Forward Osmosis Using Organic Cationic Draw Solutions for Water Recovery

by

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ABSTRACT

Title:	Forward Osmosis Using Organic Cationic Draw Solutions for Water Recovery
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Forward Osmosis (FO) is an emerging technology which has potential to operate with minimum energy input. High performance of FO systems depend on the availability of a suitable Draw Solution. Different types of Draw Solutions have been proposed, however; choosing a suitable one is still a developing area within the FO field. There is an urgent need to explore new materials in order to develop an efficient FO system. The current study aims at investigating the performance of three Draw Solutions namely, L-Alanine, DADMAC and PolyDADMAC as osmotic agents for FO. These organic cationic solutions can be used as extraction agents of water from poorer quality organic solutes such as fumaric acid solution produced in a continuous flow microbial fermentation process. The performance of the three Draw Solutions was evaluated by measuring the water flux and reverse solute diffusion at different concentrations. The viability of reconcentration of the diluted Draw Solutions was also investigated using Nanofiltration system. The performance and the efficiency of the Draw Solutions were studied via two separated bench scale systems of FO and Nanofiltration. Both Cellulose Triacetate (CTA) and Thin Film Composite (TFC) aquaporin protein FO membranes were employed under different orientations in FO set up operated for 24 hours or longer. In this study, NF90 membrane was used for reconcentration the Draw Solutions. A series of experiments were conducted to obtain the best water flux and reverse solute diffusion under various influencing operating conditions.

The experiments were designed to achieve three objectives, i.e. (i) optimum operating conditions for FO system, (ii) optimum operating conditions for the reconcentration system, and (iii) implementation of the optimum operating conditions of the FO system for water recovery from a fumaric acid solution produced by a simulated industrial fermentation process. In the initial stage, L-Alanine Draw Solution demonstrated that it was the most viable agent for FO. It was established that L-Alanine Solution at 0.085 g/mL concentration achieved the highest initial water flux and the lowest reverse solute diffusion through both CTA and TFC aquaporin protein FO membranes. In the second stage, a Nanofiltration system was proven to be effective in the reconcentration of the diluted L-Alanine Draw Solution. The average rejection of L-Alanine ions achieved by NF90 membrane was 96.00%. Drawing on the previous results, the third stage was used to investigate the viability of the FO system in water recovery from fumaric acid solution produced by continuous microbial fermentation process using L-Alanine as a Draw Solution. The reduction of water content of the fumaric acid solution made it to concentrate by 26.00% and 19.80% in 32°C and 17°C, respectively. Consequently, FO technology is an effective way to concentrate a fumaric acid solution produced by continuous microbial fermentation process. Based on the results, it is recommended that L-Alanine should be proposed in the FO process according to its reliability and effectiveness as a viable draw agent. TFC aquaporin protein membrane is also recommended to be used in recover the water from fumaric acid solution produced by fermentation processes. Further studies should be done to investigate the viability of FO in water recovery from advanced application such as downstream bioprocessing.

Keywords: Forward osmosis, water recovery, draw solution, organic cationic, PolyDADMAC, DADMAC, L-Alanine, aquaporin, Fumaric acid, downstream processing, fermentation.

DECLARATION

I **Mohammed J A Hamad**, hereby declare that this dissertation which I submit to University of Pretoria for examination in consideration of the award of a Master of Engineering (Water Utilisation Engineering) is my own original work. This work has not been submitted by me for any degree at this or other institutions.

Signature of candidate …………………………… Date ……………………………

DEDICATION

I dedicate this dissertation to my parents, sisters and brothers for their love, motivation and support. May Allah bless all of you.

I also dedicate this dissertation to my late brother soul, Khaled. I miss you so much. Rest in peace till we meet again in heaven insha’a Allah. I love you forever.

