Doctoral Dissertation

A BASIC STUDY OF MAGNESIUM CHLORIDE AS DRAW SOLUTION FOR NUTRIENT REJECTION BY FORWARD OSMOSIS

（正浸透法による栄養塩の阻止における駆動液としての塩化マグネシウムの有効性に関する基礎的研究）

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A dissertation submitted to the Division of Environmental Science and Engineering of Yamaguchi University in partial fulfillment of the requirements for the degree of Doctor of Engineering (Dr. Eng)

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ABSTRACT

Wastewater in most cases contain high levels of the nutrients: nitrogen and phosphorus. Excessive release of nutrients to the environment can cause severe environmental problem such as eutrophication leading to algal blooms, oxygen deficiency, and fish kills. The secondary treated effluent of wastewater treatment plants usually still contain nutrients at levels that commonly less strict than those for eutrophication control. In consequence, wastewater treatment plants need to implement advanced treatment.

Advanced treatment such as forward osmosis (FO) can be used to separate nutrients from secondary treated effluents. Forward osmosis uses the chemical potential across the membrane, which is the osmotic pressure gradient, to induce a net flow of water through membrane from a feed solution (FS) into a draw solution (DS). The performance of FO is affected by membrane characteristics, composition of FS and DS, and operating conditions.

First, to elucidate the effect of the FO cross flow velocity on nutrient rejection and water flux, a series of FO processes were conducted at velocities of 0.17, 0.25, and 0.34 m/s. The same concentration of 1 M magnesium chloride ($MgCl_2$) as DS was applied to the commercial membrane Hydration Technologies Inc. (HTI-NW) in these experiments. Nutrient rejection was successfully achieved by a moderate velocity of cross flow at 0.25 m/s in which reject NO_2-N, NO_3-N, NH_4-N, and PO_4-P in FS side until to 68.8%, 96.84%, 99.33%, 98.50%, respectively. The higher velocity that resulted higher flow rate is possible to increase random or mixing flow condition. This condition will increase the potential back-movement of nutrients from passing through membrane active layer surface to move back into the bulk of FS. Therefore, it reject nutrient to

transfer to the DS side and increase nutrient rejection. Temperature had less of an impact on nutrient rejection than the velocity, but temperature did have an effect on the water flux. A temperature of 25°C exhibited good nutrient rejection rates.

The second, FO process presents the results of using four kinds of variation in concentrations of DS and the two kinds of membranes for the nutrient rejection in the same cross flow velocity at 0.25 m/s and temperature 25ºC. The nutrient rejection by high concentration of DS 2 M $MgCl_2$ and membrane HTI-NW was more efficient than was process by low DS concentration and membrane HTI-ES. For instance, when low concentration $MgCl_2$ was used as 0.5 M DS, the rejection of NO_2, NO_3, NH_4 and PO_4 in membrane HTI-ES yielded lower rejection 57.47%, 83.68%, 67.57% and 71.99%, respectively than using 2 M $MgCl_2$, the rejection of NO_2, NO_3, NH_4 and PO_4 in membrane HTI-NW were measured high rejection as 60.71%, 81.61%, 99.58%, and 83.46%, respectively. The performance of nutrient rejection was supported by lower reverse solute flux rate at 3.38-5.26 g/m^2-hr and the specific reverse solute at 0.45 to 0.55 g/L in membrane HTI-NW than that in membrane HTI-ES, which could support the efficiency of the FO system. The concentration of DS $MgCl_2$ less affect to reverse solute of membrane HTI-NW than membrane HTI-ES. The reverse solute in membrane HTI-NW seemly constant along all concentration of DS $MgCl_2$ that the chloride diffusion slightly higher than magnesium. In membrane HTI-ES, the reverse solute of chloride was almost three times that of magnesium. Conversely, the water flux in membrane HTI-NW achieved lower 7.55–9.61 L/m^2-hr than in membrane HTI-ES that exceeds until 13.58-15.10 L/m^2-hr. The characteristics of the ionic nutrients, such as ion size and ion charge, and membrane morphologies affect the performance of FO process. The concentration difference between the dissociated ions of $MgCl_2$ in the DS plays a significant role in rejecting ion nutrients in the FS by the Donnan potential effect in lower concentrations DS and by diffusion constant in higher concentrations.

The third, the results in this study show a potential $MgCl_2$ as DS to enhance nutrient rejection performance. The cleaning process mostly could achieve similar performance on nutrient rejection as well as before cleaning that promisingly could extending membrane's longevity and reducing cost material. A compete price of $MgCl_2$ with NaCl r was considered with its high performance on nutrient rejection. Interestingly, using $MgCl_2$ as DS, due to the high difference of diffusion constant between Mg^{2+} and Cl^-, the Cl^- more dominantly to diffuse from DS to FS. Compare with NaCl and seawater, the common DS that have been used in FO process, Na^+ and Cl^- have very similar high diffusion constants whereas seawater contain complex diffusion constant that more difficult to predict the dominant diffusion thereby generated varied result in performance of FO. In addition several important consideration should be taken in the FO system by $MgCl_2$ for rejecting nutrient. 1) The concentrated FS contaminated by low magnesium chloride due to reverse solute should be considered, 2) The forward osmosis that considered as pre-treatment, especially in clean water production, which need further treatment of recovery $MgCl_2$ from diluted DS needs to be investigated.

学位論文要旨

廃水は多くの場合、その中に栄養塩（窒素やリン）を高い濃度で含有している。栄養塩の水環境への過剰な排出は甚大な環境問題、富栄養化によるアオコの大量発生やそれによる溶存酸素の低下、水生生物の斃死等を引き起こす。廃水処理施設からの２次処理水はまだ栄養塩を含有することが多く、閉鎖性水域の富栄養化の原因となっている。したがって、廃水処理施設での高度処理が必要とされている。

正浸透法（FO）等による高度処理は、２次処理水から栄養塩を分離することが可能である。FOは膜を通して膜の両側に位置する液体の浸透圧の差を利用し、浸透圧の低い液体（フィード液 : FS）から高い液体（ドロー液 : DS）へ水を移動させるものである。FOの性能は膜の特性、FSやDSの組成、運転条件によっても影響を受ける。

まず、FOにおけるクロスフロー速度と栄養塩阻止率および水フラックスとの関係を把握するために、クロスフロー速度を0.17、0.25、0.34m/sに変化させて実験を行った。すべての速度条件下で、DSとして1Mの塩化マグネシウム（MgCl）を用い、膜として市販されているHTI社のHTI-NW膜を用いた。栄養塩阻止率はクロスフロー速度を中程度（0.25m/s）に設定した場合に最も高い値（それぞれ、NO_2-Nが68.80%、NO_3-Nが96.84%、NH_4-Nが99.33%、PO_4-Pが98.50%：FS側）が得られた。これは、高いクロスフロー速度は当然ながら高い流量、高い混合速度となり、DS側への栄養塩の移動を抑制し栄養塩の阻止率を向上させる結果となった。水温はクロスフロー速度に比べて栄養塩の阻止に影響しなかったが、水フラックスには影響した。25℃の水温の場合に良好な栄養塩の阻止率を示した。

次に、DSの濃度を4段階に変化させて上記4種類の栄養塩の阻止に関して実験を行った。実験は2種類の市販膜（HTI社製、HTI-NWとHTI-ES）を用

い、クロスフロー速度は0.25m/s、水温は25℃にて行った。実験結果からDSの$MgCl_2$濃度を2MとしてHTI-NW膜を用いた場合に、最も高い栄養塩除去率（それぞれ、NO_2-Nが60.71%、NO_3-Nが81.61%、NH_4-Nが99.58% 、PO_4-Pが83.46%：FS側）が得られた。逆に低いDS濃度（$MgCl_2$濃度0.5 M）でHTI-ES膜を用いた場合は低い栄養塩除去率（それぞれ、NO_2-Nが57.47%、NO_3-Nが83.68%、NH_4-Nが67.57% 、PO_4-Pが71.99%：FS側）であった。栄養塩除去性能は、HTI-ES膜に比較してHTI-NW膜の低いg逆流溶質フラックス（3.38〜5.26 g/m^2-hr）と比逆流溶質濃度（0.45〜0.55 g/L）によるものである。DSの$MgCl_2$濃度はHTI-ES膜に比較してHTI-NW膜の方が逆流溶質濃度に影響しなかった。HTI-NW膜内における逆流溶質濃度はDSの$MgCl_2$濃度（マグネシウムより塩素の拡散の方が高い）に影響されなかった。HTI-ES膜内では、逆流溶質（塩素）は逆流溶質（マグネシウム）のほぼ３倍であった。一方でHTI-NW膜の水の透過量（7.55–9.61 L/m^2-hr）はHTI-ES膜のそれ（13.58-15.10 L/m^2-hr）より低くなった。イオン性物質（栄養塩）のサイズや電荷等の特徴並びに膜の表面形状は、FOの性能に影響した。DS中の$MgCl_2$の解離イオンの濃度差がドナン効果によりFS中のイオン性の栄養塩の阻止に大きく貢献した。

最後に、本研究の結果から栄養塩の阻止における$MgCl_2$のDSとしての有効性が明らかとなった。膜のクリーニングにより栄養塩阻止に関する膜の性能は十分に回復し、そのことにより膜の長寿命化、低コスト化につながる。NaClや海水に比べると$MgCl_2$の価格は高いものの、$MgCl_2$の栄養塩阻止に関する高い性能を考えれば、十分考慮に値する。興味深いことに$MgCl_2$をDSとして用いた場合に、Mg^{2+}とCl^-の間の拡散係数の違いからCl^-がDSからFSへの拡散においてより優占的となった。一般的にFOのDSとして用いられるNaClや海水に比べると、Na^+とCl^-とは非常に似た高い拡散係数を持つものの、海水は複雑な種々のイオン性物質を含むが故に様々に異なる結果を示した。加えて、

$MgCl_2$をDSとして用いたFOにおける栄養塩の阻止には以下の課題が明らかとなった。１）逆流溶質による低濃度の$MgCl_2$を含有する濃縮されたFSの適正な処理方法が解決すべき課題であり、２）FOはあくまでも前処理であり（特に清浄な水を造る場合）、希釈されたDSからの$MgCl_2$の回収（それにより清浄な水を造る）が重要な課題である。

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TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 EFFECT OF OPERATING CONDITION ON FORWARD OSMOSIS

3.3 Material and method

3.4 Result and discussion

CHAPTER 4 EFFECTS OF MAGNESIUM CHLORIDE CONCENTRATION AND MEMBRANE MORPHOLOGIES ON NUTRIENT REJECTION, WATER FLUX AND REVERSE SOLUTE IN FORWARD OSMOSIS

4.2 Material and method

CHAPTER 5 THE FEASIBILITY AND FUTURE HANDLING OF MAGNESIUM CHLORIDE AS DRAW SOLUTION AND ITS COMPARISON WITH SODIUM CHLORIDE AND SEAWATER

CHAPTER 6 CONCLUSION AND FUTURE WORK

LIST OF FIGURES

LIST OF TABLES

Chapter 1

INTRODUCTION

1.1 GENERAL

Eutrophication refers to the enrichment of a water body by nutrients, which leads to excessive phytoplankton growth (Khan, 2005). Undesirable aquatic plant overgrowth and the resulting decomposing plant matter, cause the formation of a greenish slime that reduces light penetration and re-oxygenation. Moreover, a foul smell and turbidity are produced. The excess nutrients (nitrogen and phosphorus) from wastewater or sewerage treatment and other source can cause severe environmental problem such as eutrophication that lead to oxygen deficiency, algal blooms and fish kills (Ji et al., 2013). The U.S EPA makes the following recommendations for nutrients to control eutrophication: total phosphate (as phosphorus) should not exceed 0.05 mg/L in a stream at the point at which it enters a lake or reservoirs and should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs. The Japan environmental quality standards for conservation of the living environment decided for lakes class 1 total nitrogen and total phosphorus are should not exceed 0.1 mg/L and 0.005 mg/L, respectively. The secondary treated effluent of sewerage treatment plants usually do not reach nutrients at these levels. In consequence, they could still cause eutrophication because do not meet strict recommendation described above. The standards for effluents are commonly less strict than those for eutrophication control. This problem forces sewerage treatment plants to implement further treatment.

One of the promising technologies that can be used to solve the above mentioned problem is forward osmosis (FO). The forward osmosis uses the osmotic pressure difference ($\Delta\pi$) across the membrane, rather than the hydraulic pressure difference, as the driving force for transporting water through a semipermeable membrane (Cartinella et al., 2006). The forward osmosis is the transport of water across a selectively permeable membrane from low osmotic pressure in solution of higher water chemical potential to higher osmotic pressure in solution of lower water chemical potential (Achilli et al., 2009). In the FO process, solutions of higher and lower water chemical potential are named feed solution (FS) and draw solution (DS), respectively. The studies of application of FO in the scope of wastewater treatment have been slower in the last 10 years, because the FO step is still mostly perceived as a pre-treatment process (Lutchmiah et al., 2014). However, FO has the advantages of requiring low or no hydraulic pressure, which reduces the effect of fouling, thereby requiring less cleaning and less energy; a high osmotic pressure that produces a high water flux and recovery; and a high rejection that yields a high quality product (Zhao et al., 2012). The forward osmosis has the potential to sustainably treat wastewater and produce high quality water by focusing on membrane development, a DS and operating conditions (Lutchmiah et al., 2014). One key component for successful development of FO technologies is the selection of an optimal DS (Achilli et al., 2010).

The application of FO process to retain nutrient in FS side and separate permeate water to DS side, by understanding and optimizing mechanism and relation between operating condition, membrane condition and selected DS, will investigate in this study. The assessment of the separation or rejection performance also calculated the quantity of water flux and reverse solute. To know further feasibility of this research, the cleaning efficiency, cost evaluation and comparison of selected DS with other DS would considered to evaluate.

1.2 OBJECTIVES

The aim of this study is to investigate magnesium chloride performance as a DS in forward osmosis on separating nutrient from secondary treated effluent by understanding its mechanism. In order to accomplish it, the aims is divided into three objectives as follows:

a. To investigate the optimum cross flow velocity and temperature to use during FO treatments aimed at achieving high nutrient rejection and water flux.
b. To investigate the effect of DS magnesium chloride concentration and membrane morphologies on nutrient rejection, water flux production and reverse solute process in order to understand mechanism between nutrient and magnesium chloride in the FO process.
c. To investigate the further feasibility of application FO on nutrient rejection by analyzing the cleaning process, economic and comparison of magnesium chloride with sodium chloride and seawater.

1.3 STRUCTURE OF DISSERTATION

The structure of dissertation was divided into six chapter and listed as follow:

Chapter 1 states the background, objectives and structure of dissertation,

Chapter 2 reviews literature of the background knowledge and previous study,

Chapter 3 explain the effect of operating condition that consist of cross flow velocity and temperature on the FO process,

Chapter 4 relating with Chapter 3, the optimum condition was obtained that will use in investigating the potential of magnesium chloride and membrane morphologies on retaining nutrient in FS side, water flux permeation in DS side and reverse solute in the FO process. Moreover, the mechanism between nutrient and magnesium chloride were also indicated in this chapter,

Chapter 5 to know further feasibility of application FO on nutrient rejection by analyzing the cleaning process, cost and comparison of magnesium chloride with sodium chloride and seawater,

Chapter 6 summarizes the overall results of this study and suggest the idea for future study.

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Chapter 2

LITERATURE REVIEW

2.1 WASTE WATER TREATMENT PLANT

A wastewater treatment plant operate to treat waste from municipal, residential, institutional, commercial and industrial. According to United States Environmental Protection Agency (U.S. EPA), a municipal wastewater (sewage) treatment is defined as primary, secondary, or tertiary according to the extent of pollutant removal and the mechanisms (physical, biological, or chemical) through which pollutants are removed (**Figure 2.1**). In the wastewater treatment system, the removal of biochemical oxygen demand (BOD), suspended solids, nutrients (NO_3^{-}-N,NO_2^{-}-N,NH_4^{+}-N and PO_4^{3-}-P), coliform bacteria, and toxicity are the main goal for getting purified wastewater (Raouf, 2012).

Some of wastewater treatment plant completed with preliminary treatment that extracts coarse solids and grit through screens and other filtering devices. These coarse materials are not incorporated in biosolids. A primary treatment consists primarily of physical processes (settling or skimming) that reject a significant percentage of the organic and inorganic solids from wastewater. A primary wastewater treatment usually involves gravity sedimentation of screened wastewater to reject settled solids. A half of the solids suspended in wastewater are rejected through primary treatment. The residual material from this process is a concentrated suspension which called primary sludge, which will undergo further treatment to become biosolids. A secondary treatment depends on biological action to reject fine suspended solids, dispersed solids, and dissolved organics by volatilization, biodegradation, and incorporation into sludge. In addition, a secondary treatment satisfies much of the oxygen demand of the pollutants.

A tertiary (advanced) treatment uses a variety of biological, physical, and chemical treatment approaches to reduce nutrients, organics, and pathogens.

In wastewater treatment also produce sludge as by product. After digestion, the sludge is commonly dewatered using a centrifuge which produces concentrated biosolid and a liquid stream (i.e., centrate). A centrate contains high concentrations of nutrients (e.g., ammonia, *ortho*-phosphate, organic nitrogen). In some agricultural communities, a centrate is used as a soil fertilizer, however, the common practice for centrate treatment is to return it back, to the headworks of wastewater treatment facility for re-treatment. According to Cath et al. (2006), when these species are returned to the head of the treatment facility, they increase facility loading and operation cost, and it is suspected that some of these constituent are recalcitrant and end up in the effluent as nitrogen and phosphorus species. A wastewater treatment plant employs numerous physical, chemical, and biological methods to improve effluent water quality but nutrient removal requires advanced treatment (Carey and Migliaccio, 2009).

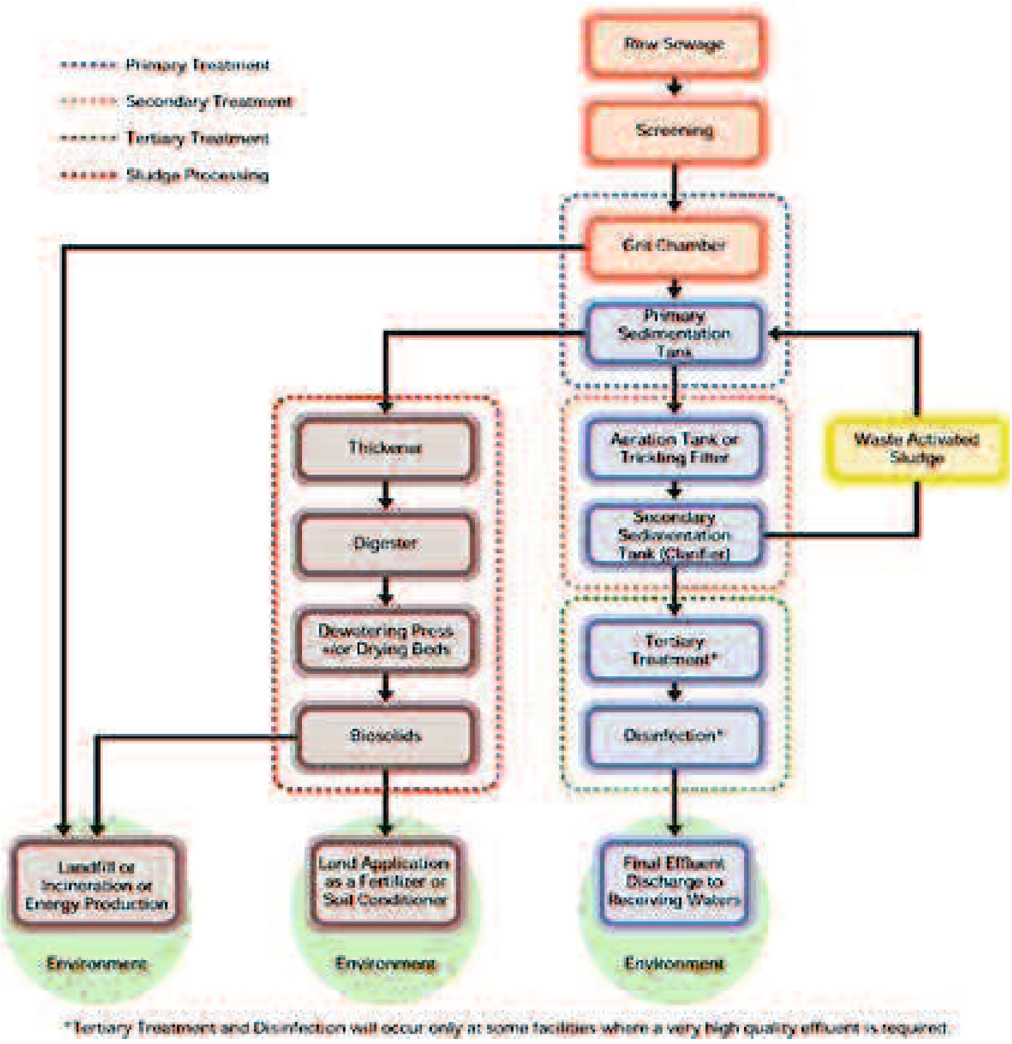


Figure 2.1 Flowchart of typical wastewater treatment (UNEP, 2015)

2.1.1 Secondary Treated Effluent

A secondary treatment is an effluent quality standard theoretically obtainable by wastewater treatment plant using both physical phase separation to reject settleable solid and a biochemical process to reject dissolved organic compounds, suspended organic compounds and nutrients. The effluent meeting this standard may be described as secondary-treated effluent. From an engineering perspective, a secondary treatment is the portion of a wastewater treatment sequence removing dissolved and colloidal compounds measured as biochemical oxygen demand (BOD). A secondary treatment is traditionally applied to the liquid portion of sewage after primary treatment has rejected settleable solids and floating material (**Figure 2.2**).

