1.
Lutchmiah, K., Verliefde, A., Roest, K., Rietveld, L.C. and Cornelissen, E.R. (2014) Forward osmosis for application in wastewater treatment: a review. Water research 58, 179-197.
Mabrouk, A.N., Fath, H., Darwish, M. and Abdulrahim, H. (2015) Desalination Updates, InTech.
Martinetti, C.R., Childress, A.E. and Cath, T.Y. (2009) High recovery of concentrated RO brines using forward osmosis and membrane distillation. Journal of Membrane Science 331(1–2), 31-39.
McCutcheon, J.R. and Elimelech, M. (2006) Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. Journal of Membrane Science 284(1–2), 237-247.
McCutcheon, J.R., McGinnis, R.L. and Elimelech, M. (2006) Desalination by ammonia–carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance. Journal of Membrane Science 278(1–2), 114-123.

Mehrabadi, A., Craggs, R. and Farid, M.M. (2015) Wastewater treatment high rate algal ponds (WWT HRAP) for low-cost biofuel production. Bioresource technology 184, 202-214.
Mi, B. and Elimelech, M. (2008) Chemical and physical aspects of organic fouling of forward osmosis membranes. Journal of Membrane Science 320(1–2), 292-302.
Mi, B. and Elimelech, M. (2010) Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents. Journal of Membrane Science 348(1–2), 337-345.
Mo, W. and Zhang, Q. (2013) Energy–nutrients–water nexus: Integrated resource recovery in municipal wastewater treatment plants. Journal of Environmental Management 127, 255-267.
Nguyen, H.T., Nguyen, N.C., Chen, S.-S., Ngo, H.H., Guo, W. and Li, C.-W. (2015) A new class of draw solutions for minimizing reverse salt flux to improve forward osmosis desalination. Science of The Total Environment 538, 129-136.
Nguyen, N.C., Chen, S.-S., Yang, H.-Y. and Hau, N.T. (2013) Application of forward osmosis on dewatering of high nutrient sludge. Bioresource technology 132, 224-229.
Nie, X., Wang, X., Chen, J., Zitko, V. and An, T. (2008) Response of the freshwater alga Chlorella vulgaris to trichloroisocyanuric acid and ciprofloxacin. Environmental toxicology and chemistry 27(1), 168-173.
Norberg, J. (2016) Progress: Ten Reasons to Look Forward to the Future, Oneworld Publications.
Ong, R.C., Chung, T.-S., de Wit, J.S. and Helmer, B.J. (2015) Novel cellulose ester substrates for high performance flat-sheet thin-film composite (TFC) forward osmosis (FO) membranes. Journal of Membrane Science 473, 63-71.
Ozalp, G., Gomec, C., Ozturk, I., Gonuldinc, S. and Altinbas, M. (2004) Effect of high salinity on anaerobic treatment of low strength effluents. Water Science and Technology 48(11-12), 207-212.
Ozgun, H., Dereli, R.K., Ersahin, M.E., Kinaci, C., Spanjers, H. and van Lier, J.B. (2013) A review of anaerobic membrane bioreactors for municipal wastewater treatment: Integration options, limitations and expectations. Separation and Purification Technology 118, 89-104.
Paerl, H. (2015) Managing Eutrophication Along the Freshwater-Marine Continuum: Why the Need for Dual Nutrient (N & P) Input Controls?
Phillip, W.A., Yong, J.S. and Elimelech, M. (2010) Reverse Draw Solute Permeation in Forward Osmosis: Modeling and Experiments. Environmental Science & Technology 44(13), 5170-5176.
Quinn, J.C. and Davis, R. (2015) The potentials and challenges of algae based biofuels: A review of the techno-economic, life cycle, and resource assessment modeling. Bioresource technology 184, 444-452.
Ruiz-Marin, A., Mendoza-Espinosa, L.G. and Stephenson, T. (2010) Growth and nutrient removal in free and immobilized green algae in batch and semi-continuous cultures treating real wastewater. Bioresource technology 101(1), 58-64.
Sagiv, A. and Semiat, R. (2005) Backwash of RO spiral wound membranes. Desalination 179(1), 1-9.