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LIST OF ABBREVIATIONS AND ACRONYMS

BDSA	2,2’-Benzidinedisulfonic acid
CECP	Cake enhanced concentration polarisation
CP	Concentration polarisation
CTA	Cellulose triacetate
DADMAC	Diallyldimethylammonium chloride
ECP	External concentration polarisation
DI	Deionized
FO	Forward osmosis
GHM	Grams per square meter per hour
HPLC	High performance liquid chromatography
HTI	Hydration technology innovation
ICP	Internal concentration polarisation
LHM	Litres per square meter per hour
MF	Microfiltration
MPD	m-Phenylene diamine
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
OMBR	Osmotic membrane bioreactor
OP	Osmotic pressure
PAA-NA	Polyelectrolyte polyacrylic acid sodium salts
PAI	Polyamide-imide
PAH	Poly(allylamine hydrochloride)
PAN	Polyacrylonitrile
PBI	Polybenzimidazole
PES	Polyethersulfone
PolyDADMAC	Poly(diallyldimethylammonium chloride)
PPD	p-Phenylene diamine
PRO	Pressure related osmosis
PSf	Polysulfone
PSS	Poly(sodium 4-styrene sulfonate)
PVP	Polyvinylpyrrolidone

RO	Reverse osmosis
RSD	Reverse solute diffusion
TDS	Total dissolved solids
TFC	Thin film composite
TMA-CO_2	Thermolytic trimethylamine carbon dioxide
TMC	Trimesoyle chloride

CHAPTER 1

Introduction

1.1 Research Rationale and Motivation

Separation and extraction processes of purified water from industrial products and polluted streams have been a subject of wide range in science and research. The debate among researchers continues posing the question as to whether the proposed processes are optimal in solving the water treatment and recovery from otherwise highly polluted water. Water recovery processes use to minimise the water content, consequently concentrate the final product. The water recovered from aqueous solutions can be used directly or after post treatment. Furthermore, water extraction processes are widely employed for conventional applications such as seawater desalination, industrial water treatment, wastewater streams, dewatering the sludge, etc. Water extraction processes are also used in other variable solutions such as food streams, protein concentration, peptides and bioprocessing (Nguyen et al. 2013; Mentzel et al. 2016).

The available technologies in water extraction include mechanical and pressure driven membrane processes. The mechanical processes involve centrifugation and filter press and the pressure driven processes include Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO). These extraction technologies have been used in various applications for water extraction purpose for decades (Baker 2012; Nguyen et al. 2013). However, these technologies are limited due to high energy requirement during the operation and irreversible membrane fouling (Nguyen et al. 2013; Nicoll 2013). In order to overcome the current limitations, a new proposal has been made which offers low energy consumption and longer operation time for the membrane system. Forward Osmosis (FO) is the new osmotically driven membrane system which allows movement of water molecules up-gradient to an extractable Draw Solution using a non-degradable, natural, or artificial draw solutes. FO is a natural process which occurs due to the variance of osmotic pressure between the two solutions separated by semi-permeable membrane. The process can be utilised in water recovery and concentration stream applications (Zhao et al. 2012; Nicoll 2013; Alsvik & Hägg 2013).

The advantage of FO lies in the low operation cost where a minimal energy consumption is required compared to pressure driven membrane processes. The intensive energy consumption of operation in pressure driven membrane processes comes from the high quantity of hydraulic pressure which is needed to overcome the osmotic pressure of solution to create the flux. However, during the FO process the osmotic pressure of the solution itself works as a driving force to create the flux across the membrane (Yong 2012). In contrast, the absence of applied hydraulic pressure during FO system minimizes the foulants accumulation which results in easy removed reversible fouling. (Cai & Hu 2016).

Although FO system is a promising technology, concentration polarisation (CP), reverse solute diffusion, and membrane fouling still pose challenges relating to the efficiency of FO. Mitigating these challenges can be achieved through the improvement of FO membrane and the development of more effective Draw Solution. (Yong 2012). Besides that, reconcentration the diluted Draw Solutions by energy efficient and commercial ways forms another challenge to the FO system. Proper processes such as low pressure driven processes are utilised in the Draw Solutions reconcentration stage, which is where the energy loses occur in the FO system, to minimize the energy consumption. This dissertation investigates the appropriate Draw Solutions, which may partially address the challenges facing FO.