A secondary treatment systems is classified into three main categories: (a) stabilization ponds, (b) fixed-film such as trickling filter, rotating biological contactor and (c) suspended-growth systems such as activated sludge, sequential batch reactor and aerated lagoons (Naidoo and Olaniran, 2014).

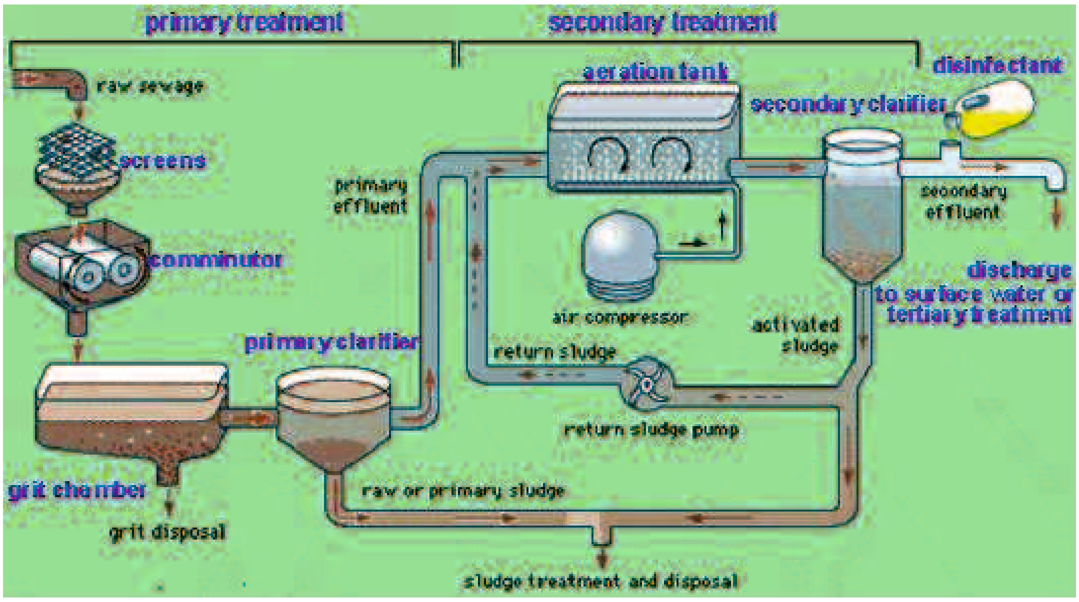


Figure 2.2 Schema of primary and secondary treatment (Bluepanet, 2015)

2.1.2 Nitrogen and Phosphorus

2.1.2.1 General

A wastewater may contain high levels of the nutrients: nitrogen and phosphorus. Excessive release to the environment can cause severe environmental problem such as eutrophication leading to algal blooms, oxygen deficiency, and fish kills (Ji, 2013). Eutrophication is a natural process, but can be greatly accelerated by human activities that increase the rate at which nutrients enter the water. Eutrophication refers to the enrichment of a water body by nutrients, which leads to excessive phytoplankton growth (Khan, 2005) such as weeds, algae and cyanobacteria (blue-green algae). A rapid growth in the population of algae, namely algal bloom, which the number unsustainable and eventually most of them die. Excessive amounts of algae grow into scum on the water surface, decreasing recreational value and clogging water-intake pipes. The decomposition of the algae by bacteria uses up so much of the oxygen in the water that most or all of the animals die, which creates more organic matter for the bacteria to decompose. The decomposition cause the formation of a greenish slime that reduces light penetration. In addition to causing de-oxygenation or oxygen deficiency, some algal species produce toxins that contaminate clean water supplies. Moreover, a foul smell and turbidity are produced. Dissolved oxygen concentrations drop too low for fish to breathe, leading to fish kills. According to Chambers et al. (2011), addition of bioavailable N and P to surface water can changes in abundance and diversity of aquatic invertebrates, fish and possibly birds and mammals dependent upon these habitats. In addition, elevated concentration of un-ionized ammonia, nitrate and nitrite may be toxic to humans and aquatic life.

Algae growth is limited by the available supply of phosphorus or nitrogen, so if excessive amounts of these nutrients are added to the water, algae and aquatic plants can grow in large quantities. In freshwater lakes and rivers, phosphorus is often the growth limiting nutrient, because it occurs in the least amount relative to the needs of plants. In estuaries and coastal waters, nitrogen is generally the growth limiting nutrient. The deep information about nitrogen and phosphorus will explained in the next sub-chapter.

Nutrient removal rates at wastewater treatment plant varied (**Table 2.1**) depending on several factors, including (1) treatment technologies used; (2) influent wastewater; (3) mechanical and operational failures; and (4) technical design limitation of facilities (Asano et al., 2007, Carey et al., 2009)

Table 2.1 Typical nutrient concentration ranges

Constituent (mg/L)	Untreated wastewater	Conventional activated sludge (include nitrification step)	Activated sludge with biological nutrient removal (tertiary treatment)	Activated sludge with biological nutrient removal (tertiary treatment), microfiltration and reverse osmosis (advanced treatment)
Total Nitrogen	20-70	15-35	3-8	≤ 1
NH_3-N	12-45	1-10	1-3	≤ 0.1
NO_3-N	0-trace	10-30	2-8	≤ 1
Total Phosphorus	4-12	4-10	1-2	≤ 0.5

Carey et al., 2009, Asano et al., 2007, Tchobanoglous et al., 2003

The advanced treatment such as reverse osmosis (RO) could be choice of treatment that have high efficiency to remove or reject nutrient. This study is investigating about forward osmosis (FO) that could be the alternative of nutrient rejection. A reverse osmosis, a commonly used desalination technology, is significantly more expensive than the standard treatment of freshwater for potable use. The new technologies such as FO seemly more competitive with freshwater treatment (McCutcheon et al., 2005).

2.1.2.2 Nitrogen

Mostly nitrogen can be removed from wastewater through biochemical processes (Carey et al., 2009) of nitrification (oxidation of NH_4-N and organic nitrogen to NO_3-N within an aerobic zone) and denitrification (reduction of NO_3-N to gaseous nitrogen in an anoxic environment). Several physical-chemical processes have been used in the past for nitrogen removal. Although under most circumstances biological treatment is the most attractive nitrogen control technology, physical and chemical processes may be technically and economically feasible in certain situations. The major processes that fall under category are breakpoint chlorination, selective ion exchange, and air stripping.

Selective ion exchange for removal of ammonia can be accomplished by passing the wastewater through a bed of ion-exchanger which exhibits a high selectively for the ammonium ion over other cations that are normally present in wastewater. Regeneration is required when all exchange is utilized and ammonium breakthrough occurs. Filtration prior to ion exchange is usually required to prevent fouling. Ammonium removal of 90 to 97 percent can be expected. Nitrite, nitrate, organic nitrogen are not affected by this process. Regeneration is accomplished by either sodium chloride, NaCl (neutral pH regeneration) or an alkaline reagent such as sodium or calcium hydroxide NaOH or $Ca(OH)_2$ (high pH regeneration). High pH regeneration is more efficient than neutral pH regeneration. However, high pH regeneration may cause precipitation of magnesium hydroxide and calcium carbonate within the ion exchange. The most feasible regenerant recovery process is air stripping with high pH regenerant.

2.1.2.3 Phosphorus

A wastewater is relatively rich in phosphorus compounds. Phosphorus is a nutrient used by organisms for growth. It occurs in natural water and wastewater bound to oxygen to form phosphates. Phosphates come from a variety of sources including agricultural fertilizers, fecal and waste material, domestic wastewater, detergents, household cleaning product, industrial process wastes and geological formations. The discharge of wastewater containing phosphorus may cause algae growth in quantities sufficient to cause taste and odor problems in drinking water supplies. Dead and decaying algae can cause oxygen depletion problems which in turn can kill fish and other aquatic organisms in streams. For this reason, phosphorus removal is an essential role of wastewater treatment plants and testing for phosphorus in the plant effluent is critical.

Phosphates are classified chemically as orthophosphates, polyphosphates and organic phosphates (on the basis of acid hydrolysis and digestion). According to physical characteristic, the type of phosphate are categorized into dissolved and particulate fractions (on the basis of filtration through a 0.45 micron membrane filter).

To remove phosphorus, it can use biological or chemical process. In this study, the phosphorus removal or rejection is based on chemical process. Therefore, it discuss more deeply about chemical phosphorus removal. Phosphate removal from wastewater involves the incorporation of phosphate into a particulate form (suspended solids, SS) and then the removal of the SS. The types of SS into which phosphate can be incorporated are either biological (micro-organisms) or chemical. The physical removal such as phosphorus sorption and desorption (Heal et al., 2004) and subsequent processing of these phosphate-containing solids should be accomplished without allowing significant release of phosphate into liquid streams that are recycled back to the wastewater stream (Sedlak, 1991).

Chemical precipitation of phosphate usually becomes necessary when the phosphorus discharge criteria are lower than those that can be achieved by primary sedimentation and secondary biological wastewater treatment. Very few instances of chemical precipitation without the involvement of biological processes exist. To achieve the standard effluent phosphorus concentration, processes additional to, or other than, conventional biological treatment must be employed.

Chemical phosphate removal commonly rely on the formation of sparingly soluble orthophosphates that can be rejected by solid separation processes. Phosphate precipitation can be classified according to their location in the process stream:

a. Pre-precipitation: addition chemical to raw wastewater and removal of the formed precipitates together with the primary sludge.

b. Simultaneous precipitation: addition chemical so that the formed precipitates are rejected together with the waste biological sludge. The point of addition are (i) primary effluent and activated sludge (ii) mixed liquor in aeration basin or following aeration but prior to secondary treatment.
c. Post precipitation: addition chemical at point after primary and secondary treatment. The formed precipitates are rejected by solid separation device: clarifier, filter.

Phosphate precipitation is achieved by the addition of the salts of the one of three metals that form soluble phosphate: Ca(II), Fe(III), Fe(II), Al(III). The salts: lime, alum, sodium aluminate, ferric chloride, ferric sulfate, ferrous sulfate, ferrous chloride, sometimes waste from steel industry contain ferrous iron in either a sulfuric or hydrochloric acid solution. Lime when used as a post precipitation process, pH adjustment is required following lime treatment to bring the effluent to within commonly stated discharge limit (pH 6 – 9) and for the prevention of scaling in downstream processes. This pH adjustment is usually achieved by re-carbonation followed by clarification to reject the $CaCO_3$ that forms in this process. Precipitation is the creation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid. When the reaction occurs in a liquid solution, the solid formed is called the 'precipitate'. The chemical that causes the solid to form is called the 'precipitant'.

2.1.3 STANDARD

The wastewater treatment aim to produce a clean effluent that can be safely discharged to water bodies. The U.S EPA makes the following recommendations for nutrients to control eutrophication: total phosphate (as phosphorus) should not exceed

0.05 mg/L in a stream at the point at which it enters a lake or reservoirs and should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs (Muller & Helsel, 1999 in Khan, 2005). The Japan environmental quality standards for conservation of the living environment decided for lakes class 1 total nitrogen and total phosphorus are should not exceed 0.1 mg/L and 0.005 mg/L, respectively. The secondary treated effluent of sewerage treatment plants usually do not reach nutrients at these levels. In consequence, they could still cause eutrophication because do not meet strict recommendation described above. The standards for effluents are commonly less strict than those for eutrophication control as shown in **Table 2.2**. This problem forces sewerage treatment plants to implement further treatment.

Table 2.2 Comparison standard of nutrient effluent

Nutrient	National Effluent Standard Japan	EPA : to control eutrophication	Environmental Quality Standard for conservation of the living environment
Nitrite (NO_2^-)	Ammonia, ammonium compounds, nitrate and nitrite compound : 100 mg/L (standard that related to the protection of human health)		
Nitrate (NO_3^-)			
Ammonia (NH_3)			
Total nitrogen (T-N)	120 mg/L or daily average 60 mg/L (standard that related to the protection of the living environment)		For lakes Class I $\leq$ 0.1 mg/L Class II $\leq$ 0.2 mg/L Class III $\leq$ 0.4 mg/L Class IV $\leq$ 0.6 mg/L Class V $\leq$ 1 mg/L
Phosphate (PO_4^-)	Organic phosphorus compound (parathion, methyl parathion, methyl demeton and EPN only) : 1 mg/ L		
Total phosphorus (T-P)	16 mg/L or daily average 8 mg/L (standard that related to the	< 0.05 mg/L (at the point at which it enters a lake or	For lakes Class I $\leq$ 0.005 mg/L

Nutrient	National Effluent Standard Japan	EPA : to control eutrophication	Environmental Quality Standard for conservation of the living environment
	protection of the living environment)	reservoir < 0.1 mg/L (in streams that do not discharge directly into lakes or reservoir)	Class II ≤ 0.01 mg/L Class III ≤ 0.03 mg/L Class IV ≤ 0.05 mg/L Class V ≤ 0.1 mg/L

2.2 DRAW SOLUTION

Draw solution (DS) is the concentrated solution on the permeate side of the membrane that has source of the driving force in the FO process (Cath et al., 2006). Different terms are used in the literature to name this solution including DS osmotic agent, osmotic media, driving solution, osmotic engine, sample solution, or just brine. When selecting DS, the criterion:

- DS has a higher osmotic pressure than the feed solution (FS), the diluted DS should be able to be easily and economically re-concentrated and/or recovered, low cost, and low reverse solute permeability (Cath et al., 2006)
- DS should exhibit minimized ICP in the FO processes, zero toxicity, no damaged to membrane, good bio-fouling resistance, inertness and stability at or near natural pH, and the solution diffusivity, ion/molecule size, and viscosity (physicochemical properties) of DS should be considered or characterized (Zhao et al., 2012)
- in typical environmental engineering applications, because of the complex ion matrix of the feed solution, DS that contain scale precursors are not recommended (Achilli et al, 2010)

The solutes for DS that have been used are shown in **Table 2.3**

Table 2.3 The DS used in FO and their recovery method since 2005

DS Type	Example	Advantages	Disadvantage
Inorganic substance	Salts	• High solubility • Low cost • High osmotic pressure	• Salt leakage may inhibit anaerobic digestion • Clogging/scaling/fouling • ICP • Recovery is not often feasibly
Highly soluble zwitter ionic substances	Glycine	• High flux, low leakage • Leakage beneficial to biology in subsequent energy-generating units	• Limited storage time due to biodegradation
High charge compounds	EDTA	• High water flux • Low reverse leakage • Re-concentration via less energy consuming processes, i.e. NF	• More expensive than common salts • pH dependency • Questionable environmental repercussions
Nutrient-rich substances	Fertilizer	• Direct fertilization • No recovery necessary	• Osmotic equilibrium limits • Dilution of nutrients
Readily available sources	Seawater, RO brine	Abundant source	• TEP fouling • Seawater: only cost-efficient if applied near coastal area
Thermo-lytic solutes	Ammonium bicarbonate	• High solubility in water • Recovery by moderate heat	• Toxic thermo-lytic product • High diffusive loss
Engineered DS	Magnetic nanoparticles	High osmotic pressures at low concentration • No leakage • Overcomes scaling • Crystallization issue in membrane distillation	• Agglomeration during magnetic separation • Ultra-sonication weakens magnetic properties • Viscosity of solution reduces effective driving forces and the flux

Lutchmiah et al., 2014

In this study, the DS use magnesium chloride ($MgCl_2$) with these following reasons:

a. $MgCl_2$ has highest osmotic pressure among of several solution for DS that were calculated using OLI Stream Analyzer 2.0, OLI system Inc. Morris Plains, NJ (Cath et al., 2006) and are presented in **Figure 2.3**

b. According to Achili et al. (2010), $MgCl_2$ may be the best DS for most water and wastewater application, so should be further investigated for environmental engineering application. The use of $MgCl_2$ in FO application is no risk of scaling.

c. The role of $MgCl_2$ in the FO process of wastewater treatment, especially for nutrient from secondary treated effluent and its rejection mechanism, has been rare investigated. Some previous experiments used $MgCl_2$ in FO process, for membrane test using $MgCl_2$ as DS and deionized (DI) water as FS (Yang et al., 2009; Saren et al., 2011; Qiu et al., 2011; Qiu et al., 2012).

d. According to Lay et al. (2010) and Lee et al. (2010) multivalent ions (e.g. Ca^{2+} and Mg^{2+}) solution with lower diffusion coefficients may be preferable in some specific applications in which high rejection is desired. The drawback of multivalent ions solutions are may interfere with the foulants in the feed solution after reverse diffusion which is likely to aggravate membrane fouling; may also introduce more severe ICP because of their larger ion sizes and lower solution diffusion coefficients.

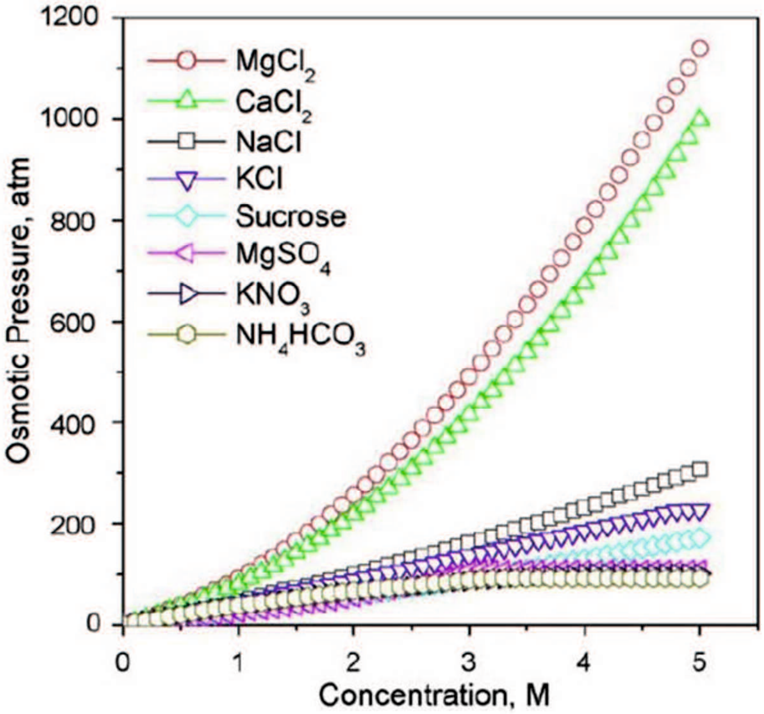


Figure 2.3 Osmotic pressure as a function of a solution concentration at 25°C for various potential DS (Cath et al., 2006; Zhao et al., 2012).

Magnesium chloride is the name for the chemical compound with the formula $MgCl_2$ and its various hydrates $MgCl_2(H_2O)_x$. These salts are typical ionic halides, being highly soluble in water. The hydrated magnesium chloride can be extracted from brine or sea water. The composition of the synthetic sea salt (Cath et al., 2009) was calculated from the data provided by the manufacturer and for example, is summarized in **Table 2.4.** Magnesium chloride, as the natural mineral bischofite, is also extracted (via solution mining) out of ancient sea-beds. Some magnesium chloride is made from solar evaporation of seawater.

Table 2.4 Magnesium chloride source from sea water.

Ion	Instant Ocean (@ 35 g/L TDS) (mg/L)
Chloride	19,290
Sodium	10,780
Sulfate	2,660
Magnesium	1,320
Pottasium	420
Calcium	400
Carbonate/bicarbonate	200
Bromide	56
Strontium	8.8
Boron	5.6
Fluriode	1

Cath et al., 2009

2.3 MEMBRANE

Different material are used for FO membranes. The widely-used membrane is cellulose triacetate (CTA). The new generation is thin film composite (TFC) membrane that reportedly superior than CTA (Klaysom et al., 2013) in term of permeability and stability at broader pH ranges. The difference of CTA and TFC membrane is showed in **Table 2.5**. Most FO membranes have an asymmetric structure with two different layer: an active layer (AL) and support layer (SL). The AL is generally the dense selectively layer, while the porous SL provides the mechanical support. In FO mode, the AL facing the FS.

Table 2.5 Comparison of CTA and TFC membrane

	CTA	TFC
Characteristic and Advantages	– the thickness of membrane is less than 50 µm with the thin layer in support layer (Cath et al., 2006) – Relatively high hydrophilicity – High water flux – Low fouling propensity – Good mechanical strength – Wide availability – Good resistance to degradation by chlorine and other oxidant (Zhao et al., 2012)	– Very thin overall thickness (~50µm) – Asymmetric – Made of CTA – Higher water flux than CTA – Consist three parts : a. A thin layer on one side b. A relatively support layer on other side c. An embedded mesh in the middle – Distinctively different from the conventional TFC membrane – Embedded polyester mesh rather than thick support layer (Zhao et al., 2012) – Good pH stability and resistance to hydrolysis and biological degradation (Lutchmiah et al., 2014, McCutcheon et al., 2008)
Disadvantages	– Poor resistance to hydrolysis and biological attach (Zhao et al., 2012)	

This study will use two kinds of commercial membrane from Hydration Technologies Inc. (HTI):

a. The cellulose triacetate non-woven (CTA-NW) membrane

According to Wei et al., 2011,

- Asymmetric CTA layers supported by a non-woven fabric
- The CTA layer ~60 µm in thickness, and non-woven fabric layer had a thickness ~80 µm.
- CTA–NW has slightly less porous

- The larger structural parameter (s value) is consistent with its lower porosity and larger overall thickness due to the presence of the non-woven fabric layer

b. Thin film composite membrane (TFC-ES) membrane

This type of membrane is thin film composite with embedded polyester screen support that can support wide range of pH 2-11. According to HTI, the water permeation is 18 L/m^2-hr for FO mode and 36 L/m^2-hr in unpressurized PRO mode.