Shaffer, D.L., Jaramillo, H., Romero-Vargas Castrillón, S., Lu, X. and Elimelech, M. (2015) Post-fabrication modification of forward osmosis membranes with a poly(ethylene glycol) block copolymer for improved organic fouling resistance. Journal of Membrane Science 490, 209-219.
Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Marinas, B.J. and Mayes, A.M. (2008) Science and technology for water purification in the coming decades. Nature 452(7185), 301-310.
Shen, Q., Wall, J.D. and Hu, Z. (2016a) Solids Retention Time Dependent Phototrophic Growth and Population Changes in Chemostat Cultivation Using Wastewater. Water Environment Research 88(1), 5-12.
Shen, X.-F., Liu, J.-J., Chauhan, A.S., Hu, H., Ma, L.-L., Lam, P.K.S. and Zeng, R.J. (2016b) Combining nitrogen starvation with sufficient phosphorus supply for enhanced biodiesel productivity of Chlorella vulgaris fed on acetate. Algal Research 17, 261-267.
Shen, Y., Linville, J.L., Urgun-Demirtas, M., Mintz, M.M. and Snyder, S.W. (2015) An overview of biogas production and utilization at full-scale wastewater treatment plants (WWTPs) in the United States: Challenges and opportunities towards energy-neutral WWTPs. Renewable and Sustainable Energy Reviews 50, 346-362.
Stern, D.I., Common, M.S. and Barbier, E.B. (1996) Economic growth and environmental degradation: the environmental Kuznets curve and sustainable development. World development 24(7), 1151-1160.
Sun, Y., Tian, J., Zhao, Z., Shi, W., Liu, D. and Cui, F. (2016) Membrane fouling of forward osmosis (FO) membrane for municipal wastewater treatment: A comparison between direct FO and OMBR. Water research 104, 330-339.
Tang, C.Y., She, Q., Lay, W.C.L., Wang, R. and 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(1–2), 123-133.
Tang, T. and Hu, Z. (2016) A comparison of algal productivity and nutrient removal capacity between algal CSTR and algal MBR at the same light level under practical and optimal conditions. Ecological Engineering 93, 66-72.
Tiraferri, A., Yip, N.Y., Phillip, W.A., Schiffman, J.D. and Elimelech, M. (2011) Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure. Journal of Membrane Science 367(1–2), 340-352.
Van der Bruggen, B., Vandecasteele, C., Van Gestel, T., Doyen, W. and Leysen, R. (2003) A review of pressure-driven membrane processes in wastewater treatment and drinking water production. Environmental progress 22(1), 46-56.
Vergili, I., Kaya, Y., Sen, U., Gönder, Z.B. and Aydiner, C. (2012) Techno-economic analysis of textile dye bath wastewater treatment by integrated membrane processes under the zero liquid discharge approach. Resources, Conservation and Recycling 58, 25-35.
Wang, Z., Zheng, J., Tang, J., Wang, X. and Wu, Z. (2016) A pilot-scale forward osmosis membrane system for concentrating low-strength municipal wastewater: performance and implications. Scientific Reports 6, 21653.
Wei, J., Qiu, C., Tang, C.Y., Wang, R. and Fane, A.G. (2011) Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes. Journal of Membrane Science 372(1), 292-302.

Wintgens, T., Melin, T., Schäfer, A., Khan, S., Muston, M., Bixio, D. and Thoeye, C. (2005) The role of membrane processes in municipal wastewater reclamation and reuse. Desalination 178(1), 1-11.
Wong, M.C.Y., Martinez, K., Ramon, G.Z. and Hoek, E.M.V. (2012) Impacts of operating conditions and solution chemistry on osmotic membrane structure and performance. Desalination 287, 340-349.
Xie, M., Lee, J., Nghiem, L.D. and Elimelech, M. (2015) Role of pressure in organic fouling in forward osmosis and reverse osmosis. Journal of Membrane Science 493, 748-754.
Xie, M., Nghiem, L.D., Price, W.E. and Elimelech, M. (2014) Toward resource recovery from wastewater: extraction of phosphorus from digested sludge using a hybrid forward osmosis–membrane distillation process. Environmental Science & Technology Letters 1(2), 191-195.
Xie, M., Price, W.E., Nghiem, L.D. and Elimelech, M. (2013) Effects of feed and draw solution temperature and transmembrane temperature difference on the rejection of trace organic contaminants by forward osmosis. Journal of Membrane Science 438, 57-64.
Xu, M., Li, P., Tang, T. and Hu, Z. (2015) Roles of SRT and HRT of an algal membrane bioreactor system with a tanks-in-series configuration for secondary wastewater effluent polishing. Ecological Engineering 85, 257-264.
Xue, W., Tobino, T., Nakajima, F. and Yamamoto, K. (2015) Seawater-driven forward osmosis for enriching nitrogen and phosphorous in treated municipal wastewater: Effect of membrane properties and feed solution chemistry. Water research 69, 120-130.
Yip, N.Y., Tiraferri, A., Phillip, W.A., Schiffman, J.D. and Elimelech, M. (2010) High Performance Thin-Film Composite Forward Osmosis Membrane. Environmental Science & Technology 44(10), 3812-3818.
Zhang, S., Wang, K.Y., Chung, T.-S., Chen, H., Jean, Y.C. and Amy, G. (2010) Well-constructed cellulose acetate membranes for forward osmosis: Minimized internal concentration polarization with an ultra-thin selective layer. Journal of Membrane Science 360(1–2), 522-535.
Zhao, S. and Zou, L. (2011) Relating solution physicochemical properties to internal concentration polarization in forward osmosis. Journal of Membrane Science 379(1–2), 459-467.
Zhao, S., Zou, L. and Mulcahy, D. (2011) Effects of membrane orientation on process performance in forward osmosis applications. Journal of Membrane Science 382(1), 308-315.
Zhao, S., Zou, L., Tang, C.Y. and Mulcahy, D. (2012) Recent developments in forward osmosis: Opportunities and challenges. Journal of Membrane Science 396, 1-21.
Zhou, Z., Lee, J.Y. and Chung, T.-S. (2014) Thin film composite forward-osmosis membranes with enhanced internal osmotic pressure for internal concentration polarization reduction. Chemical Engineering Journal 249, 236-245.