1.2 Problem Statement

The fundamental requirement for effective FO lies in selecting a suitable Draw Solution. The competent Draw Solution is a key factor of high performance and viability of FO technology, consequently mitigating environmental externalities. In terms of the environment, Draw Solution is required to be environmental friendly, non-toxic and stable. In terms of performance, the characterisation of the Draw Solution is based on the size and function of the molecular size. On the one hand, the Draw Solution is characterised by a large molecular size enough to minimise the reverse solute diffusion through the active layer of the membrane. On the other hand, it is required to be of a small molecular size, which is enough to alleviate the effect of Internal Concentration Polarisation (ICP) inside the support layer of the membrane. Furthermore, the ability of the Draw Solution to produce high osmotic pressure for high water flux and be easily reconcentrated by techniques at hand is also required (Shaffer et al. 2015). Among these several and sometimes conflicting properties, a wide range of materials have been proposed as novel Draw Solutions such as inorganic and organic solutes, magnetic nanoparticles, polymers and others (Cai & Hu 2016). However, choosing the optimal draw osmotic agent is still debatable issue. The question arises as to whether the appropriateness of organic cationic draw solutions may propose viable solution for FO.

1.3 Project Aim and Objectives

This dissertation aims at investigating the performance of three organic cationic solutions namely, L-Alanine, DADMAC and PolyDADMAC as osmotic agents for FO. Thereafter, utilises the competent Draw Solution to recover the water from fumaric acid solution produced by continuous microbial fermentation process via FO. This has been realised by the following specific objectives:

i. Exploring the FO performance under the influence of various operation conditions, (including Draw Solution type, Draw Solution concentrations, membrane type, membrane orientations, and the pattern of pumping the solutions)
ii. Identifying the optimum operating conditions for FO system among the previous operating conditions, where the highest water flux and lowest reverse solute diffusion were achieved.
iii. Evaluating FO system for recovering water from fumaric acid solution produced by continuous microbial fermentation process.
iv. Identifying the impact of membrane fouling and changing the temperature on concentrating fumaric acid solution produced by continuous microbial fermentation process.
v. Investigating the availability of reconcentration of the diluted Draw Solution using stirred dead end NF membrane cell.

1.4 Scope

The scope of this dissertation focuses on three organic cationic solutions, namely DADMAC, PolyDADMAC, and L-Alanine, within two focal points. The first investigates the most suitable solution to be used as a draw osmotic agent in FO. The second investigates whether the water recovery from fumaric acid solution produced by continuous microbial fermentation process can be achieved via FO.

The first focal point has been dealt with by testing the three organic cationic solutions with different concentrations in order to determine the most efficient Draw Solution for water extraction application. Several bench scale experiments were performed using CTA and TFC aquaporin protein flat sheet FO membranes. The diluted Draw Solutions were tested for their reconcentration potential by using NF membrane process.

The second focal point was addressed by using L-Alanine at a concentration of 0.085 g/mL as a Draw Solution and the TFC aquaporin protein flat sheet membrane in FO set up. L-Alanine at a concentration of 0.085 g/mL achieved the highest distilled water flux with the lowest reverse solute diffusion through the TFC aquaporin protein flat sheet membrane. Besides that, diluted Draw Solutions of L-Alanine was effectually reconcentrated by NF system. The average ion rejection of L-Alanine by NF90 membrane was 96.00%. The distilled water Feed Solution was replaced with fumaric acid solution produced by continuous microbial fermentation process to examine the viability of L-Alanine Draw Solution in extracting the water from it via FO process.

1.5 Main Findings

The main findings of this dissertation are categorised according to three phases of experiments which in the first phase intended to identify the best water flux and the lowest reverse solute diffusion various operating condition. Fundamentally, this phase identifies L-Alanine solution with 0.085 g/mL concentration as the best Draw Solution. L-Alanine with 0.085 g/mL concentration achieved the highest initial water flux through both CTA and TFC aquaporin protein flat sheets membranes with 22 $\mathrm{L/m^2}$. hr (cited to as LMH) and 17 LMH, respectively. The same concentration of L Alanine had the lowest reverse solute diffusion across both membranes. It changed from 0.05 $\mathrm{g/m^2}$. hr (cited to as GMH) at the beginning of experiment to 0.01 GMH at the end of experiment.