Generally, any dense, non-porous, selectively permeable material can be used as a membrane for FO. The desired characteristics of membrane for FO would be high density of the AL for high solute rejection, a thin membrane with minimum porosity of the SL for low internal CP, and therefore, higher water flux, hydrophilicity for enhanced flux and reduced membrane fouling, and high mechanical strength to sustain hydraulic pressure when used for PRO (Cath et al., 2006). For wastewater treatment, the FO membrane need to address fouling propensity, fast transport of water towards the draw side, with ideally no migration of solutes between the FS and DS especially in closed-loop application. Other ideal characteristics are a dense, ultra-thin, active separating layer for high solute rejection, open, thin, hydrophilic SL with high mechanical stability, sustaining long-term operation and reducing ICP, high affinity for water (hydrophilicity) for enhanced flux and reduced fouling propensity (Lutchmiah et al, 2014).

2.4 FORWARD OSMOSIS

2.4.1 DEFINITION

Forward osmosis (FO) membrane technology research has grown remarkably in the last decade. FO is a membrane contactor process that uses osmotic pressure difference ($\Delta\pi$) across the membrane, rather than hydraulic pressure difference (as in reverse osmosis, RO) as the driving force for transport of water through a semipermeable membrane (Cartinella et al., 2006). FO, or simply osmosis, is the transport of water across a selectively permeable membrane from a solution of higher water chemical potential (low osmotic pressure) to a solution of lower water chemical potential (higher osmotic pressure) (Achilli et al., 2009). FO uses the chemical potential across the membrane, which is the osmotic pressure gradient, to induce a net flow of water through membrane into draw solution, DS (Yang et al., 2009).

Conventionally, osmosis is physical phenomenon that defined as the net movement of water across a selectively or semi-permeable membrane driven by a difference in osmotic pressure across the membrane. The term osmosis describes the natural diffusion of water through a semi-permeable membrane from a solution of a lower concentration to a solution with a higher concentration. Diffusion involves the movement of particles or molecules from an area of high concentration to an area of low concentration. FO uses a semi-permeable membrane to separate water from dissolved solutes effectively. A selectively or semi-permeable membrane allows passage of water, but rejects solute molecules or ions (Cath et al., 2006). The semi-permeable membrane acts as a barrier that allows small molecules such as water to pass through while blocking larger molecules like salts, sugars, starches, proteins, viruses, bacteria, and parasites.

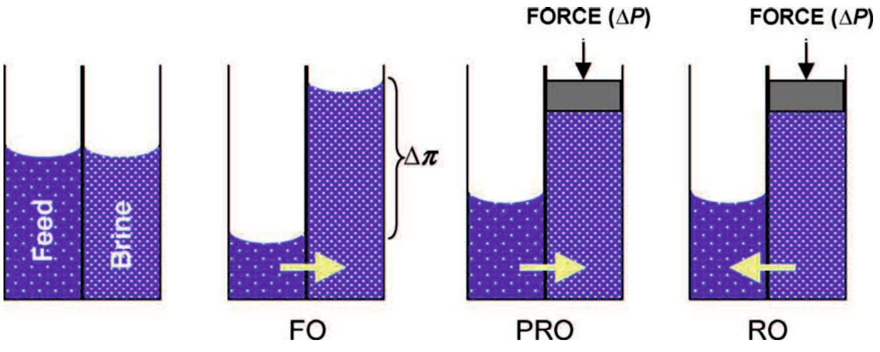
2.4.2 COMPARISON OF REVERSE OSMOSIS (RO), PRESSURE RETARDED OSMOSIS (PRO) AND FORWARD OSMOSIS (FO)

In the field of water treatment, Reverse Osmosis (RO) is more familiar than osmosis. The RO uses hydraulic pressure of an aqueous feed solution to produce purified water

(Sourirajan in Cath et al., 2006). Other treatment is Pressure Retarded Osmosis (PRO) that exploiting the osmotic pressure difference of two solutions by membrane based to generate power (Zhao et al., 2012). Osmotic pressure (π) is the pressure which if applied to the more concentrated solution, would prevent transport of water across the membrane. The simplest equation describing the relationship between osmotic and hydraulic pressures and water flux is:

$$Jw = A(\Delta\pi - \Delta P) \tag{2–1}$$

Where Jw is water flux, A is the hydraulic permeability of the membrane, $\Delta\pi$ is the difference in osmotic pressures on the two sides of the membrane, and ΔP is the difference in hydrostatic pressure (negative values of Jw indicating reverse osmotic flow). The flux directions of the permeating water in FO, PRO, and RO are illustrated in **Figure 2.4.** The advantages and drawback of FO summarized in **Table 2.6.**



$\Delta P=0$ $\Delta P < \Delta\pi$ $\Delta P > \Delta\pi$

ΔP = hydraulic pressure differential; $\Delta\pi$ = osmotic pressure differential

Figure 2.4 The permeate water flow in FO, PRO, and RO (Cath et al*.,* 2006)

The relation between the water flux and osmotic pressure difference is expressed by the following equation (2–2):

$$Jw = A.\sigma.\Delta\,\pi \tag{2–2}$$

where A is the water permeability coefficient (L/(m^2-hr bar)), σ is the reflection coefficient, and $\Delta\pi$ is the osmotic pressure difference (bar). More specifically, the relation between the osmotic pressure and concentration is explained by the Van't Hoff equation derived from the Morse equation. The osmotic pressure is linearly related to the concentration of the solution that is determined by equation (2–3):

$$\pi = iMRT = i\left(\frac{n}{V}\right)RT \tag{2–3}$$

where π is the osmotic pressure, i is the Van't Hoff factor, M is the molar concentration of solute particles, which is equal to the ratio of the number of solute moles (n) to the volume of the solution (V), R is the gas constant of 8.3145 J K^{-1} mol^{-1}, and T is the absolute temperature.

Table 2.6 The advantages and drawback of FO

Process	Advantages	Drawbacks
FO	low hydraulic pressure	requires special membrane
	low fouling	need to re-concentrated and replenish DS
	reduce cleaning	need periodically to clean membrane
	low energy	
	high osmotic pressure	
	high water flux and high recovery	
	high rejection	
	high quality product	

Holloway et al., 2006; Cath et al., 2006; Zhao et al., 2012

2.4.3 OPERATING CONDITION

In FO process, membrane, DS, and operating conditions should be optimized to increase the efficiency and to decrease concentration polarization (Lutchmiah et al., 2014) which will explain clearly in sub chapter 2.4.4.4. The operating condition of FO related with temperature, pH hydraulic operating condition and membrane orientation.

Temperature is an important factor relating mass transfer in FO process (Xie et al., 2013). In several practical application of FO, there can be significant temporal and spatial variation in the temperature of FS such as secondary treated effluent. Similarly, DS can be at higher temperature than the FS as a result of thermal separation and recycling of the DS or using higher temperatures to increase the solubility of the DS. Generally, water and salt permeability increased with increasing temperature in the FO process (Zhao et al., 2011, Xie et al., 2013). Water flux increased significantly by increasing DS temperature (Phuntsho et al., 2012).

The hydraulic operation related with velocity and or flow rate of FO process. Mass transport boundary layer theory was utilized to predict theoretical hydraulic flux at system operating condition (Anastasio and McCutcheon, 2013). The type or speed of the flow defined the boundary layer that called a momentum boundary layer. The boundary layer describes the actual region of interaction between a surface and a fluid. The momentum boundary layer defined by flow type is the region between a surface and the point where flow changes from laminar to turbulent. The momentum boundary layer can also be defined by water flow speed as the region above a surface which ranges from 0% to 99% of mainstream flow. Stated simply it is the region where flow slows down. In some cases the boundary layer may be more turbulent than laminar so the definition of a boundary layer in terms of velocity is preferred. There is another separate boundary layer which can be described in terms of the concentration of a particular substance which is called a *diffusion* boundary layer. The diffusion boundary layer is (arbitrarily) defined as the region above a surface which contains the change in the concentration of a particular substance. Organisms continually absorb and release substances from their surfaces into the water column so the concentration of a substance can either increase or decrease as you move away from the surface. Regardless of the definition used, the thickness of the momentum and diffusion boundary layers depends on the velocity water flow. In fast condition, turbulent flow there will be more mixing and the boundary layers will be thinner. In slow, laminar flow there will be less mixing.

The FS and DS in the FO system utilized tube to flow to the rectangular channel of membrane module. The applied velocity in selected diameter of circular tube can determine the flow rate by using equation as follows:

$$Q = A_{tube}.u_{tube} = \frac{1}{4}\pi d^2.u_{tube} \tag{2–4}$$

where Q is flow rate (m^3/s), A_{tube} is cross section area of the tube (m^2), u_{tube} is velocity in the tube (m/s) and d is diameter of the tube (m). The velocity in the rectangular channel membrane module is based on the flow rate and rectangular cross section area that expressed as below:

$$u_{rect} = \frac{Q}{A_{rect}} = \frac{Q}{b \times h} \tag{2–5}$$

where u_{rect} and A_{rect} are velocity (m/s) and cross section area of rectangular channel (m^2), respectively. The b is width of channel (m) and h is height of flow in rectangular channel (m).

On fundamental level, the mass transfer coefficient, k (m/s), is determined by evaluate Sherwood number, Sh.

$$k = \frac{D.S_h}{d_h} = \frac{D.S_h}{L} \tag{2–6}$$

where d_h is hydraulic diameter of the system (m), L is characteristic length of the channel (m) and D is molecular diffusivity constant (m^2/s).

In the rectangular channel, the hydraulic radius, R can be expressed as

$$R = \frac{A}{P} = \frac{b.h}{2(b+h)} \tag{2–7}$$

where A is flow area (m^2) and P is wetted perimeter (m). For rectangular channel, the hydraulic diameter, d_h can be calculated as (Papautsky et al., 1999):

$$d_h = 4\frac{A}{P} = 4\,\frac{b.h}{2(b+h)} = \frac{2.b.h}{(b+h)} \tag{2–8}$$

The Sherwood equation for the appropriate flow regime in a rectangular channel is defined below (McCutcheon et al., 2006, McCutcheon and Elimelech, 2006)

$$Sh = 1.85 \left(Re\, Sc\, \frac{d_h}{L}\right)^{0.33} \qquad \text{(laminar flow)} \qquad (2\text{–}9)$$

$$Sh = 0.04\, Re^{0.75} Sc^{0.33} \qquad \text{(turbulent flow)} \qquad (2\text{–}10)$$

Where Re is the Reynolds number and Sc is the Schmidt number. Schmidt number is expressed by

$$Sc = \frac{\mu}{\rho . D} \qquad (2\text{–}11)$$

Where μ is dynamic viscosity (mPa.s or kg/(m.s)) and ρ is density of fluid (kg/m^3). To characterize different flow regimes within similar fluid, such as laminar or turbulent flow can use Reynolds equation that shown below (Papautsky et al., 1999):

$$Re = \frac{u.d_h}{\nu} = \frac{\rho.u.d_h}{\mu} \qquad (2\text{–}12)$$

Where u is velocity of the object relative to the fluid (m/s), d_h is hydraulic diameter or can change with L the travelled length of the fluid (m) and ν is kinematic viscosity (m^2/s).

2.4.4 MECHANISM OF FORWARD OSMOSIS

2.4.4.1 FO performances: rejection, water flux and reverse solute

FO is engineered process utilizing natural osmosis pressure differences across membranes. In FO, both of side membrane operate at equal hydraulic pressure ($\triangle$P=0). The concentration of FS and highly concentrated solution DS provide the driving force for separation of the process. When two solution with high and low osmotic pressure that separated by membrane, water will spontaneously diffuses from FS to DS to equilibrate the chemical potential of water on both sides membrane.

The percentage of rejection, R, is calculated from the final concentration of the nutrients in the diluted DS and the initial concentration of the nutrients in the FS before the FO cross flow process (McCutcheon et al., 2005; McCutcheon et al., 2006; Holloway et al., 2007; Yang et al.; 2009; Yip et al., 2010; Tiraferri et al., 2011; Wei et al., 2011; Xie et al., 2012a). The equation is:

$$R = 100\left(1 - \frac{C_P}{C_F}\right) \tag{2–13}$$

where C_P and C_F are final nutrients concentration in diluted DS after the FO process and the initial nutrients concentration in the FS before the FO process, respectively. The equation (2–13) is showing nutrient rejection/retention excluded the dilution of draw solution.

The next derivation of rejection equation was considered the permeate water, A (m/s.Pa), solute permeability, B (m/s), hydraulic pressure difference, △P (Pa) and osmotic pressure difference △π (Pa), that have been used in some previous researches (Zou et al., 2011, Jin et al., 2011, Saren et al., 2011, Jin et al., 2012, Han et al., 2012), as shown in equation (2–14):

$$R = \frac{1}{1+\frac{B}{A(\Delta P-\Delta\pi)}} \tag{2–14}$$

According to Jin et al. (2011), Jin et al. (2012), Xue et al. (2015), the rejection equation could be derived from equation (2–13) as follows

$$C_p = \frac{J_P}{J_w} \tag{2–15}$$

Where Jp is solute flux. Substituting equation (2–15) for C_p in Equation (2–13) gives an expression

$$R = 1 - \frac{J_P}{J_w C_F} \tag{2–16}$$

The Jp was defined as

$$J_p = \frac{B}{1+\frac{B}{J_w}} . C_F \tag{2–17}$$

Substituting equation (2–17) for Jp in equation (2–16) yields an expression for the rejection

$$R = 1 - \frac{B}{\left(1+\frac{B}{J_w}\right)} \cdot \frac{\cancel{C_F}}{J_w \cancel{C_F}}$$

$$R = 1 - \frac{B}{(J_w+B)} \qquad (2\text{–}18)$$

Other derivation of rejection equation is considering the dilution factor, D_F as shown in equation (2–19). A D_F value is introduced to calculate target solute such as nutrients in permeate sample. The equation (2–13) would be completing as (Xie et al., 2013):

$$D_F = \frac{V_{DS\,final}}{V_P} \qquad (2\text{–}19)$$

$$R = \left(1 - \frac{D_F \times C_P}{C_F}\right) \times 100 \qquad (2\text{–}20)$$

Where $V_{DS\ \mathrm{final}}$ is the final volume of the DS and V_P is the volume of permeate.

The permeate concentration of target solute such as nutrients in the FO process is diluted by the DS. Therefore, the apparent concentration of target solute in the DS overestimates the actual rejection performance. Hence, the actual (corrected) concentration of target solute, $C_{s(t)}$ can be obtained by taking into the dilution using a mass balance (Xie et al., 2012a, Xie et al., 2012b):

$$C_{s(t)} = \frac{C_{DS(t)}V_{DS(t)} - C_{DS(t-1)}V_{DS(t-1)}}{V_{w(t)}} \qquad (2\text{–}21)$$

where $C_{DS(t)}$ is the measured concentration of target solute in the DS at time (t), $C_{DS(t-1)}$ is the measured concentration of target solute in the DS at time (t-1), $V_{DS(t)}$is the volume of DS at time (t), $V_{DS(t-1)}$ is the volume of DS at time (t-1) and $V_{w(t)}$ is permeate volume of water to the DS at time t. The solute rejection as shown in equation (2–13) is calculated using the actual permeate concentration, yielding:

$$R = 100\left(1 - \frac{C_{S(t)}}{C_{F(t)}}\right) \qquad (2\text{–}22)$$

where $C_{F(t)}$ is the concentration of target solute in the FS at t time.

The transport of solute through membrane can pose substantial limitation to implementation FO process solute in both side. The bi-directional diffusion of solute must be considered. The rate of reverse diffusion of specific ions across the membrane should be considered. Forward diffusion occurs when solutes move from the FS (wastewater) into the DS, while reverse diffusion (solute leakage) occurs from the DS into the FS (Cath et al, 2009). The reverse solute flux was affected by concentration difference between FS and DS. This phenomenon can be described by Fick's Law in equation (2–23) (Achilli et al., 2010):

$$Js = B\Delta C \tag{2–23}$$

where Js is the reverse solute flux (g/m^2-hr), B is the solute permeability coefficient (L/m^2-hr) and $\triangle$C is the concentration difference across the membrane (g/L).

The structure of the membrane support layer and the diffusion constant play a significant role in determining the internal concentration polarization (McCutcheon et al., 2006). The equation (2–24) describes the solute resistance to diffusion within the membrane support layer, K:

$$K = \frac{t\tau}{\varepsilon D} \tag{2–24}$$

where t, τ, and $\boldsymbol{\varepsilon}$ are thickness, tortuosity, and porosity of the support layer of the membrane, respectively, and D is the bulk diffusion constant. The higher is the resistance of the solute to diffusion within the membrane support layer, lower is the reverse solute flux.

According to Cath et al. (2009), the key mechanism for rejection in depth are electrostatic repulsion, size exclusion, adsorption, steric hindrance. In FO still unknown and required additional research for mechanism. The rejection is affected by membrane characteristic (porosity, surface charge, hydrophobicity), rejected particle characteristic (size, charge, molecular weight), hydraulic operating condition and feed water matrix. The small, neutral, hydrophilic compound are poorly rejected, whereas the large, charged, hydrophobic compound are better to rejected.Water flux is influenced by DS solution (concentration, viscosity, diffusivity, etc.), temperature, and membrane characteristic (porosity, tortuosity, thickness).

2.4.4.2 Donnan potential

The Gibbs–Donnan effect, also known as the Donnan's effect, Donnan law, Donnan equilibrium, or Gibbs–Donnan equilibrium, is a name for the behavior of charged particles near a semi-permeable membrane that sometimes fail to distribute evenly across the two sides of the membrane. The usual cause is the presence of a different charged substance that is unable to pass through the membrane and thus creates an uneven electrical charge. Some ionic species can pass through the barrier while others cannot (**Figure 2.5**). The solutions may be gels or colloids as well as solutions of electrolytes, and as such the phase boundary between gels, or a gel and a liquid, can also act as a selective barrier. The electric potential arising between two such solutions is called the Donnan potential.

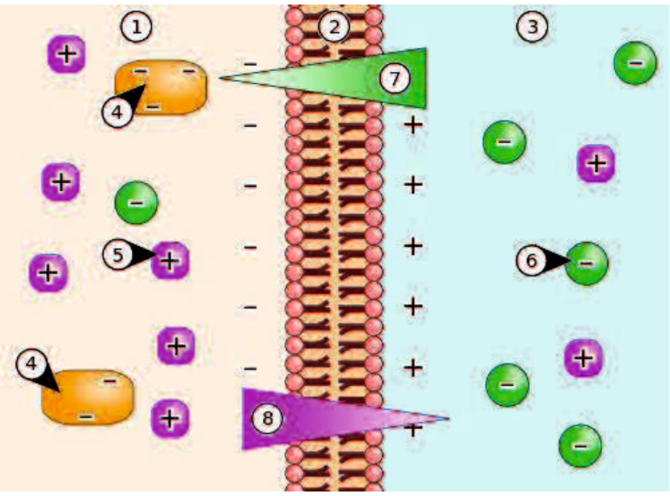


Figure 2.5 Donnan potential
(http://commons.wikimedia.org/wiki/File%3AGibbs-donnan-2.svg)

A potential difference is generally established between two electrolyte solutions at different concentrations separated by semi-permeable membrane. This potential difference called the membrane potential. As is well known, in the stationery state the membrane potential arises both from the diffusion potential and from the membrane boundary potential. The total membrane potential is described as total of Donnan potential differences on the membrane-solution interface and the diffusion potential difference in the membrane (Higa et al., 1998a). The Donnan potential that depend on the membrane charge density affect membrane selectivity with related to the valence of ion whereas diffusion potential depend on the ionic mobility in the membrane and affect the transport of ion in the membrane. The transport of ion against its own concentration gradient driven by the third driving electrolyte added to the system is called counter-transport of ions. Higa et al., 1998b in their study concluded that the counter-transport of ions has three mode (1) the counter-transport opposite to the overall driving potential gradient due to the Donnan potential (2) the counter-transport along the potential gradient due to diffusion potential generated by the diffusion of the driving electrolyte (3) the alternation of the direction of the counter-transport.

2.4.4.3 Diffusion constant

The fluid in different concentration has a viscosity value that is considered to the diffusion constant calculation. The diffusion constant can be expressed as

$$D = \frac{K_B\ T}{6\pi\eta r} \tag{2–25}$$

where D is the diffusion constant, K_B is the Boltzmann constant (1.381 x 10^{-23} m^2kg/s^2K), T is the absolute temperature, η is the viscosity, and r represents the radius of spherical particles.

2.4.4.4 Concentration polarization

In osmotic driven membrane processes, concentration polarization (CP) is caused by the concentration difference between the feed solution and the DS trough an asymmetric FO membrane (Zhao et al., 2012). CP is unique problem in the FO processes, arises as the water flux in FO has an opposite direction to the solute flux (Wei et al., 2011). Two types of concentration polarization:

1. External concentration polarization (ECP) :
    a. Concentrative ECP : membrane support layer (SL) is facing the DS
    b. Dilutive ECP : membrane SL is facing the FS

    The ECP reduces the net driving force due to increased osmotic pressure at the membrane active layer (AL) interface on the feed side of the membrane and decreased osmotic pressure at the membrane AL surface on the DS side.
2. Internal concentration polarization (ICP) :
    a. Concentrative ICP : membrane AL is facing the DS, where the solutes from the feed solution accumulate in the porous SL as a result of their rejection by the active rejection layer
    b. Dilutive ICP : membrane AL is facing the feed, caused by the dilution of the DS inside the SL

    The ICP can contributed by the solutes the diffuse from the high concentration DS to the low concentration feed for a low rejection membrane.

In this study, the FS is facing the AL of membrane. The possibility of CP are concentrative ECP and dilutive ICP as seen in **Figure 2.6**

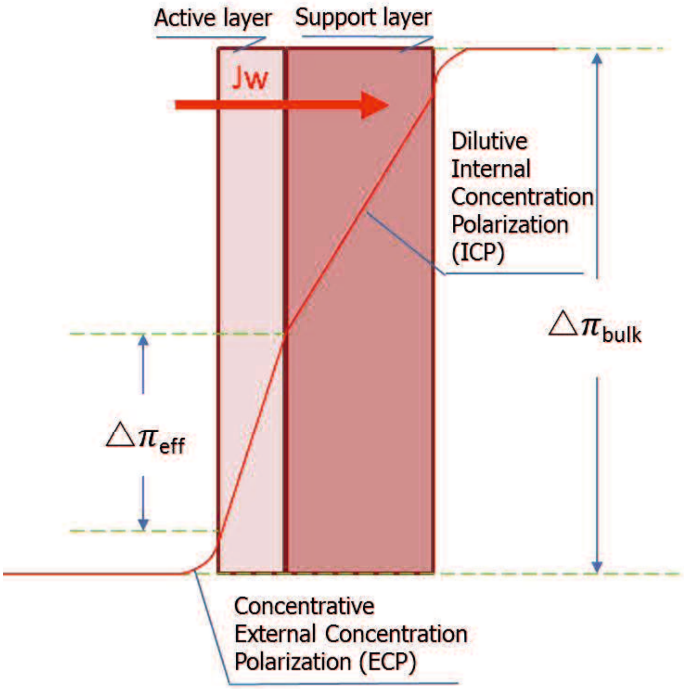


Figure 2.6 Illustration of CP when FS facing AL membrane (Cath et al., 2009)

2.4.4.5 Cleaning

Due the high rejection of FO membrane, a large amount of salt solute is retained in the feed water, which causes the increase in salt concentration, particularly at the membrane surface. When the solute concentration exceeds its solubility limits in the water, the excess solute precipitates on the membrane surface, forming scales and causing membrane pore blocking. Hence, it is necessary to minimize the formation of foulants and prevent solute precipitation on membrane surface, and develop effective methods for membrane cleaning to achieve high and sustainable membrane performance.

In membrane use, one of problem is irreversible fouling that occurs during long-term filtration process such as wastewater treatment. To achieving sustainable operation of FO, cleaning is need to develop (Wang et al., 2015). Chemical cleaning agents, acid or alkaline, such as sodium ethylenediaminetetraacetic acid or EDTA, alconox, NaOCl, NaOH, HCl, citric acid, sodium dodecyl sulfate or SDS, have been applied for cleaning membrane CTA and TFC (Wang et al., 2015, Valladares et al., 2013, Yoon et al., 2013). The detrimental to the integrity of membrane and irreversible fouling still need a solution in cleaning research. The mixed chemical cleaning reagents would enhanced the cleaning efficiency (Wang et al., 2015).

The physical cleaning usually less effective than chemical cleaning (Yoon et al., 2013). Some studies reported increasing the hydraulic condition without chemical cleaning agent could easily cleaned the fouled FO membrane (Mi and Elimelech, 2010, Lee et al., 2010).The fouling layer formed in FO mode is less compact due to the lack of hydraulic pressure. Membrane materials also play an important role in controlling membrane fouling and cleaning behavior in FO (Mi and Elimelech, 2010).

2.5 ECONOMIC FEASIBILITY

FO is an emerging water purification technology that could be used to reject biological, inorganic, and organic contaminant (Cath et al., 2006). In his study, Butler (2012) evaluate the point of use water treatment with FO for emergency and population migration relief that have six aspect should be considered: (1) system operation and maintenance (2) technology for contaminant deactivation (3) total lifecycle cost of materials, distribution, training and follow up (4) material availability (5) flexible production capacity (6) community-technology interaction. According to Butler (2012), in term of lifecycle cost, for cost model the draw solution and membrane module are the two primary material costs. These costs are related to the total cost per volume of drink produced (C_{total}):

$$C_{total} = \left(\frac{C_m}{L_m}\right)\left(\frac{1}{Q}\right) + \left(\frac{C_b}{V_b}\right)\left(\frac{1}{D}\right) \qquad (2–26)$$

Where C_m is the cost of the membrane module, L_m is the lifetime of the membrane module, Q is the drink product flow rate, C_b is the cost of the draw solution per bag of draw solution, V_b is the volume of draw solution per bag of draw solution, D is the dilution factor, which is equivalent to the total volume of product produced divided by the volume of draw solution used to produce that product, and $\frac{C_m}{L_m}$ and $\frac{C_b}{V_b}$ are considered the membrane and draw solution cost constants, respectively. Since product flow rate and dilution factor are related inversely, there must be a cost minimal operating condition according the equation (2–26). This equation do not consider cleaning reagent and pretreatment system cost.

In wastewater treatment terms, generally there are two types of costs to build facilities: capital cost and operation and maintenance (O&M) cost. The capital cost consist of material and construction cost, while O&M calculated from chemical, energy, personnel, maintenance, disposal and others. Cleaning and recovery could reduce the cost of O&M. The high cost of capital and O&M should be compensate with damage environmental cost. For example, in England and Wales, damage cost of freshwater due to eutrophication reached \$ 105 – 160 million/year. In Seto inland Japan, the maximum fishery damage was 7.1 billion yen (about US \$60 million).

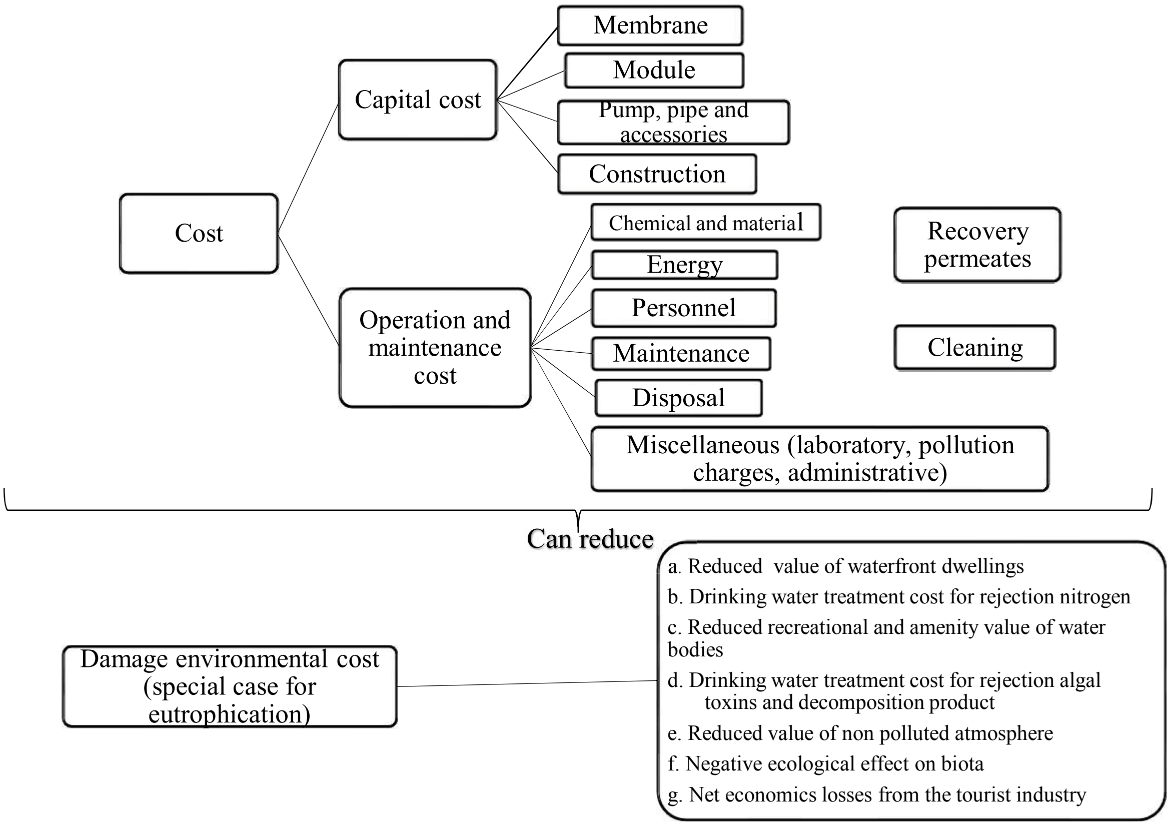


Figure 2.7 Schema of forward osmosis cost for prevent environmental damage

The damage environmental cost especially for eutrophication case can reduce value of waterfront dwellings, increase drinking water treatment cost for rejection nitrogen, reduce recreational and amenity value of water bodies, increase drinking water treatment cost for rejection algal toxins and decomposition product, reduce value of non-polluted atmosphere, cause negative ecological effect on biota and net economics losses from the tourist industry. The FO technology hopefully can reduce the damage environmental cost related to rejection nitrogen and phosphorus.

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CHAPTER 3

EFFECT OF OPERATING CONDITIONS ON FORWARD OSMOSIS

3.1 INTRODUCTION

FO is kind of physic-chemical process using membrane and chemical potential to treat water. The performance of FO is affected by the membrane characteristics, composition of the FS and DS, and operating conditions. Hence, these factors should be optimized to increase the efficiency of the process and decrease concentration polarization or CP (Lutchmiah et al., 2014). The CP is caused by the concentration difference between the FS and DS troughs across an FO membrane (Zhao et al., 2012). The CP arises as the water flux in FO has an opposite direction to the reverse solute flux (Wei et al., 2011). Since the effect of the membrane, DS, and operating conditions on the FO efficiency are closely related to each other, all these factors must be investigated.

The lower FS cross flow velocities in FO may generate higher concentrative ECP (Loeb et al., 1997, McCutcheon et al., 2006). A low velocity of cross flow will minimize reverse solute transport from DS to FS, but it may also reduce water flux by increasing the external CP and creating conditions conducive to membrane fouling. The ECP affected by both FS and DS flow, resulting in maximum water flux at higher and equal flow velocities on both side of the membrane (Hancock and Catch, 2009). However other studies have shown that different flows in FO did not change the water flux (Qin et al., 2010, Tan and Ng, 2008).

Membrane module configuration is the packing of a membrane into a module to maximize the surface to volume area and reduce particle deposition by sufficient cross-flow (Degremont, 2011 in Lutchmiah et al. 2014). The simplest device for packing flat sheet membranes is a plate-and frame module. The advantages of plate and frame module are can be constructed in different sizes and shapes ranging from lab-scale devices to full scale system (Cath et al., 2006), well-suited to wastewater applications, less complicated in design, better backwashing and higher cross flow velocities (Lutchmiah et al., 2014). The limitation of plate and frame module are limited operation to low hydraulic pressure and /or operation at similar pressures on both sides of the membrane (requiring relatively high process control), low packing density lead to a larger system footprint, higher capital costs, and higher operating cost (labor for membrane replacement), problem with internal and external sealing, difficulty in monitoring membrane integrity and limited range of operating condition such as flow velocities and pressure (Cath et al., 2005)

In the FO process, increasing temperatures will increase the water flux because of the increase of DS osmotic pressure and the decrease in wastewater viscosity (McCutcheon and Elimelech, 2006). Hence, the reverse solute increase due to increase in solute diffusion constant through the membrane and lower ICP. In wastewater application using FO, an increase in temperature will concentrate the wastewater faster, but this may lead to greater fouling of the membrane (Lutchmiah et al., 2014). Thus, the optimal temperature for concentrate of nutrients needs to be investigated.

Based on the aforementioned reasons, this study aims in this chapter is to investigate the optimum velocity and temperature that compatible with module membrane design for the further experiments.

3.2 DESIGN OF MEMBRANE MODULE

To obtain the purpose in this study, membrane module was designed with considering the compatibility and the thickness of structure material, the easiness for replace the membrane and minimization of leaching. **Figure 3.1** showed the design of module of membrane.

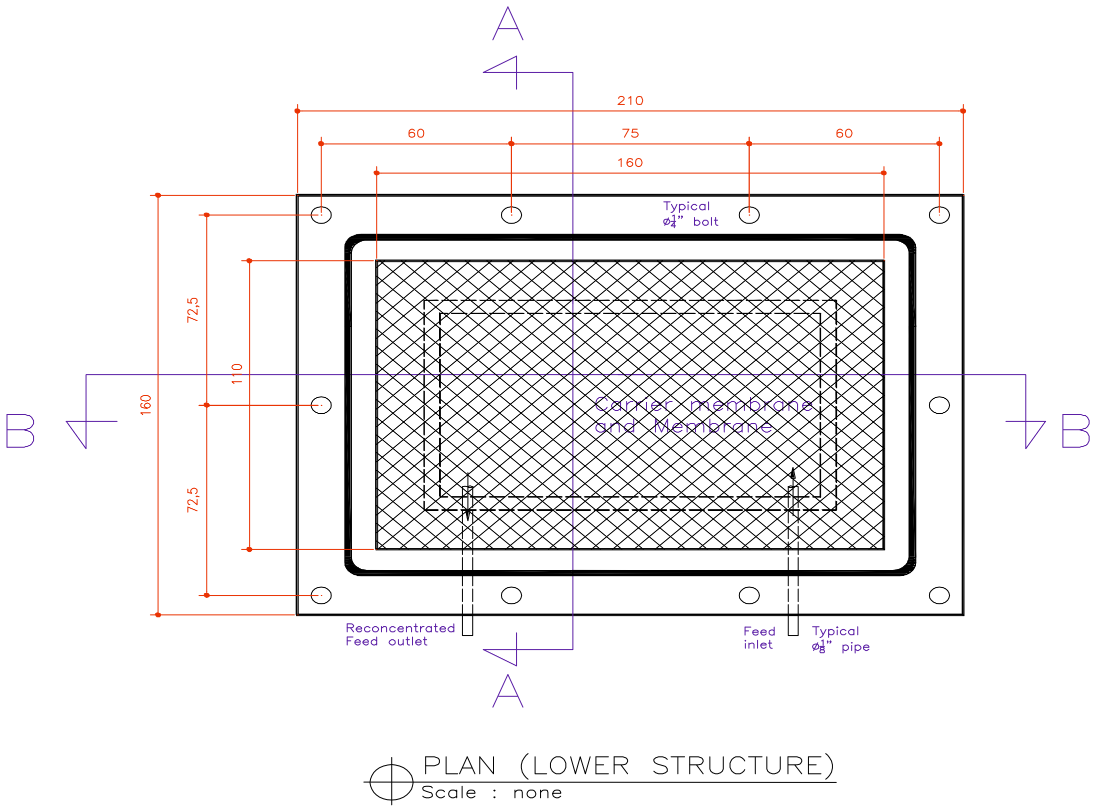

Figure 3.1 The lower part of module membrane

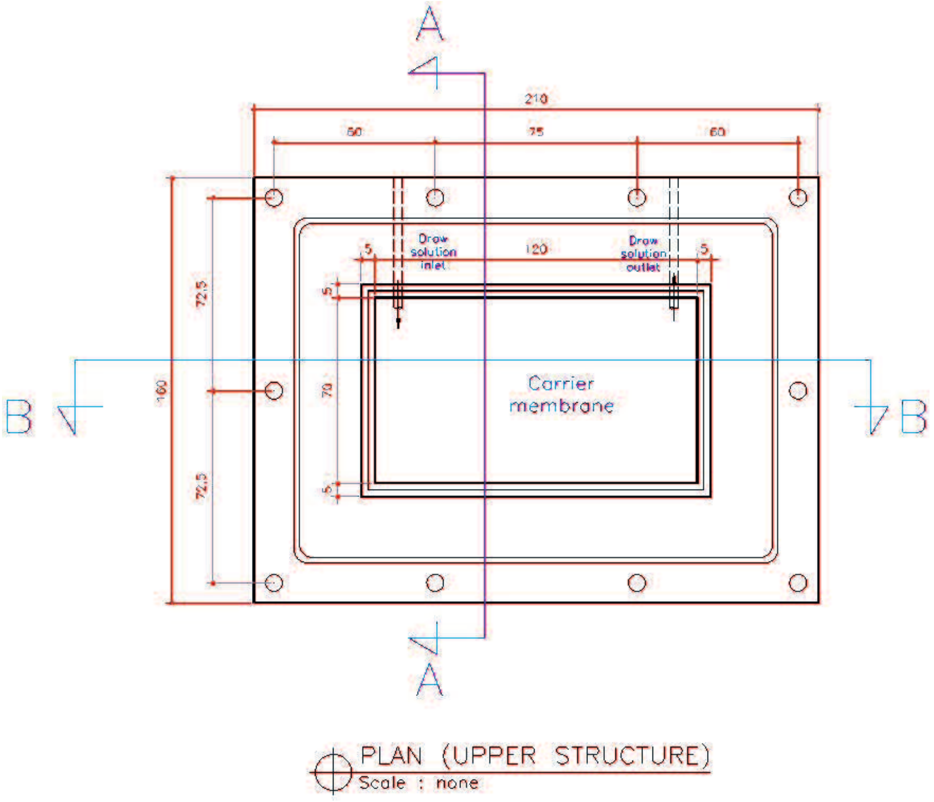

Figure 3.2 The upper part of membrane module

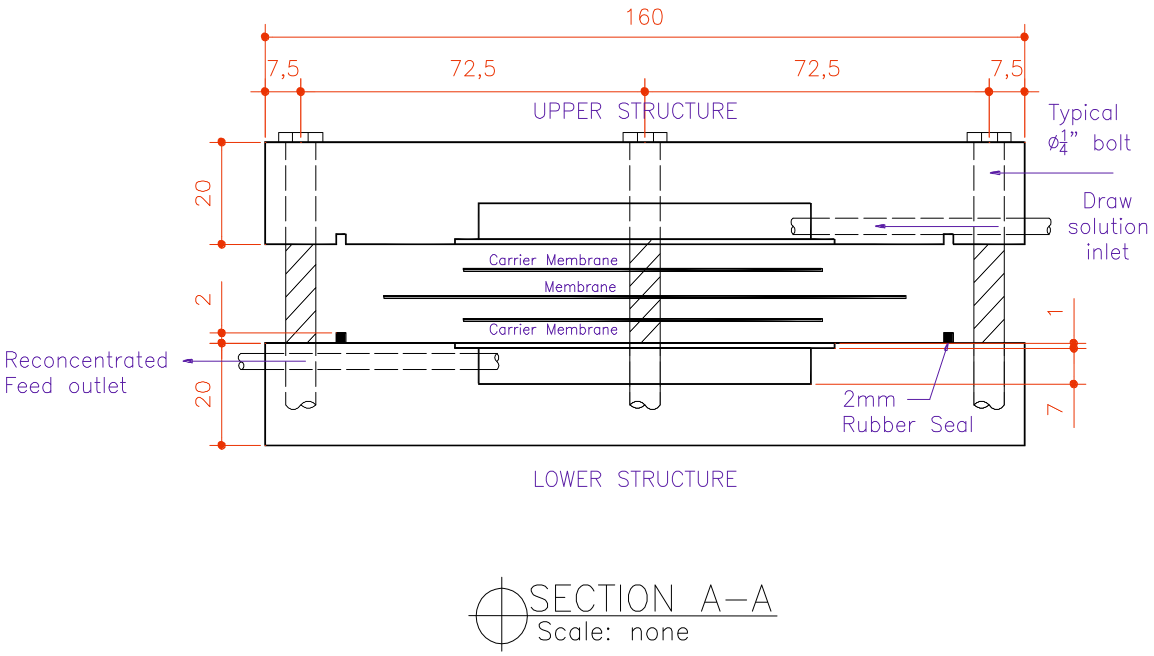

Figure 3.3 Width cross section of membrane module

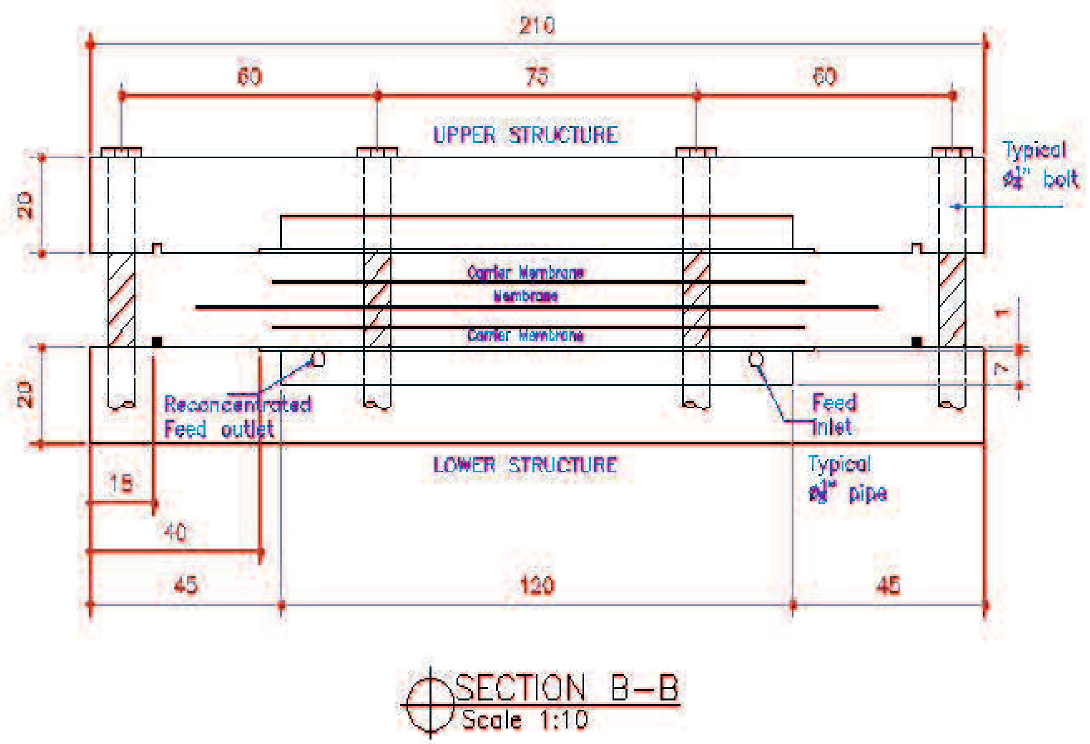

Figure 3.4 Length cross section of membrane module

3.3 MATERIAL AND METHOD

3.3.1. Feed and draw solutions

An actual sample of secondary treated effluent from the Eastern Municipal Wastewater Treatment Plant in Ube City, Yamaguchi, Japan was collected for analyses. The concentration, i.e., nitrogen content (nitrite, nitrate, and ammonium) and phosphorus (phosphate) content, was measured as shown in **Table 3.1.** This research did not consider about organic content from secondary wastewater treatment.