The second phase investigates the ability of concentration the diluted Draw Solution produced in FO system. In this phase it was demonstrated that Nanofiltration system was effective method to reconcentrate the diluted L-Alanine solution. The average rejection of L-Alanine ions achieved by NF90 membrane was 96.00%.

The third phase explores the viability of the FO system in water recovery from fumaric acid solution produced by continuous microbial fermentation process experiments. This phase was intended to establish that FO is an effective way to recover the water from the feed solution by using L-Alanine as a Draw Solution. As a result, Fumaric acid solution produced by continuous microbial fermentation process concentrated by 26.00% and 19.80% at 32℃ and 17℃, respectively. In the same vein, high residual concentration of glucose in the biological process limited the high water recovery from the fumaric acid feed solution. The limitations were due to the reduction of the net driving osmotic force through the membrane.

1.6 Research Outline

- Chapter 2 investigates previous studies pertaining to FO technology and membrane processes and their structure, recent developments in materials and preparation of methods of FO membranes, various types of responsive and non-responsive Draw Solution, and the limitations of FO performance.
- Chapter 3 presents the experimental plan, experimental protocol and set up of both FO and NF systems, all materials and analytical methods used to conduct the research.
- Chapter 4 summarises the experimental findings and discussions of each FO system, reconcentration system, and the potential application which is concentrate fumaric acid solution produced by continuous microbial fermentation process via FO system.
- Chapter 5 presents the conclusions of research and important recommendations for future works

CHAPTER 2

Literature Review

This chapter presents a brief background of membrane technologies in separation and extraction processes. It also provides for the principles of FO technology, FO membrane structure and the materials, which are used to prepare the membrane. Furthermore, the chapter details information on a wide range of materials used as draw agents. The limitations of FO process including concentration polarisation, reverse solute diffusion (RSD), and membrane fouling are discussed.

2.1 Background

Membrane Technology has been used as a separation and purification tool since the dawn of human civilisation (Mohanty & Purkait 2011). However, utilising the membranes in large scale industrial applications was considered seriously about 1970 for desalination and purification purpose to produce high quality water (Strathmann et al. 2006). Membrane processes are applied to control the permeation of the mixture components movement by allowing specific components to go through the membrane structure freely, whilst trapping the other components behind the membrane (Baker 2012).

Efficient membrane processes are necessary to supply the residential and industrial sectors with high quality water, to remove toxic contaminants and to recover valuable components from the industrial downstream. Membrane processes are utilised mainly in three areas ranging from traditional to advanced applications. The first area covers wastewater treatment, desalination applications and production ultrapure water. The second area focuses on separation and purification the valuable components in food and medication industry. The third area includes the usage of membrane in medical devices and artificial organs such as artificial kidney (Strathmann et al. 2006; Ansari et al. 2017). Nowadays the use of membrane technology in petrochemicals and production green energy is rabidly increasing. However, more contributions are still needed in this area to enhance the performance of membranes in advanced applications (Mohanty & Purkait 2011).

The characters of membrane processes make it favourable compared to other separation processes such as distillation, crystallization and ion exchange. Membrane processes are more energy efficient and easy to operate than the others. It works at ambient temperature and without adding chemicals. Therefore, membrane processes are attractive tools compared to conventional separation processes because it can be used to separate and purify the temperature-sensitive components in medication industry and downstream processing.

Membranes can be natural membranes, which are part of living objects such as cells membrane, or man-made synthetic membranes. The early studies of membranes were done using natural materials such as gum elastics and animals bladders. Natural membranes are characterised with high efficiency of transport molecules and minimal energy consumptions. The first study on membrane permeation was recorded on the middle of the eighteenth century by Nollet. He noticed that ethanol passes pig's bladder while it was used as a barrier between water-ethanol mixture on one side and pure water on the other side. This early observation demonstrated the relations between mass transport through semi permeable barriers and osmotic pressure. More studies on osmotic phenomena and mass transport through semipermeable membranes were carried out by Fick and van't Hoff. Fick (1855) explained that the liquids diffusion was a result of concentration gradients. Later, van't Hoff (1887) introduced the osmotic pressure equation of dilute solutions based on thermodynamic explanation (Strathmann et al. 2006).