Table 3.1. Concentration of nutrients in an actual secondary treated effluent sample

Nutrient	Concentration (mg/L)
Nitrogen	
Nitrite (NO_2-N)	0.1
Nitrate (NO_3-N)	11.4

Nutrient	Concentration (mg/L)
Ammonium (NH_4-N)	3.4
Phosphorus	
Phosphate (PO_4-P)	2.7

An artificial secondary treated effluent was prepared for use as the FS; this solution contained the same concentrations of nutrients that were determined for the actual secondary treated effluent. The sources of nitrite, nitrate, ammonium, and phosphate were sodium nitrite ($NaNO_2$) 0.03 mM, potassium nitrate (KNO_3) 2.8 mM, ammonium chloride (NH_4Cl) 0.85 mM, and potassium hydrogen phosphate (KH_2PO_4) 0.3 mM, respectively. The chemicals added for nitrite, nitrate, ammonium, and phosphate were sodium nitrite ($NaNO_2$) at 0.03 mM, potassium nitrate (KNO_3) at 2.8 mM, ammonium chloride (NH_4Cl) at 0.85 mM, and potassium hydrogen phosphate (KH_2PO_4) at 0.3 mM, respectively. For the DS, magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) was mixed with deionized (DI) water (SA 2100E Eyela Japan) to achieve a final concentration of 1 M.

3.3.2. Membranes

In this chapter, commercial non-woven flat sheet membranes from Hydration Technologies Inc. (HTI) were used in the experiments. The membrane chemistry is proprietary, though it is believed to consist of asymmetric cellulose triacetate (CTA) with a non-woven (NW) support layer. The contact angle for the HTI-NW membranes is 64° (Qiu et al., 2011) and they are stable at a pH range of 3–8 (Lutchmiah et al., 2014). The other HTI membrane that also used in this study which is TFC with embedded polyester screen support (HTI-ES) could not afford the high cross flow velocity (0.34 m/s) due to its low thickness. The deep discussion will focus on membrane HTI-NW.

3.3.3 Forward osmosis cross flow set-up

The membrane was installed in a membrane module consisting of two rectangular sides with the dimensions 135 mm long, 90 mm wide, and 4 mm deep and an effective membrane area of 0.012 m^2 that permitted the FS and DS to flow to the membrane. In FO application mode, the active and support layers of the membrane were facing the FS and DS, respectively (Cath et al., 2006). Two peristaltic pumps equipped with a speed controller (Eyela, RP-2100) were used to recirculate the FS and DS. Three cross flow velocities of 0.17 m/s, 0.25 m/s and 0.34 m/s were applied. The water that permeated through the membrane into the DS was allowed to overflow into a beaker that was placed on a balance meter (PJ3000 Mettler-Toledo USA). The change of weight on the balance was recorded to calculate the water flux through the membrane. A 3.5 L flask was used to contain the artificial FS and a 1 L flask for the DS. The complete experimental apparatus that was constructed for measuring the FO cross flow is showed in **Figure 3.5.** The time for conducting a single cross flow experiment was 8 hours (Achilli et al., 2009, Holloway et al., 2007). The temperature tested included 20°C, 25°C, and 30°C. A water bath and magnetic stirrer were used to maintain the temperature. The temperature and pH were monitored intermittently with a pH-meter/thermometer (Horiba D-13). At the end of the cross-flow process, permeates were collected, and analyzed for nitrogen (NO_2 -N, NO_3 -N, and NH_4 -N), and phosphorus (PO_4 -P). Nutrient rejection was calculated by subtracting the initial concentration from the final concentration.

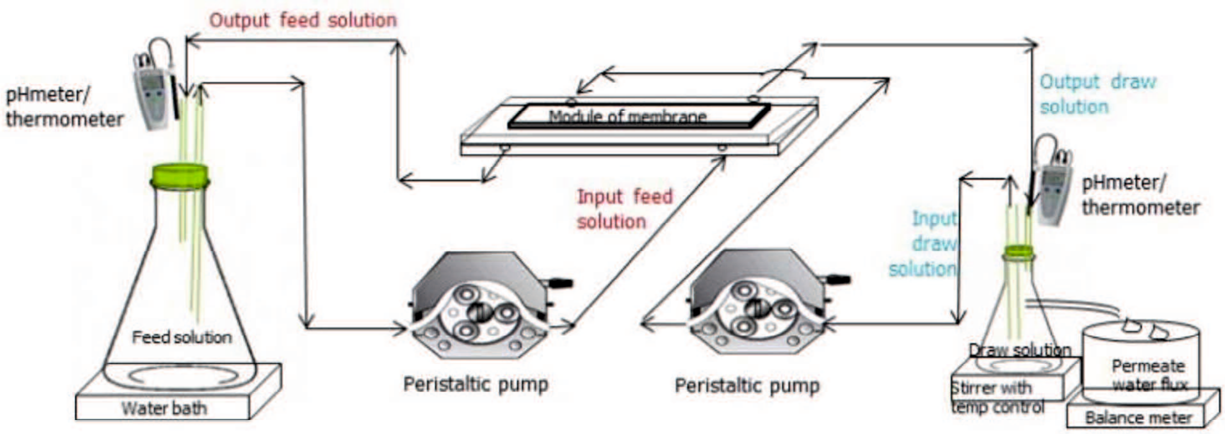

Figure 3.5 Forward osmosis experimental apparatus

3.3.4 Cross flow velocity determination

In previous studies, FO cross flow velocity or flow rate and effective membrane area were varied. Holloway et al. (2007) used 1.5 L/min and 139 cm^2, while Xue et al. (2015) used 8.3 cm/s and 60 cm^2. This experiment used a circular tube diameter of 7.94 mm, an effective membrane area of 120 cm^2, and various flow rate were achieved by adjusting the speed of peristaltic pump. Refer to equation (2-4), the applied cross flow velocities in a selected circular tube generated flow rates that shown in **Table 3.2**

Table 3.2 Applied tube cross flow velocities and flow rate in FO experiment

Cross flow velocity in tube		Flow rate	
(cm/s)	(m/s)	(L/h)	(L/min)
16.8	0.168	30	0.5
25	0.25	44.5	0.75
33.7	0.337	60	1

3.3.5. Nutrients rejection

According to McCutcheon et al., the determination of rejection nutrient in the FS is performed by collecting a sample of diluted DS after a complete FO run (McCutcheon, 2006). Based on the final concentration of the nutrients in the diluted DS and the initial concentration of the nutrients in the FS before the FO cross flow process, the percentage of rejection, R is calculated using equation (2-20) that included the dilution factor (Xie et al., 2013).

The nitrogen (NO_2 -N, NO_3 -N, and NH_4 -N), and phosphorus (PO_4 -P) content of the FS and DS were determined according to standard methods (APHA, 1998) with a UV-Vis spectrophotometer (Hitachi U-1800). All samples were diluted to allow for measurement within the standard calibration range.

3.3.6 Water flux calculation

Osmosis leads to water flux from FS to DS across the FO membrane, and this results in increase in the weight of the DS. The water flux can be calculated using equation (3–1), where the change in weight of DS was converted to a volume and then the value is divided by the membrane area and time duration; this equation is as follows:

$$Jw = \frac{W_e - W_0}{\rho \, . \, A_m \, . \, t} \tag{3–1}$$

where J_w is the water flux (L/m^2h), W_e the final weight of DS at the end of the FO process (g), W_0 is the initial weight of DS (g), ρ is the density of fluid (kg/m^3), A_m is the membrane area (m^2), and t is the time duration (h).

3.4 RESULT AND DISCUSSION

3.4.1 EFFECT OF THE CROSS FLOW VELOCITY

To elucidate the effects of the FO cross flow velocity on nutrient rejection and water flux, a series FO processes were conducted at velocities of 0.17 m/s, 0.25 m/s, and 0.34 m/s. The experiment used membrane HTI-NW. The membranes HTI-ES did not further investigated because could not functioned at high cross flow velocity (0.34) m/s.

The effects of cross flow velocity on water flux are shown in **Figure 3.6.** While a water flux of 6.3 L/m^2-h was achieved at a cross flow velocity of 0.17 m/s, the water flux was around 30% higher (i.e., 8.4 L/m^{2}h) at a cross flow velocity of 0.25 m/s. At a cross flow velocity of 0.34 m/s, the water flux increased again by 30% (i.e., 11.3 L/m^{2}h). The boundary layer thickness would have been higher at lower cross flow velocities (Zou et al., 2011), and thus, CP likely occurred under those conditions. Notably, CP can adversely affect the water flux (McCutcheon and Elimelech, 2006). During the FO process, internal CP acts to diminish the driving force across the membrane and decrease water flux (Loeb et al., 1997). In this study, at the low cross flow velocity of 0.17 m/s, the water flux did not decrease substantially, which was probably a result of the short time used for the FO process.

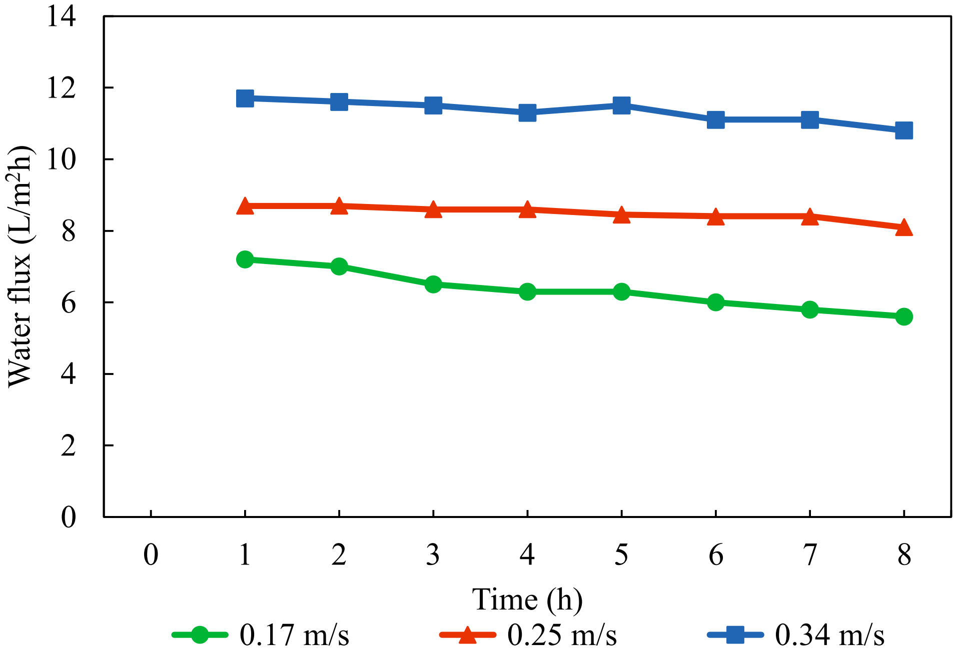

Figure 3.6 Water flux with the HTI-NW membrane for a 1 M $MgCl_2$ DS at different cross flow velocities of 0.17 m/s, 0.25 m/s, and 0.34 m/s

As shown in **Figure 3.7**, the rejection percentages for nitrogen (NO_2-N, NO_3-N, and NH_4-N) and phosphorus (PO_4-P) during FO differed for the different cross flow velocity conditions. Rejection percentages for NO_2-N, NO_3-N, NH_4-N, and PO_4-P at 0.17 m/s were 56.09%, 93.56%, 55.62%, and 91.24%, respectively, whereas for 0.25 m/s, the rejection percentages increased to 68.82%, 96.84%, 99.33%, and 98.50%, respectively. When the FO cross flow velocity was increased to 0.34 m/s, the rejection percentages slightly increased for NO_3-N (98.59%) and NH_4-N (99.81%), but the percentages decreased for NO_2-N (66.13%) and PO_4-P (95.07%). Given the varying levels of rejection for nutrients in this study, the cross flow velocity of 0.25 m/s was considered to be the optimal condition for mixing and mass transfer in the flow pipe and the membrane area of 0.012 m^2.

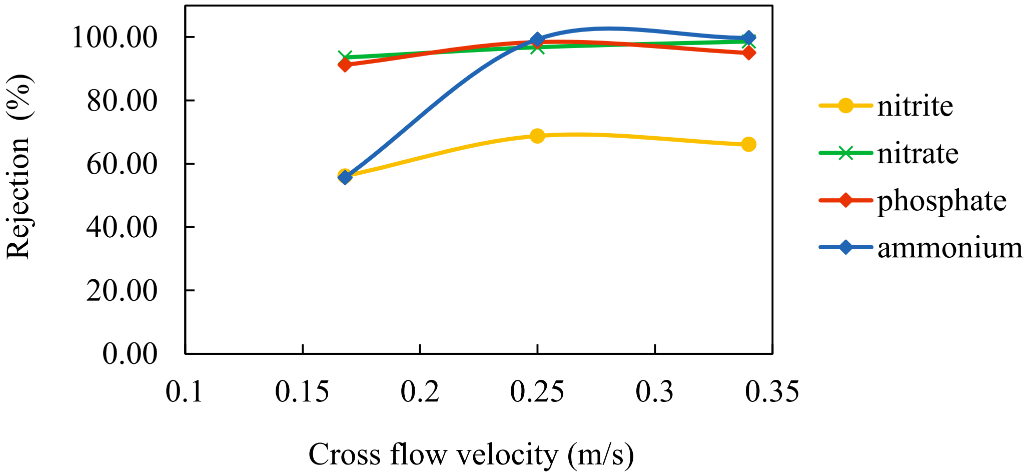

Figure 3.7 Rejection of nutrients by the HTI-NW membrane with a 1 M $MgCl_2$ DS at different cross flow velocities of 0.17 m/s, 0.25 m/s, and 0.34 m/s

The rejection of NO_2-N and NH_4-N was low when the effluent was treated with a low cross flow velocity because of the effect of small molecular weight compounds and hydrated ion diameters, which makes the transfer across the FO membrane easy in low mixing conditions. The NO_2 molecular weight and hydrated ion diameter are 46.01 g/mole and 0.3 nm, respectively, whereas those of NH_4 are 18.01 g/mole and 0.25 nm, respectively. Conversely, the higher molecular weights and hydrated ion diameters for NO_3 (62.01 g/mole and 0.3 nm) and PO_4 (94.97 g/mole and 0.4 nm) resulted in higher rejection rates owing to attenuated transfer across the membrane. The increased cross flow velocity at 0.25 m/s increased mixing and reduced nutrient transfer; therefore, the rejection percentages were higher. The highest velocity of 0.34 m/s resulted in decreased rejection for some of the nutrients; thereby this value represents the limiting condition for this experiment given the flow pipe size and membrane dimension. Further increases in velocity might ruin the membrane. Ultimately, an operating velocity of 0.25 m/s is suggested for further experiments and applications. These findings agree with the selected velocity for the proposed FO methodology (Cath et al., 2013).

Mass transfer in cross flow filtration is largely an unknown parameter because of the variations that result from changing experimental circumstances such as the membrane channel and FS and DS flow rates. The cross flow velocity has a direct influence on the mixing and mass transfer in the flow channel (Cath et al., 2013). To obtain reliable mass transfer coefficient relations directly from experimental data, one method that can be used is based on the variation in observed rejection when cross flow velocity changes were applied (Berg et al., 1989). Mass transfer coefficients also can be estimated from many different theoretical equations, correlations, and analogies that are functions of material properties, intensive properties, and flow regimes (laminar or turbulent flow). However, there are some factors such as aspect ratio between height and width of channel that must be considered for friction, which do not investigated further in this study. Hence, the Reynolds number to show flow regime, whether laminar or turbulent, cannot perfectly represented.

In this study, to help elucidate the effects of the cross flow velocity in the FO process, the flow rates and velocities in rectangular membrane module were calculated. The velocity in rectangular membrane module was determined by dividing flow rate with hydraulic radius of rectangular membrane module. The cross section area for both sides by the FS and DS was 3.6×10^{-4} m^2, and this was derived from dimensions of the rectangular membrane module with the assumption that the width of the channel is 90 mm and the height of flow is 4 mm.

All of the velocities at membrane module were seemly low, as shown in **Table 3.3**. A higher cross flow velocity, higher flow rate generated that possible to increase random or mixing flow condition. This condition increase the potential back-movement of nutrients from membrane active layer surface into the bulk of FS. Therefore, it restrain nutrient to transfer to the DS side and increase nutrient rejection. In higher flows and at high DS concentrations, the thickness of the boundary layer will be diminished, thus decreasing the severity of internal CP and increasing the water flux (Anastasio and McCutcheon, 2013). However, the mechanical strength of the membrane should be considered as one of the main limitations of high mixing that affect performance of nutrient rejection. Conversely, Park et al. (2011) in their study concluded that development performance of the membrane might be the most efficient way to maximize FO performance, rather than through optimizing operation conditions such as FS and DS velocity.

Table 3.3 Calculation of velocity at rectangular membrane module

Flow rate (L/min)	Velocity at rectangular membrane module (m/s)
0.5	0.023
0.75	0.033
1	0.047

3.4.2 EFFECT OF TEMPERATURE

The effect of temperature on the rejection of nutrients by forward osmosis was investigated. Three set of FO experiments using three kinds of temperature 20°C, 25°C, and 30°C on both FS and DS side were conducted. In all experiments, the same concentration of 1 M $MgCl_2$ DS was used and HTI-NW membranes were employed. The results showed that the rejection of ion nutrients was varied to temperature variations (**Figure 3.8)** for example, the negative ion phosphate rejection amount only increased slightly with increases in temperature; specifically, the rejection percentages were 95.72%, 99.58%, and 99.78% at temperatures of 20°C, 25°C, and 30°C, respectively. However, the positive ion ammonium rejection amount did increase more pronouncedly with increases in temperature; specifically, the rejection percentages were 83.00%, 99.33%, and 98.09% at temperatures of 20°C, 25°C, and 30°C. The chloride ion diffusion from DS to FS gave electrostatic attraction to the ammonium ion, thereby increasing ammonium rejection. Nevertheless, the varied results indicate that temperature does not play a significant role in charged ion nutrient rejection. In aqueous solutions, charged ions are hydrated and the hydration of the charged ions results in size exclusion. In addition to size exclusion, negative membranes and electrostatic interactions can be important rejection mechanisms for charged ions or solutes (Alturki et al., 2013, Xie et al., 2013). This finding is supported by previous study results that found that solution temperature and transmembrane temperature differences only exerted a small influence on the rejection of charged trace organic contaminants by CTA and thin film composite (TFC) membranes, whereas neutral trace organic contaminants were significantly affected by temperature (Xie et al., 2013). For further experiment, due to practical reason of experiment condition in room temperature, the 25°C was chosen as experiment temperature.

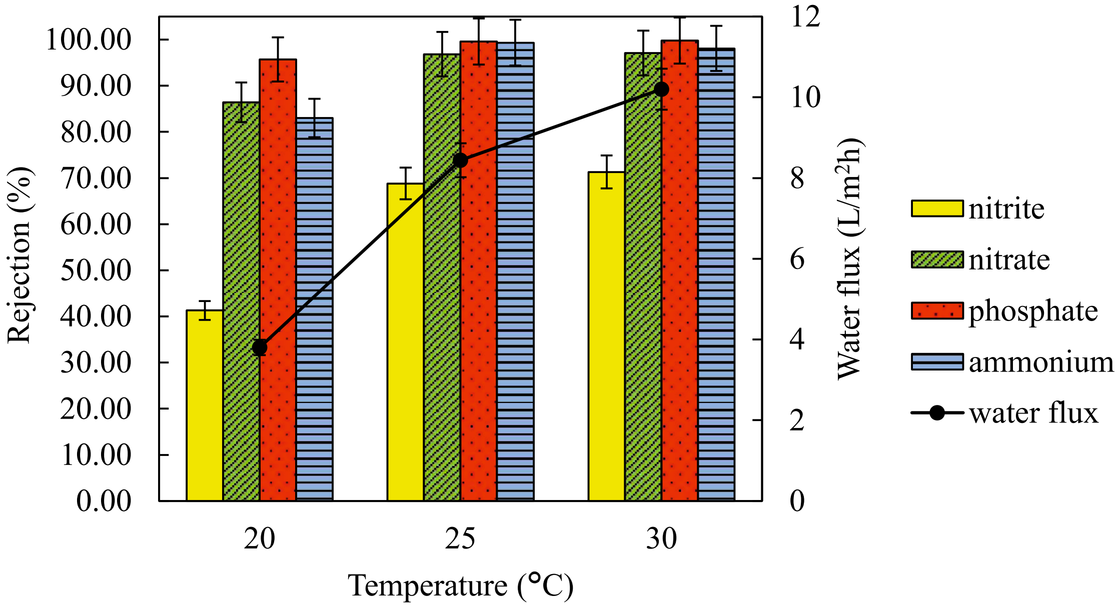

Figure 3.8 Nutrient rejection and water flux at varying temperatures at 20°C, 25°C, 30°C. Experiment condition: DS $MgCl_2$ 1 M, membrane HTI-NW, cross flow velocity 0.25 m/s.

In contrast to lack of effect on nutrient rejection, water flux was significantly impacted by temperature changes in the FS and DS. The increase of temperature in the FS enhanced the diffusivity of water molecules, thereby increasing the water flux. At the same time, the increase of DS temperature decreased DS viscosity and increased the DS diffusivity constant as shown in equation (2–25), thereby increasing the water flux (Cornelissen et al., 2008, Xie et al., 2013). The viscosity is influenced by temperature and the concentration of the solution. Further experiments should be conducted to investigate the effects of DS concentration variations. The DS concentration must be eventually optimized as well because the water flux is non-linearly related to the concentration of DS (Cornelissen et al., 2008).

3.5 CONCLUSION

This chapter investigated the optimum cross flow velocity and temperature to use during FO treatments aimed at achieving high nutrient rejection rates. Nutrient rejection was successfully achieved more than 95% except nitrite, by a moderate velocity of cross flow at 0.25 m/s. The higher velocity that resulted higher flow rate will restrained nutrient transfer to the DS side, thereby increasing nutrient rejection. A water flux of 6.3 L/m^2-h was achieved at a cross flow velocity of 0.17 m/s, and this increased to around 30% and 60% at cross flow velocities of 0.25 m/s and 0.34 m/s, respectively. The increasing temperature had less of an impact on nutrient rejection, but temperature did have an effect on the water flux. A temperature of 25°C exhibited good nutrient rejection rates.

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Chapter 4

EFFECTS OF MAGNESIUM CHLORIDE CONCENTRATION AND MEMBRANE MORPHOLOGIES ON NUTRIENT REJECTION, WATER FLUX AND REVERSE SOLUTE IN FORWARD OSMOSIS

4.1 INTRODUCTION

Forward osmosis (FO) membrane technology research has grown remarkably in the last decade. In FO, solutions of higher and lower hydro-chemical potential are named feed solution (FS) and draw solution (DS), respectively. Natural osmotic difference drives water from FS to DS through membrane. The membrane, DS, and operating conditions should be optimized to increase the efficiency and to decrease concentration polarization (Lutchmiah et al., 2014). The concentration polarization is caused by the concentration difference between the FS and DS troughs across an FO membrane (Zhao et al., 2012). The concentration polarization arises as the water flux in FO has an opposite direction to the reverse solute flux (Wei et al., 2011). Since the effect of the membrane, DS, and operating conditions on the FO efficiency are closely related to each other, these aspects must be considered. According to Ge et al. (2013), the resolution of high efficiency FO membranes and suitable DS, related to the molecular solution, is required.

This research used $MgCl_2$ as a molecular solution DS for the following reasons. $MgCl_2$ has a relatively high osmotic pressure that has been tested for the prediction of the properties of solutions over a wide range of concentrations and temperatures (Cath et al., 2006). Achilli et al. (2010) in their experiments concluded that $MgCl_2$ may be the best DS for most water and wastewater applications, and suggested that it warranted further investigation to be used in environmental engineering applications. The role of

$MgCl_2$ in the FO process of wastewater treatment, especially for nutrient from secondary treated effluent and its rejection mechanism, has been rare investigated. Some previous experiments have been conducted for membrane test by using $MgCl_2$ as DS and deionized (DI) water as FS (Loeb et al., 1997, Qiu et al., 2012, Yang et al., 2009, Saren et al., 2011).

Mostly the previous studies used sodium chloride (NaCl) and sea salt as DS. A study by Cath et al. (2010), investigating the rejection of ammonia and nitrate by FO membrane, showed that rejections of 74% and 78%, respectively, were achieved with sea salt as DS and secondary effluent as FS. In their study, combined FO and RO membrane was also used that resulted in higher rejection of 94% for ammonia and 97% for nitrate. Holloway et al. (2007) investigated the rejection of ammonia, total kjeldahl nitrogen (TKN), and orthophosphate by a cellulose triacetate membrane that uses NaCl as DS. Their study indicated that 82.9%, 91.6% and 99.8% rejection of ammonia, TKN, and orthophosphate were achieved, respectively, for FO treated centrate increasing the feed concentration. Xue et al. (2015) investigated enriching nitrogen and phosphorus with synthetic seawater as DS. They concluded, at water reduction 50%, dissolved organic carbon and phosphate were 2.3-fold concentrated, ammonia 2.1-fold concentrated, while nitrite and nitrate were 1.9-fold and 1.3-fold, respectively. Retention of ammonia by cellulose triacetate (CTA) membrane were approximately 90% and negative retention by thin film composite (TFC) membrane in active layer-feed solution orientation.

Ideally, a FO membrane is able to provide high rejection, high water flux, and low reverse solute flux, such that the internal concentration polarization is essentially reduced. However, depending on DS's characteristic, the reverse solute of DS may result in a lower osmotic driving force and further concentration polarization.

Based on the aforementioned reasons, this study aims to investigate the efficiency and mechanism of nutrient rejection in the FO process with $MgCl_2$ and membranes and optimum operating conditions. The comprehensive review of the efficiency of nutrient rejection, water flux, and reverse solute flux by $MgCl_2$ in the FO process with various membrane morphologies is needed. This chapter established an understanding of the mechanism and relation of membrane characteristic and DS concentration, to provide further insight into the rejection of nutrients by the FO process. This can be potentially useful for future application in wastewater treatment plants.

4.2. Material and methods

4.2.1 Feed and draw solutions

The concentration of nitrite, nitrate, ammonium, and phosphate in real secondary treated effluent was investigated by collecting and measuring a grab sample of secondary treated effluent from the Eastern Municipal Wastewater Treatment Plant in Ube City, Yamaguchi Japan. The concentrations that were measured for these nutrients in an actual sample of secondary treated effluent are 0.1 mg/L, 11.4 mg/L, 3.4 mg/L and 2.7 mg/L for nitrite (NO_2 -N), nitrate (NO_3 -N), ammonium (NH_4-N), and phosphate (PO_4 -P), respectively. In our FO process, an artificial secondary treated effluent was used as FS, which was prepared by referring to the actual concentrations of secondary treated effluent. The sources of nitrite, nitrate, ammonium, and phosphate were 0.03 mM sodium nitrite ($NaNO_2$), 2.8 mM potassium nitrate (KNO_3), 0.85 mM ammonium chloride (NH_4Cl), and 0.3 mM potassium hydrogen phosphate (KH_2PO_4), respectively. The DS was prepared by dissolving magnesium chloride hexahydrate ($MgCl_2.6H_2O$) in DI water (SA 2100E Eyela Japan) at concentrations of 0.5 M, 1 M, 1.5 M, and 2 M.

Standard solution was prepared in the desired concentration range using stock standard and dilute DI water. Samples were diluted to facilitate the measurement within the standard calibration range. The nitrogen (NO_2-N, NO_3-N, and NH_4-N) and phosphorus (PO_4-P) contents were determined by referring to the standard methods (APHA, 1998) using a UV-Vis spectrophotometer principle (Hitachi U-1800). The viscosity of FS and DS was measured by a viscometer (TVC-5 Toki Sangyo Japan).

4.2.2 Membrane

Two of the FO membranes used in this study were acquired from Hydration Technology Innovations (HTI, Albany, OR). The membrane chemistry are proprietary, though it is believed that the membranes were asymmetric CTA nonwoven support layer (HTI-NW) and TFC with embedded polyester screen support (HTI-ES), and negatively charge surface (Ge et al., 2013). The surface-active layer, support layer, and cross section of the membranes were observed using Scanning Electron Microscopy (SEM) (Keyence VE 8800). In FO mode, active layer will facing feed solution (AL-FS) and in PRO mode, active layer will facing draw solution (AL-DS). The PRO mode that applied is unpressurized pressure retarded osmosis membrane orientation.

4.2.3 Forward osmosis cross flow set-up

The set-up of FO cross flow in this chapter was similar as Chapter 3. Cross flow velocities of 0.25 m/s were applied. Two proportional flasks were used to store 3.5 L artificial FS and 1 L DS. The weight of both of these flasks and their contents were measured (PB5001-5 Mettler Toledo USA) at initial and final stages of the FO process to calculate reverse solute flux. In the reverse solute flux calculation, not only initial and final volume of FS but also their conductivities (Horiba ES-14) were measured.

The permeate water from FS through the membrane into the DS was allowed to overflow into a beaker placed on a balance meter (PJ3000 Mettler-Toledo USA). The change in weight on the balance was recorded for the measurement of the water flux through the membrane. The FO cross flow apparatus in this chapter was completed with conductivity meter and balance meter. This apparatus showed in **Figure 4.1**. A single cross flow experiment was carried out in 8 hours (Cath et al., 2009, Holloway et al., 2007). During the experiment, the room temperature was maintained at $25\pm1.0^{\circ}$C. The pH of FS and DS were 7.2 ± 0.2 and 6.3 ± 0.2, respectively. The temperature and pH were monitored intermittently with a thermometer and pH-meter (Horiba D-13), respectively. At the end of the cross-flow process, permeates were collected and analyzed for nitrogen (NO_2-N, NO_3-N, and NH_4-N), and phosphorus (PO_4-P) content. The calculation for each rejection was done by subtracting the initial concentration from the final concentration.

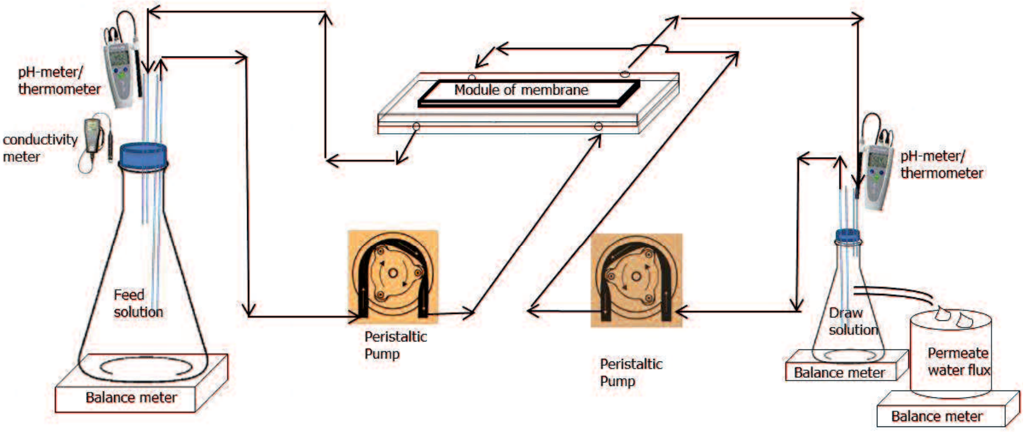


Figure 4.1 FO cross flow apparatus

4.2.4 Nutrients Rejection

The determination of nutrient rejection in the FS is carried out by collecting a sample of dilute DS after a complete FO run (McCutcheon et al., 2006*)*. The equation is follow equation (2-20) that considering the dilution factor for nutrient rejection (Xie et al., 2013).

4.2.5 Water flux calculation

The performance of FO process also can expressed by water flux. The water flux was calculated using equation (3–1).

4.2.6 Reverse solute calculation

The transported solute from the DS to the FS is named reverse solute. A conductivity meter and a balance meter were used to determine the concentration and volume of FS, respectively, before and after the FO process. Thus, the characteristics of the reverse solute were measured. The concentration, which is measured in mS/cm, was converted to g/L TDS and then divided by the membrane area (m^2) and the operation time (hours). The reverse solute flux was determined using mass balance calculation as seen on equation (4–1):

$$Js = \frac{C_t V_t - C_0 V_o}{A_m \, . \, t} \tag{4–1}$$

where Js is the reverse solute flux (g/m^2h); C_0 and C_t are the concentration of solute in the FS before and after the FO process, respectively; V_0 and V_t are the volume of the FS before and after the FO process, respectively.

The specific reverse solute can be used to investigate membrane performance that indicated the amount of solute loss per unit of water produced. The specific reverse solute was measured by dividing the reverse solute flux rate by the water flux rate (Js/Jw). To investigate diffusion constant of ion Mg^{2+} and Cl^-, analysis of these ion were conducted using Optical Emission Spectrometry Inductively Coupled Plasma (OES ICP Optima 3300) and ethylenediaminetetraacetic acid or EDTA titrimetric method for Mg^{2+} and argentometric method for Cl^-.

4.3 RESULT AND DISCUSSION

4.3.1 Nutrients rejection

Osmosis is the result of diffusion across a semi-permeable membrane that allows the spontaneous net movement of water to move from a low concentration solution to high concentration solution to equilibrate the chemical potential of the two solutions (Ge et al., 2013). Whereas, diffusion involves the movement of particles or the molecules from high concentration solution to low concentration solution. The driving force for the FO process is the natural osmotic pressure difference between the FS and DS across the membrane. The membrane allows water to pass from the FS to DS, but does not allow molecules to pass through. Hence, the nutrients were expected to be retained in the FS. In reality, because of the complexity and variability of particles or molecules, especially in wastewater, the efficiency of process varies depending on the characteristics of the FS, DS, and membrane.

To determine whether the induced nutrient rejection by DS concentration variation was related to the membrane characteristics, data of percentage rejection from the four kinds of variation in concentration of DS and the two kinds of membranes were generated. The **Figure 4.2** show the nutrients rejection percentage based on the equation (2–20).

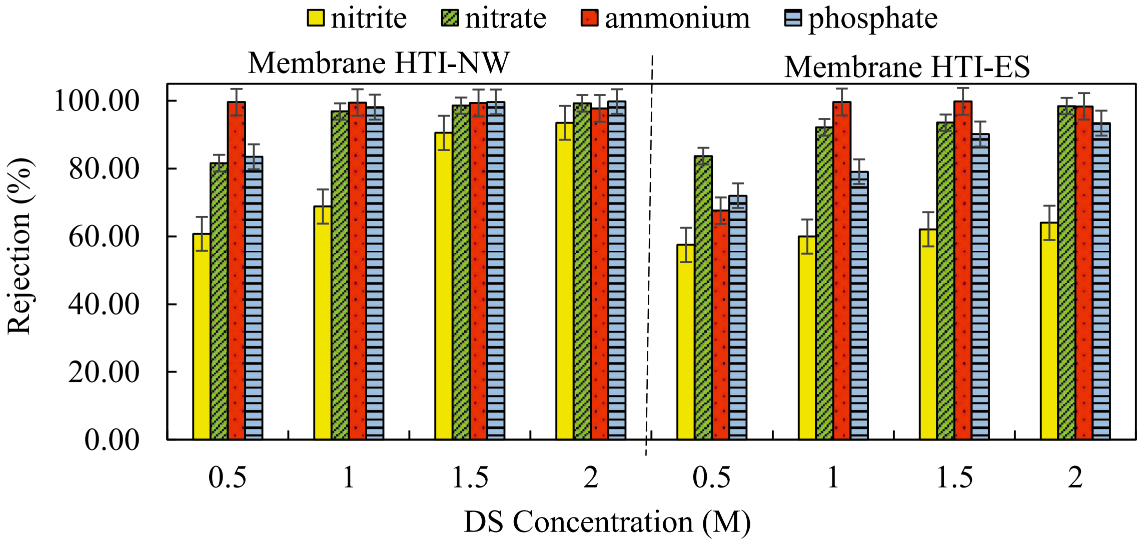


Figure 4.2 Rejection nutrients based on variation of DS $MgCl_2$ concentration at 0.5M, 1 M, 1.5 M and 2 M using membrane HTI-NW and HTI-ES. Experiment condition: cross flow velocity 0.25 m/s, temperature 25±1.0°C.

When low concentration of $MgCl_2$ was used as 0.5 M DS, the rejection of NO_2, NO_3, and PO_4 in membrane HTI-NW were 60.71%, 81.61% and 83.46%, respectively. Whereas, NH_4 rejection reached 99.58%. Using membrane HTI-ES, the experiment yielded lower rejections than that of HTI-NW 57.47%, 83.68%, 71.99% and 67.57% of NO_2, NO_3, PO_4 and NH_4, respectively.

In both the membranes, a low concentration of DS mostly does not achieve high nutrients rejection. The nutrient sources in FS and $MgCl_2$ in DS include polyatomic ions that could dissociate in water. In ionized water, the monovalent, negatively charge, low molecular weight ions, such as NO_2^- and NO_3^- anions, were rejected less than both the PO_4^{3-} anion (multivalent, negatively charge, large molecular weight) and NH_4^+ cation (monovalent, positively charge, and low molecular weight). These findings indicate that low concentration of DS does not dominantly affect the nutrient rejection. The Donnan potential is caused by the presence of multiple ions with varying charges in the FS in which electrical potential at the interfaces of the FS active layer membrane and the DS support layer membrane resulted from the adsorption difference of cations and anions. It prevents some of the ions to pass through the FO membrane and is identical to the rejection process. It, thus, creates an uneven electrical charge. In this process, since the FS does not contain $MgCl_2$, the Mg^{2+} and Cl^- ions try to diffuse along the concentration gradient. However, due to the low concentration difference between FS and DS and the tortuosity of the support membrane morphologies (**Figure 4.3 (b) and 4.4 (b)**), the diffusion constant does not strongly establish the electronegativity in the interface of the membrane. In this study, the smallest anion (NO_2^-) easily passed through the membrane from the FS, unlike the other small cation (NH_4^+). Large anions, such as NO_3^- and PO_4^{3-}, do not easily pass through the membrane. All of these reasons also explained the lower rejection of NO_2^- as compare to NO_3^- and PO_4^{3-}. The two positively charge hydrogen atoms (electronegativity 2.20) of the water molecule expand and weakly attract the negatively charge ions, such as NO_2^-, NO_3^-, and PO_4^{3-}. Even though NH_4^+ is attracted to the negatively membrane, it is not bound due to the low negativity of interface membrane caused by Cl^-. The FS with 3.5 L water consists of negatively charge oxygen (electronegativity 3.44) resulting from the polar water molecules, which are strongly attracted to positively charge ions, such as NH_4^+ (Nguyen, 2013). This situation would explain the high rejection rate of NH_4^+, compared to the other ions in membrane HTI-NW. All these results are consistent with a previous study that concluded the Donnan potential to be the dominant cause of the nutrient rejection mechanism in low concentrations of DS (Bian, 2014).

The rejection increased with increasing concentrations of DS. Thus, by using 2 M $MgCl_2$, the rejection of NO_2, NO_3, NH_4, and PO_4 in membrane HTI-NW were measured as 93.46%, 99.24%, 97.74%, and 99.78%, respectively; whereas in membrane HTI-ES, the nutrient rejections were 63.99%, 98.42%, 98.33%, and 93.40%, respectively. A high concentration of the DS will increase the osmotic pressure difference, thereby increasing the driving force, which in turn results in the enhancement of water flux from the FS to DS, and the reverse solute from the DS to FS by the diffusion constant. This diffusion constant is produced by the imbalance in the concentration between the anion and cation nutrient concentrations in the FS and the DS. This affects the ionic strength of the membrane. To determine the difference diffusion constant between Mg^{2+} and Cl^{-}, it can calculated by using (2–25) with $T = 25^{\circ}C$ or 298.15 K, $\eta = 1.0$ mPa.s or 1.10^{-3} kg/m.s for 1 L DS initially ($MgCl_2$), and r as the hydrated ionic radius. The value of the hydrated diameter ion of Mg^{2+} and Cl^{-} are 0.8 nm and 0.3 nm, respectively (Achilli, 2010). The respective diffusion constants are 0.55×10^{-9} m^2/s for Mg^{2+} and 1.5×10^{-9} m^2/s for Cl^{-}. It seems that Cl^{-} controlled the diffusion into the negatively charge membrane, creating a layer of Cl^{-} into the membrane. Using equation (2–25), below is calculation of Mg^{2+} and Cl^{-} diffusion constant based on concentration of DS $MgCl_2$ (**Table 4.1**) The electrostatic repulsion of the negatively charge nutrient ions, NO_2^{-}, NO_3^{-}, and PO_4^{3-} anions, increased, and this resulted in an increase in nutrient rejection. The positively charge nutrient ions, NH_4^{+} cation, was high rejection in both of the membranes because this cation do not across faster into the DS to balance higher Cl^{-} diffusion from DS to FS (Coday et al., 2013).