In the first decade of the twentieth century membrane preparation entered a new phase. A new technique of preparing synthetic membranes was developed by Bechhold (1908). He prepared the first synthetic membrane by digging a filter paper in a solution of nitrocellulose dissolved in glacial acetic acid. Subsequent research utilised Bechhold's membranes, however with different pore sizes to study the diffusion phenomena and separate molecules from aqueous solutions. Rapid developments of synthetic membranes manufacturing occurred in conjunction with the progress of polymer chemistry. Various structures of synthetic polymeric membranes have become available in the industry with efficient mass transport properties and excellent stability. Polymers such as polyamide, polyethersulfone, polysulfone, polyethylene, etc. were used in synthetic membranes manufacture. These synthetic polymeric membranes demonstrate high mechanical, thermal and chemical stability compared to the membranes based on cellulose asters. However, the milestone of membrane development was the preparation of the first reverse osmosis membrane using cellulose acetate. In 1964 Loeb and Sourirajan prepared an anisotropic cellulose acetate membrane for reverse osmosis desalination application with high permeability and high solute rejection under moderate hydrostatic pressures.

The permeability of membrane for certain component is defined as the transport rate of that component through membrane structure under particular conditions of pressure, concentration, temperature and/or electric effect. The transport mass rate of different components depends on many parameters such as membrane structure, size and concentration of permeating components, type of electrical charge of both membrane and components and the driving force (Strathmann et al. 2006). The diversity of membrane processes results from the use of different membrane structures and driving forces such as pressure, concentration, thermal, and electrical gradients across the membrane. The electrical potential driving force targets only the charged elements in the queues solutions. However, other driving forces inducing pressure, concentration, and thermal gradients affect equally on all the solutions components. Membrane processes classification based on driving forces demonstrates in table 2.1 (American Water Works Association & James Edzwald 2011).

Table 2.1: Classification of the membrane processes by driving force

Driving force	Examples of membrane processes
Pressure gradient	MF, UF, NF, RO.
Concentration gradient	Dialysis, pervaporation, FO.
Temperature gradient	Thermo-osmosis, distillation (thermal).
Electrical potential	Electrodialysis, electro-osmosis.

Choosing an appropriate membrane process depends strongly on the composition feed solution. For example, in seawater desalination applications the pressure driven membrane processes especially RO and NF compete with distillation and electrodialysis processes. This is due to the significant heat energy required for distillation process as well as high electrical energy for electrodialysis. Moreover, the electrodialysis process can not eliminate viruses, bacteria and other fine particles from the feed solution which can be removed effectively by RO and NF. In contrast, RO and NF are more commercial, energy efficient and easy to handle. Pressure driven membrane processes are run easily and achieve high quality final products at ambient temperature without any change or degradation of the sensitive components. In this regards, in some stages of wastewater treatment and surface water purification, the MF and UF processes are recommended to be used instead of conventional processes such as flocculation and sand bed filtration in order to achieve higher quality of the final product; similarly for separation and concertation of food products, industry downstream and medical applications.

Nonetheless, membrane processes still face challenges which limit its performance. The high hydraulic pressure applied during pressure driven membrane processes overstrains the membrane and reduces the long term reliability. The formation of irreversible fouling on the membrane surface declines the function of membranes. Pre-treatment processes are required to eliminate the effects of the fouling which increases the energy and the cost. Concentration polarisation is also considered as a major contributing factor forming serious constraints on the membranes function (Strathmann et al. 2006).

Recently, significant progress has been made in developing the membrane processes to improve the performance, the stability, and the minimal need of energy. The desirable development contributes to the required increasing water flux at low energy and achieve long life of membranes (Li et al. 2008). The development in membrane processes enticed engineering and membrane technology research for the potential separation efficiency such as FO. FO has invigorated membrane industry strongly for its merits including low or no energy consumption, high water flux, solute rejection, and less prone to membrane fouling (American Water Works Association & James Edzwald 2011; Nicoll 2013). The purpose of this work is focused on FO process and more detailed information is provided in the following sections.