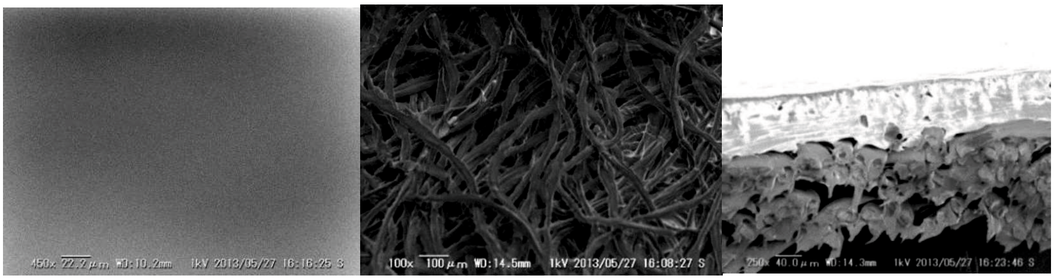
Table 4.1 Mg^{2+} and Cl^{-} diffusion constant based on concentration of DS $MgCl_2$ and viscosity value

$MgCl_2$ (M)	Initial Viscosity (mPa.s) at 25^{O}C	D Mg^{2+} (m^2/s) based on initial viscosity	D Cl^{-} (m^2/s) based on initial viscosity
0.5	1	0.55×10^{-9}	1.5×10^{-9}
1	1.1	0.5×10^{-9}	1.32×10^{-9}
1.5	1.3	0.42×10^{-9}	1.12×10^{-9}
2	1.5	0.36×10^{-9}	0.97×10^{-9}

The most commonly used DS is NaCl. The diameter of the hydrated Na^+ ion is 0.45 nm, resulting in a higher diffusion constant than Mg^2. In comparison, Na^+ and Cl^- have very similar high diffusion constants, because of their some similar hydrated diameters or nearly equimolar (Phillip et al., 2010). Therefore, difference in diffusion constants between both of them is very small. In previous study, Coday et al. (2013), in the CTA membrane, reverse flux of Na^+ was higher than that of Cl^- throughout all test with TFC membrane that resulted lower cation rejection than anion rejection. The seawater seemly has more various diffusion constant due to the complexity of ions. It worth noting that in this study, only Cl^- seemly higher diffuse than that of Mg^{2+} in HTI-NW (CTA) and HTI-ES (TFC) due to an indication of high NH_4^+ cation rejection. The detail discussion explained in sub chapter 4.3.2.

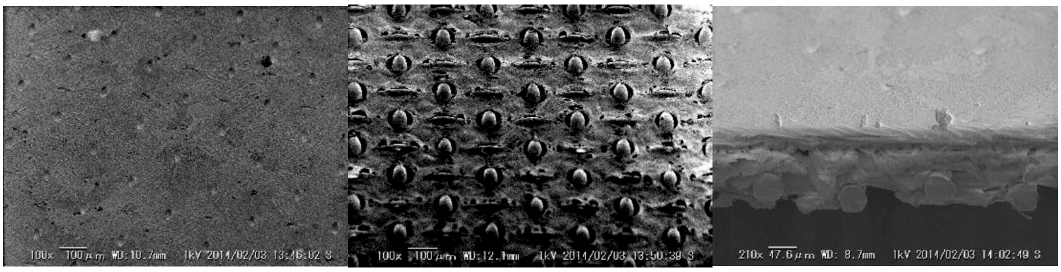
Then, the electrical double layer that formed in the pores was compressed, and in an attempt to maintain electroneutrality, it is likely that the paired Mg^{2+} cation try diffused to the membrane, causing the entire pore volume to become neutral and the Donnan potential to decrease. Therefore, in high concentrations, the effect of the diffusion constant is more dominant, compared to that of that Donnan potential, for nutrient rejection.

The percentage of rejection varies for membrane HTI-NW and HTI-ES, and the difference between the two could be explained by membrane morphologies. The surface of the active layer, support layer, and a cross-sectional area of the membrane HTI-NW are shown in **Figure 4.3 (a), (b),** and **(c)**, respectively,; and those for membrane HTI-ES are shown in **Figure 4.4(a-c),** with the help of SEM. The active layer membrane HTI-NW appears smoother and less porous (**Figure 4.3 (a)**) resulting in a good nutrient rejection efficiency than that of membrane HTI-ES (**Figure 4.4 (a)**).



(a) (b) (c)

Figure 4.3 SEM images of the HTI-NW membrane produced by HTI (a) surface layer of active layer (b) surface layer of support layer (c) cross–sectional area



(a) (b) (c)

Figure 4.4 SEM image of HTI-ES membrane by HTI (a) surface layer of active layer (b) surface layer of support layer (c) cross-sectional area

4.3.2 Water flux and reverse solute

To determine whether the $MgCl_2$ concentration and membrane morphologies were related to water flux and reverse solute, the data of **Figure 4.5** were generated. When the experiment using the same FS concentration and higher DS concentration, the concentration difference between FS and DS increases, the difference in osmotic pressure increases, and generates a higher water flux through the membrane due to the driving force that was verified by equation (2-2). Moreover, the importance of $MgCl_2$ in driving the water flux was confirmed by equation (2-3), according to which a DS with a higher Van’t Hoff factor could produce a higher osmotic pressure. Thus, the osmotic pressure difference would be increased, and this would result in an increase in the water flux. For example, $MgCl_2$ has a higher Van't Hoff factor (i=3) than NaCl (i=2), which is commonly used as the DS solute. The higher Van't hoff factor would increase the osmotic pressure, which is the driving force, and finally increase the water flux. The water flux in membrane HTI-NW achieved 7.55–9.61 L/m^{2}h and in membrane HTI-ES, it exceeds 13.58-15.10 L/m^{2}h. These findings indicate that the membrane morphologies affect the water flux. Membrane HTI-ES resulted higher water flux than membrane HTI-NW, which were likely to be affected by the porous condition of active layer and support layer. The active layer of membrane HTI-NW appears to be smooth and less porous (**Figure 4.3 (a)**), resulting in lower water flux than in case of membrane HTI-ES (**Figure 4.4 (a)**). The lower water flux is likely related to higher possibility of the occurrence of concentration polarization. The nonlinear dependence of flux on osmotic pressure investigated in FO mode is primarily a result of internal concentration polarization (Phillip et al, 2010). The concentrated FS coupled rapid permeation to DS caused diluted internal concentration polarization at the membrane interface in the support layer (Wang et al, 2015). This occurs when the difference in concentration across the active layer of the membrane varies from the difference in concentration in the DS (Cath et al., 2009). The porous support layer contributes to the internal concentration polarization (McCutcheon et al., 2006), along with porosity, tortuosity, and thickness. The internal concentration polarization depends on the diffusion coefficient and on the membrane support layer (Cath et al., 2009).

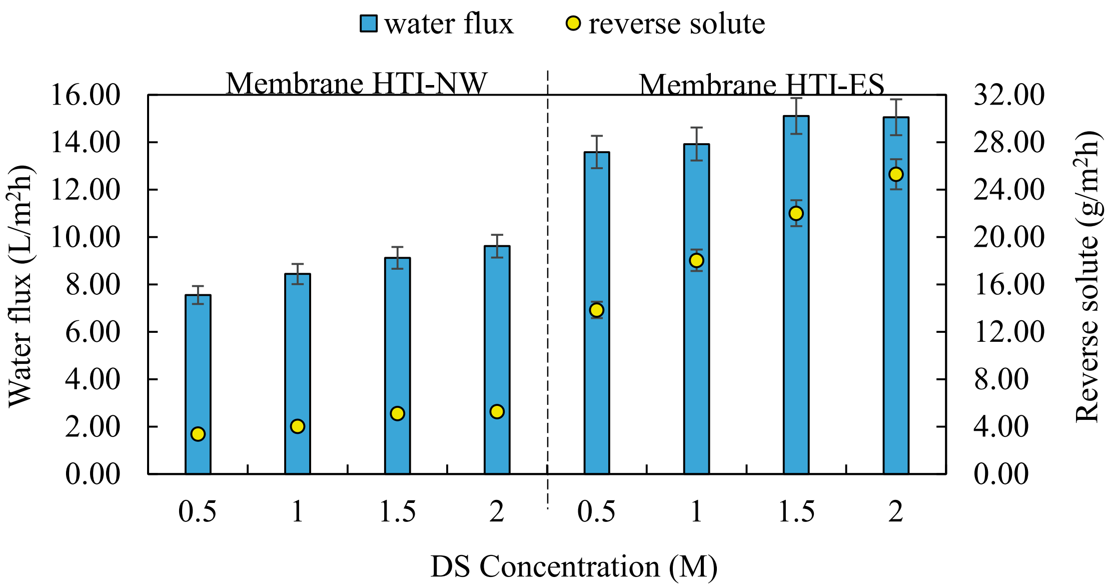


Figure 4.5 Water flux and reverse solute flux based on variation of DS $MgCl_2$ concentration at 0.5M, 1 M, 1.5 M and 2 M using membrane HTI-NW and HTI-ES. Experiment condition: cross flow velocity 0.25 m/s, temperature 25±1.0°C.

When the concentration difference between FS and DS increases, the water flux, along with the reverse solute flux, increases as explained in equation (2–23). In the FO process, the reverse movement of the solute from the DS to the FS through the membrane is unavoidable. This is because of the difference of concentrations (Zhao et al, 2012). In this study, the reverse solute flux rate reached 3.38-5.26 g/m^2h in membrane HTI-NW and increased considerably to 13.84-25.29 g/m^2h in membrane HTI-ES. These results indicated that the other factors strongly affect the reverse solute. The morphologies of the support layer of the membrane that faces the DS affected the reverse solute flux. The support layer with high resistance of the solute to diffusion will result in low reverse solute flux. **Figure 4.3 (b)** is the SEM image of the support layer of membrane HTI-NW, in which the tortuosity seems higher and less porous, which makes it more capable of restraining the reverse solute flux, as compared to membrane

HTI-ES (**Figure 4.5 (b)).** In equation (2–24), the resistance of the solute to the diffusion within the membrane support layer explained the lower reverse solute flux in case of high tortuosity and less porous of membrane HTI-NW as compared to HTI-ES, which is characterized by lower tortuosity and higher porosity. A low porosity, high tortuosity and high thickness of membrane HTI-NW determined its higher structural parameter than membrane HTI-ES which are owing high porosity, low tortuosity and low thickness. A high rejection and low reverse solute can achieved by membrane HTI-NW, however water flux generated was minimum. A membrane HTI-ES with the increasing the void fraction and decreasing the thickness and tortuosity, can improve the water flux, but a small ion such as nitrite cannot rejected well. The further improvement of FO membrane performance is still needed.

The other way, to increase the performance of high water flux, the experiment of un-pressurized retarded osmosis (PRO) in which active layer of membrane facing the DS (AL-DS), was conducted. The PRO experiment used 1 M DS $MgCl_2$ and membrane HTI-ES and applied cross flow velocity at 0.25 m/s and temperature at 25+1.0°C. The result as shown in **Figure 4.6** indicated that the nutrient rejection in PRO mode achieved lower than FO mode, but resulted higher water flux.

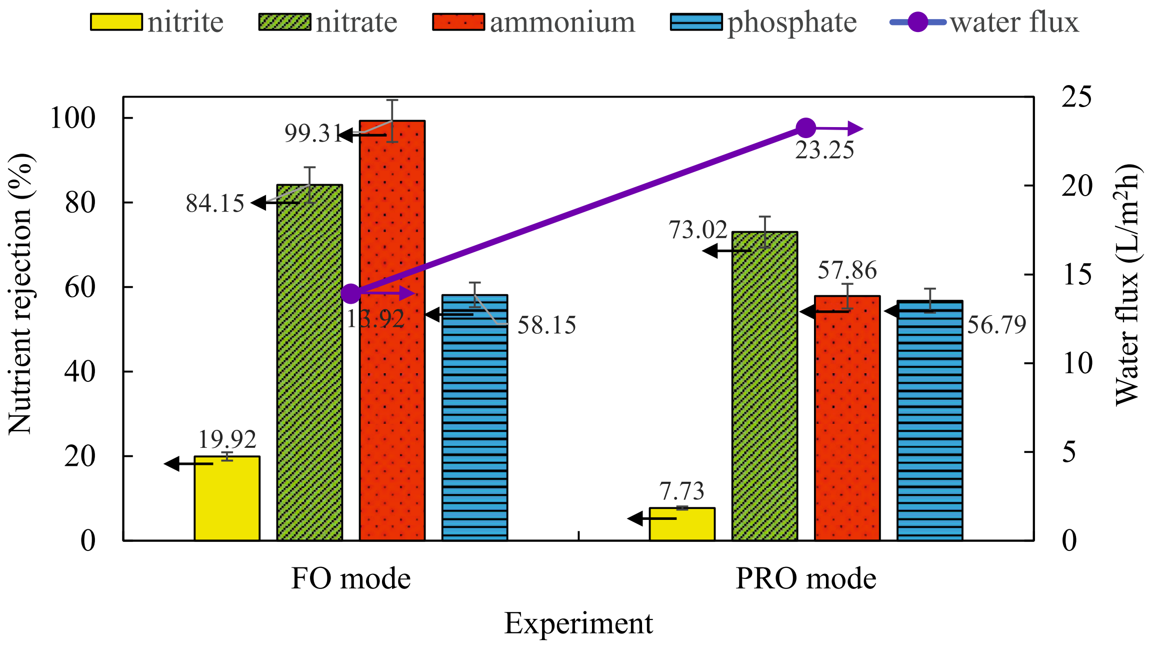
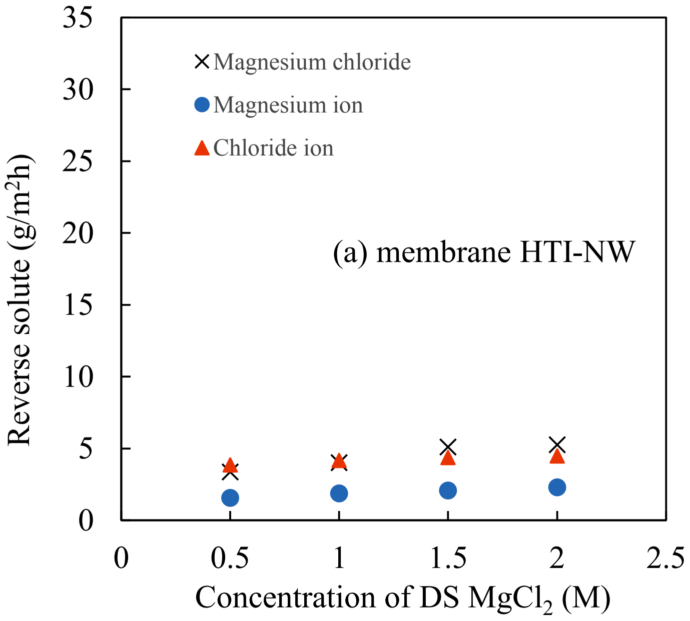


Figure 4.6 Nutrient rejection and water flux in FO mode and PRO mode. Experiment condition: 1 M DS $MgCl_2$, membrane HTI-ES, cross flow velocity 0.25 m/s, and temperature 25$\pm$1.0°C.

The investigation of reverse solute (**Figure 4.7)** was measured by monitoring increasing FS conductivity for $MgCl_2$ and through titrimetric analysis for magnesium and chloride ion. The result indicated that concentration of DS $MgCl_2$ less affect to reverse solute of membrane HTI-NW than membrane HTI-ES. The reverse solute in membrane HTI-NW seemly constant along all concentration of DS $MgCl_2$. The chloride diffusion slightly higher than magnesium. In membrane HTI-ES, the reverse solute of chloride was almost three times that of magnesium. This chloride diffusion explained the cation nutrient NH_4^+ was higher rejection than anion nutrient such as NO_2^-, NO_3^-, and PO_4^{3-}.On the contrary, those anion were lower rejection than its cation due to diffusion into the DS to maintain neutrality.

Coday et al., 2013, in their research using NaCl as DS, resulted reverse salt of sodium was higher than that of chloride in TFC membrane and in the contrary, chloride higher diffuse than sodium in CTA membrane. This phenomenon possible to occurred due to sodium and chloride were nearly equimolar (Phillip et al., 2010) resulted similar diffusion constant, thereby difficult to differentiate the dominant effect, whether sodium or chloride. Xue et al., 2015 using synthetic seawater as DS, resulted nutrient retention mostly achieved high retention 60-90% and only TFC membrane give negative result for ammonium retention. The hypothesis to explain the negative result are greater ammonium permeability to TFC membrane and high negative zeta potential of TFC membrane that similar level to that of a cation exchange membrane (Xue et al., 2015, Xie et al., 2011). The other possibility is complex composition of seawater that not as effective as a NaCl solution as DS (Zhang et al., 2011). The use single DS such as $MgCl_2$ with high osmotic pressure potential seemly promising especially to reject charged ion such nutrient ions NO_2^-, NO_3^-, NH_4^+ and PO_4^{3-} due to predictable dominant ion in rejection mechanism.



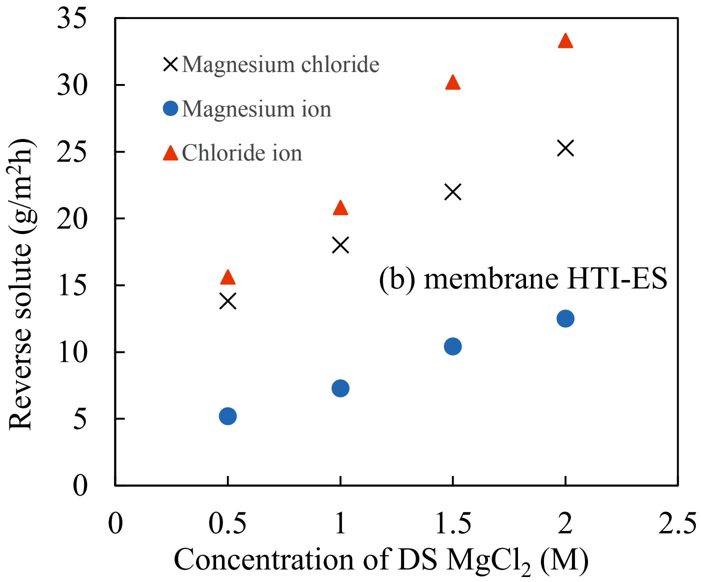


Figure 4.7 Reverse solute flux based on investigation $MgCl_2$ (conductivity meter), ion Mg^{2+} (EDTA titrimetric method), and ion Cl^- (argentometric method) on membrane HTI-NW and HTI-ES. Experiment condition: DS $MgCl_2$ concentration at 0.5M, 1 M, 1.5 M and 2 M, cross flow velocity 0.25 m/s, temperature 25±1.0°C.

The higher water flux may contribute to the higher reverse solute flux. This statement can be supported by the values of the specific reverse solute flux, as represented in **Figure 4.8**, in which it can be seen that this value of reverse solute flux-water flux ratio increases as the DS concentration increases. This ratio indicates the amount of solute loss per unit water flux. The specific reverse solute showed low values ranging from 0.45 to 0.55 g/L on membrane HTI-NW, which could support the efficiency of the FO system. On membrane HTI-ES, the specific reverse solute flux showed higher values that ranged from 1.02 to 1.68 g/L. These findings confirm that membrane HTI-NW have better performance for nutrient rejection using $MgCl_2$ than membrane HTI-ES. As summary, the result of FO performance in this chapter as shown in **Table 4.2**

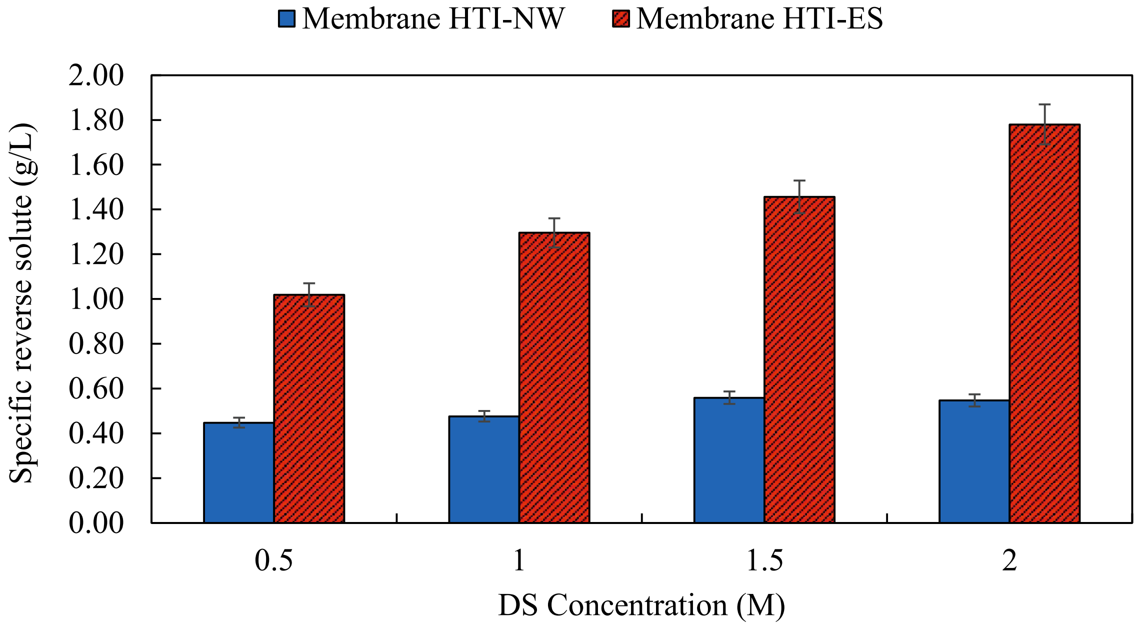


Figure 4.8 Specific reverse solute based on variation of DS $MgCl_2$ concentration at 0.5M, 1 M, 1.5 M and 2 M using membrane HTI-NW and HTI-ES. Experiment condition: cross flow velocity 0.25 m/s, temperature 25±1.0°C.

Table 4.2 Summary FO performance using two kind membrane and variation concentration of DS $MgCl_2$

Membrane	DS $MgCl_2$ (M)	Rejection (%)				Water flux (L/m^{2}h)	Reverse solute (g/m^{2}h)	Specific reverse solute (g/L)
		Nitrite	Nitrate	Ammonium	Phosphate			
HTI-NW	0.5	60.71	81.61	99.58	83.46	7.55	3.38	0.45
	1	68.82	96.84	99.47	98.11	8.44	4.02	0.48
	1.5	90.53	98.53	99.37	99.65	9.11	5.10	0.56
	2	93.46	99.24	97.74	99.78	9.61	5.26	0.55
HTI-ES	0.5	57.47	83.68	67.57	71.99	13.58	13.84	1.02
	1	59.95	92.15	99.65	79.09	13.92	18.03	1.3
	1.5	62.08	93.55	99.82	90.20	15.10	22.00	1.46
	2	63.99	98.42	98.33	93.40	14.58	26.01	1.78

4.4 CONCLUSION

The rejection of nitrogen (NO_2, NO_3, and NH_4) and phosphorus (PO_4) nutrients can be achieved by using $MgCl_2$ in the FO process. Specifically, the results support that a concentration of 2 M $MgCl_2$ effectively reject nitrite, nitrate, ammonium, and phosphate. The characteristics of the ionic nutrients, such as ion size and ion charge, affect the performance of rejection. Furthermore, concentration difference between the dissociated ions of $MgCl_2$ in the DS plays a significant role in rejecting ion nutrient. The increasing concentration difference between FS and DS generates higher water flux and reverse solute flux. The lower reverse solute flux and high rejection of nutrient on membrane HTI-NW as compared to HTI-ES, indicating better efficiency of membrane HTI-NW owing to the membrane morphologies, but still need improvement on increasing water flux. The PRO mode achieved lower nutrient rejection than FO mode, but resulted higher water flux. The chloride diffusion higher than magnesium diffusion that support nutrient rejection.

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Chapter 5

THE FEASIBILITY AND FUTURE HANDLING OF MAGNESIUM CHLORIDE AS DRAW SOLUTION AND ITS COMPARISON WITH SODIUM CHLORIDE AND SEAWATER

5.1 INTRODUCTION

Membrane filtration is widely applied on purification because of the versatility of technology and because membrane produce a consistent end product with less energy use and at lower cost (Lamminen et al., 2006). One of drawback of membrane filtration is fouling that can decrease performance. Membrane fouling has significant impact on the operational sustainability and economics of the process. Lower membrane fouling implies longer operation and more water production, less cleaning, and longer membrane life (Lay et al., 2010). Therefore, fouling phenomenon requires cleaning of membrane using hydraulic, chemical, mechanical or other treatment. In FO, water flows from FS side to the DS side across the FO membrane and at the same time, salt and contaminant in the FS being removed or rejected. The FO process has the potential to use lower energy and present lower fouling than pressure-driven membrane process such as RO (Wang et al., 2015) thereby need less cleaning and longer membrane life. The extending membrane's longevity can decrease the membrane material cost as part of capital cost (Butler, 2012). Cleaning is one of process that affect cost of membrane.

The other material cost is draw solution. FO process generate dilution of DS. These dilution affect a lower osmotic pressure as driving force, and subsequently would make lower water flux production or flow rate. Furthermore, conversely, if FO operated to produce clean water, the dilution has a lower osmotic pressure and enables production of more water at the same applied hydraulic pressure, thus reducing the energy requires to produce a unit volume of product water (Hancock et al., 2012).

Mi and Elimelech (2010) in their study, suggested to understand unique salt transport phenomena. The discussion in Chapter 4 about magnesium chloride, sodium chloride and sea water as DS in FO process showed these transport phenomena. The performance of nutrient rejection by previous studies and this study will summarized in this chapter. The comparison of DS cost and the performance should be considered. In wastewater treatment term, not only the capital cost and operation maintenance cost should be considered, but also the environmental impact.

This chapter is aimed to investigate nutrient rejection after cleaning process and to compare the performance and cost of $MgCl_2$, NaCl and synthetic sea water. Furthermore, the future handling of concentrated nutrients in a FS and a diluted DS will indicated in this chapter.

5.2 MATERIAL AND METHOD

5.2.1 CLEANING

The material and method was similar as explained in Chapter 3 and Chapter 4. The forward osmosis cross flow with 1 M $MgCl_2$ was conducted in 8 and 18 hours. At the end of process of 18 hours, without switchover of the membrane, the DS was flushed out from cross flow with DI water and replaced with sodium hydroxide solution 5 g/L (Achilli *et al*., 2009) for total time 90 minute. The FS was substituted with DI water. After cleaning, FS and DS were loaded with fresh FS contain nutrients and DS $MgCl_2$, respectively and cross flow was conducted identical to the previous process. A final permeate was also investigated.

5.2.2 COMPARISON OF MAGNESIUM CHLORIDE, SODIUM CHLORIDE AND SEAWATER

The comparison of $MgCl_2$, NaCl and synthetic sea water can discussed by considerate the nutrient rejection, water flux production and the price. The price of three of these DS were presented in industrial grade price and analytical grade price.

5.3 RESULT AND DISCUSSION

5.3.1 CLEANING

To investigate the performance of nutrient rejection after cleaning, one set FO process was conducted using DS $MgCl_2$ 1 M, membrane HTI-NW, cross flow velocity 0.25 m/s, and temperature 25$\pm$1.0°C. The FO process time conducted in 8 hours, continued to 18 hours and cleaning process implemented. The result as shown in **Figure 5.1** indicate that performance of nutrient rejection seemly constant and can reached similar performance as its previous before cleaning.

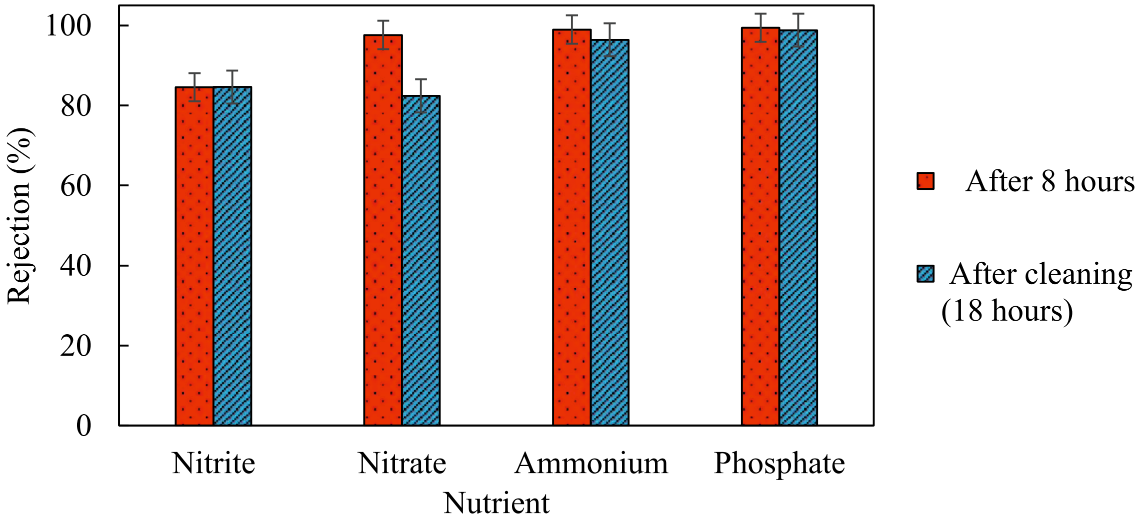

Figure 5.1 Nutrient rejection after 8 hours and after cleaning. Experiment condition: DS $MgCl_2$ 1 M, membrane HTI-NW, cross flow velocity 0.25 m/s, temperature 25$\pm$1.0°C, deionized water and NaOH as cleaning agent

In cleaning process, the NaOH can disintegrate large-size foulants into fine particles and/or soluble organic substances, which can be further hydrolyzed and solubilized into small molecules under alkaline condition. At a higher pH, the functional group of foulants can be deprotonated and become negatively charged, and the repulsive interaction among foulants can facilitate the cleaning process (Wang et al., 2015). The constant performance of membrane after cleaning can support the membrane's longevity that decrease the membrane material cost.

5.3.2 COMPARISON OF MAGNESIUM CHLORIDE, SODIUM CHLORIDE AND SEAWATER

Studies of nutrient rejection by forward osmosis have been conducted using NaCl and seawater. The comparison of these studies include present study is presented in **Table 5.1**

Table 5.1 Comparison nutrient rejection research

Item	Material/Quantity/Variation			
	Holloway et al., 2007	Cath et al., 2010	Xue et al., 2015	This study
Feed solution	Anaerobic digester centrate : a. Raw a.1 Constant feed concentration a.2 Increasing feed concentration b. Pre Treated (filtered) b.1 Constant feed concentration b.2 Increasing feed concentration	• Secondary treated effluent • Tertiary treated effluent • Effluent-impacted surface water	• A synthetic FS • A real effluent sample from membrane bioreactor treating municipal wastewater	Secondary treated effluent : increasing feed concentration, no pre treatment
Draw solution	NaCl 70 g/L, 1 L and gradually varied down	Synthetic seawater salt 5 –	Synthetic seawater	$MgCl_2$ 0.5 M (47.61 g/L) ;

Item	Material/Quantity/Variation			
	Holloway et al., 2007	Cath et al., 2010	Xue et al., 2015	This study
	until reach 30 g/L	70 g/L		1 M (95.21 g/L); 1.5 M (142.82 g/L); 2 M (190.42 g/L)
Membrane	CTA HTI membrane 139 cm^2	Flat sheet FO membranes HTI 0.062 m^2	a. TFC HTI b. CTA-1 HTI c. CTA-2 HTI 60 cm^2	a. HTI-NW 102 cm^2 b. HTI-ES 102 cm^2
Flow rate/velocity	1.5 L/min	1.4 L/min	8.3 cm/s	0.75 L/min
Cross flow time	8 h per each cycle (until 5 cycles)	4 h	2.5 h	8 h (1 cycle)
NO_2 rejection	Not investigated	Not investigated	Based on membrane a. >90% b. >60% c. >60%	Based on membrane a.89.0% b.25.8%
NO_3 rejection	Not investigated	78%	Based on membrane a. >95% b. ±60% c. >85%	Based on membrane a.98.7% b.96.7%
NH_4 (NH_3) rejection	Based on FS, NH_3 rejection a1. 84.7% a2. 92.1% b1. 88.0% b2. 82.9%	74%	Based on membrane, NH_3 rejection a. negative b. >90% c. >90%	Based on membrane, NH_4 rejection a. 99.4% b.99.6%
PO_4 rejection	Based on FS Orthophosphate rejection a1. 99.6% a2. 99.9% b1. 99.8% b2. 99.8%	Not investigated	Based on membrane a. >90% b. ±90% c. >95%	Based on membrane a.99.6% b.86.4%
Water flux	Based on FS a1. ±14 L/m^2h a2. ±14 L/m^2h b1. ±14 L/m^2h b2. ±12 L/m^2h	9 L/m^2h	Based on membrane a. 8.2 L/m^2h b. 7.4 L/m^2h c. 5.3 L/m^2h	Based on membrane a. 9.61 L/m^2h b. 15.10 L/m^2h

The comparison showed that in nutrient rejection, $MgCl_2$ compete tightly with NaCl and present better performance than seawater. The nutrient rejection achieved almost >95% by $MgCl_2$ except nitrite due to its small size that hardly to remove. Cath et al. (2006) indicate that an NaCl is very often selected because its high solubility and is relatively easy to re-concentrate to high concentration using a conventional desalination process e.g. RO or distillation without risk of scaling. Zhang et al. (2011) in their study resulted that seawater when use as a DS is not as effective as a NaCl solution. The lower conductivity and complex composition of seawater especially the presence of nonconductive compound make unfavorable for water flux because a lower osmotic pressure will slow down the water movement or water flux. Sea water contains numerous particles and microorganism which may foul the reconcentration system (in closed-loop system) or cause (bio)fouling /contamination in the FO unit, hindering performance (Lutchmiah et al., 2014). Interestingly, based on diffusion constant phenomenon in mass transfer, the knowing FS with existing charged nutrient ion, whether anion (NO_2^- , NO_3^- PO_4^{3-}) or cation (NH_4^+), and a single DS such as $MgCl_2$ with high difference diffusion potential between Mg^{2+} and Cl^-, could be predicted which ion that have dominant role, then performance of rejection could be try to enhanced. However, a single use of DS such as NaCl, due to similarly diffusion constant would give varied in mass transfer and performance. The complexity of seawater composition cause less effective on rejection performance.

The list of raw material price of DS $MgCl_2$, NaCl and synthetic sea water was shown in **Table 5.2**. The price of raw material of $MgCl_2$ was 1.3 times higher than NaCl. The applied of real sea water is feasible due to abundant source and no cost for raw material, but cost-efficient if applied near coastal area. According to equation (2–26), if assumed that cost and lifetime of the membrane module and flow rate are constant, total cost will more consider cost of DS and volume related with water flux. A higher difference osmotic pressure of $MgCl_2$ resulted higher water flux (dilution) than NaCl and seawater. The dilution factor of $MgCl_2$ was 1.07 times higher than $MgCl_2$ and 1.67 times higher than synthetic sea salt. The higher water flux will increase dilution and decrease cost. Hence, the total cost of $MgCl_2$ was 1.2 times higher than NaCl.

Table 5.2 Price of DS $MgCl_2$, NaCl and synthetic sea water

DS	Industrial grade price (¥/metric ton)	Analysis grade price (¥/500 gr)
$MgCl_2$	11,500	1,600
NaCl	8,400	850
Synthetic sea salt	59,600	850
Sea water	No cost	

The rejection of nutrients by three kinds of these DS can achieve moderate to high performance. The dilution of DS is still debated since it need further recovery or in other words the FO process is perceived as a ‘pre-treatment’ process. The diluted sea water is possible to be discharged into the sea and no need for regenerating the draw solution (Xue et al., 2015). A sodium chloride and magnesium chloride are possible to discharge into the sea because their source also from the sea as shown in **Table 2.4**. However, further study of regeneration especially magnesium chloride is desired to conduct. The simultaneous fresh water can be recovered from wastewater effluents using forward osmosis membranes.

5.3.3 FUTURE HANDLING OF DILUTED DRAW SOLUTION AND CONCENTRATED FEED SOLUTION

Membrane bioreactors (MBRs) that operated with low pressure such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) are produce product which produce non potable reuse water, use hydraulic pressure and in limit condition to reject low molecular weight constituents e.g. trace organic compound, ions and viruses (Ottoson et al., 2006). Conversely, the FO have advantages such as low membrane fouling, can act as multiple barrier treatment for indirect and direct potable reuse, excellent rejection of macromolecules, trace organic compound and ions and just use osmotic pressure (Holloway et al., 2015). The RO system is high susceptibility to the membrane fouling and scaling, therefore need intensive chemical cleaning that increase treatment cost and decrease membrane lifetime.

The integrated/hybrid process is processes where one of more membrane processes are coupled with other unit process (Ang et al., 2015). The hybrid FO-NF or FO-RO or UF-FO-MBR can reduce weakness in certain process by other processes in the integrated/hybrid system. A combined FO/RO model was developed by Cath et al. (2009) that can be configured to either increase water flux through the RO system (constant energy) or decrease the energy demand of the RO system (constant flux). The FO could be used to increase the production of an existing desalination facility. Diluting the RO influent while maintain a constant pressure on the RO will increase the flux through the membranes, and thus increase permeate flow. The four major benefits of dilution of sea water as draw solution from permeate water of impaired water (FO process) before desalination (RO process) are lower energy desalination of seawater, multi-barrier protection of drinking water, reduction in reverse osmosis membrane fouling due to impurities in impaired water and an opportunity for safe and beneficial reuse of impaired water (Cath et al., 2010). Dilution of saline water provides another method to reduce energy demand during RO desalination of highly saline water; dilution decrease the osmotic pressure that must be overcome to produce RO permeate.

The relatively low salinity of most impaired water makes them good candidates for use in diluting saline streams before desalination. The FO process as pretreatment step, can significantly reduce the membrane fouling, which is one of the most challenging problems in membrane processes for wastewater treatment, resulting in lower treatment cost (Zhao et al., 2012). Pilot system modelling was performed by Holloway et al. (2007) to estimate the power and membrane area requirement to treat 190.000 L/day of centrate. FO system consume constant power whereas RO system consume power which increase to achieve certain recovery. The FO system required more membrane area than RO system because the driving force for mass transport constantly decrease as FS became more concentrated and DS was diluted. RO system need constant membrane area. The economic calculation for FO-RO in seawater desalination (Blandin et al., 2015) resulted that FO-RO hybrid can be beneficial comparatively to stand-alone RO, only for high energy cost and/or substantial cost savings. A flux threshold of 30 L/m^2h was defined for FO economic viability. Unfortunately, current membrane do not match the fixed minimum flux threshold.

Furthermore, the concentrated feed solution can used for beneficial purposes e.g. further dewatering to produce high grade soil fertilizer (Holloway et al., 2007). Nutrients (primarily nitrogen and phosphorus) have been successfully harvested from wastewater and used as plant fertilizers in-place of conventional chemical fertilizers (Lubello et al.,2004). Other ways to manage the concentrated feed solution are returned to a wastewater treatment plant (Cath et al., 2010), recycled of nutrient for industrial and agriculture contribution (Liu et al., 2011), treated anaerobically to recover energy in form of biogas, and recovery of nutrient such as magnesium ammonium phosphate/MAP ($MgNH_4PO_4.6H_2O$) or struvite crystallization process (Doyle and Parsons, 2002; Song et al., 2007; Core et al., 2007; Diwani et al., 2007; Xie et al., 2014, Zhou et al., 2015)

5.4 CONCLUSION

To knowing the feasibility of $MgCl_2$ as DS in FO process can indicated from nutrient rejection and water flux performance that compare with other DS. The constant performance of membrane after cleaning can support the membrane's longevity that decrease the membrane material cost. The $MgCl_2$ compete tightly with NaCl and present better performance than seawater on nutrient rejection. The material cost of $MgCl_2$ was 1.3 times higher than NaCl. The dilution factor of $MgCl_2$ was 1.07 times higher than NaCl and 1.67 times higher than synthetic sea salt. The total cost of $MgCl_2$ was 1.2 times higher than NaCl. The applied of sea water is feasible due to abundant source and no cost for raw material, but cost-efficient if applied near coastal area. The hybrid technology of FO with other treatment and the handling of concentrated nutrient in FS can applied to produce clean water and other beneficial purposes, respectively.

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Chapter 6

CONCLUSION AND FUTURE WORKS

6.1 CONCLUSION

The remarkably technology forward osmosis is applied to reject the nutrients from secondary treated effluent using magnesium chloride as draw solution. The nutrient rejection was successfully achieved by the moderate velocity of cross flow 0.25 m/s. The higher velocity that resulted higher flow rate is possible to increase random or mixing flow condition. This condition increase the potential back-movement of nutrients from membrane active layer surface into a bulk of FS. Therefore, it restrain nutrient to transfer to the DS side and increase nutrient rejection. Temperature had less of an impact on nutrient rejection than the velocity, but temperature did have an effect on the water flux. The temperature on 25°C exhibited good nutrient rejection.

A nutrients consist of nitrogen (nitrite, nitrate, and ammonium) and phosphorus (phosphate) in feed solution were rejected with an efficiency of more 95% except the nitrite. The nutrient rejection is successfully achieved by the magnesium chloride 2 M as draw solution on forward osmosis process. The characteristics of the ionic nutrients, such as ion size and ion charge, affect the performance of rejection. Furthermore, concentration difference between the dissociated ions of $MgCl_2$ in the DS plays a significant role in rejecting ion nutrients in the FS. Interestingly, using $MgCl_2$ as DS, due to the high difference of diffusion constant between Mg^{2+} and Cl^-, the Cl^- more dominantly to diffuse from DS to FS. The chloride diffusion higher than magnesium diffusion that support nutrient rejection. The increasing concentration difference between FS and DS generates higher water flux and reverse solute flux. The lower reverse solute flux and high rejection of nutrient on membrane HTI-NW as compared to HTI-ES, indicating better efficiency of membrane HTI-NW owing to the membrane morphologies, but still need improvement on increasing water flux. The water flux in membrane HTI-NW achieved lower 7.55–9.61 L/m^2h than in membrane HTI-ES that exceeds until 13.58-15.10 L/m^2h.

The cleaning process mostly could achieve similar performance on nutrient rejection as well as before cleaning that promisingly could extending membrane's longevity and reducing cost material. A compete price of $MgCl_2$ with NaCl was considered with its high performance on nutrient rejection. The hybrid technology of FO with other treatment and the handling of concentrated nutrient in FS can applied to produce clean water and other beneficial purposes, respectively.

6.2 FUTURE WORKS

Some several important consideration should be considered in the FO system by $MgCl_2$ for removing nutrient:

1) Investigate the concentrated feed solution contaminated by low magnesium chloride due to reverse solute
2) Further experiment should be conduct with considering that FO as pre-treatment, especially in clean water production term, which need further treatment of recovery $MgCl_2$ from diluted draw solution
3) Life cycle cost of magnesium chloride possible to conduct when it applied in forward osmosis to remove nutrient from wastewater effluent.