2.2 Forward Osmosis Theory

The principle of osmosis phenomenon is transmission of water molecules through semi permeable barrier from region of low solute potential to region of higher solute potential. It is the movement of liquid water from a low osmotic pressure region to higher osmotic pressure region. This is illustrated by placing two compartments with different osmotic pressures separated by a semi permeable membrane, the water molecules move spontaneously to the compartment with higher osmotic pressure till the balance is achieved. The osmosis phenomenon takes place widely in nature in trees and plants to get the water up from the soil through its roots. This natural process has recently attracted more attention for its potential use in industrial processes (Nicoll 2013).

Osmosis phenomenon was first explained in 1897 by the physicist Gibbs according to the water potential of the system. It has been demonstrated that the water potential of solution decreases gradually by adding more solutes. The water potential (Ψ_w) then becomes the main parameter that controls the water flux across the membrane and can be expressed as

$$\Psi_w = \Psi_p + \Psi_s + \Psi_g + \Psi_m \qquad \text{Eq. 2.1}$$

where is Ψ_p is the pressure potential (hydrostatic pressure P);

Ψ_s is the solute potential;

Ψ_g and Ψ_m are the gravitational and matric potentials, respectively. These parameters are neglected due to their small magnitude.

It is apparent from this equation that the water potential of the system is directly proportional to the concentration of solute and external hydrostatic pressure. The dissolution occurs by binging solute molecules to water molecules via hydrogen bonds. Some of the potential energy of the system is consumed to create these hydrogen bonds which lead to decrease in the total water potential. Increasing the solute concentration in the solution leads to more energy consumption and consequently a significant decrease in the water potential. Difference of water potentials between two solutions produces unbalanced force which grants water molecules the tendency to move forward to the side with low water potential (high solute concentration) seeking the balance (Boundless Biology Boundless 2016).

Fig 2.1 illustrates the movement of water molecules through semi permeable membrane in many cases. When the solute is added (Fig 2.1, b) or external positive pressure is applied on the left side of the U-tube (Fig 2.1, c), the water shifts to the right side. Shifting of water molecules occurs due to the osmotic pressure of solutes or the external applied pressure, respectively. Conversely, if the external applied pressure becomes negative (Fig 2.1, d), the water will move to the left side of the U-tube. The mechanism of water flux through the membrane structure in FO process (as an example of osmotically driven processes) is demonstrated clearly in Fig 2.2.

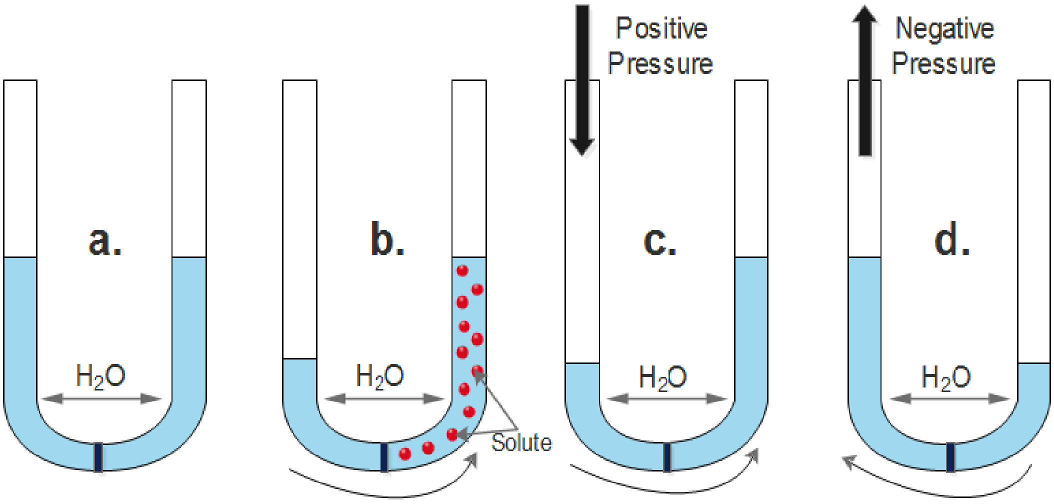


Figure 2.1: Water flux through semi preamble membrane under various condition: (a) osmotic equilibrium, (b) osmotically driven process, (c) and (d) pressure driven process

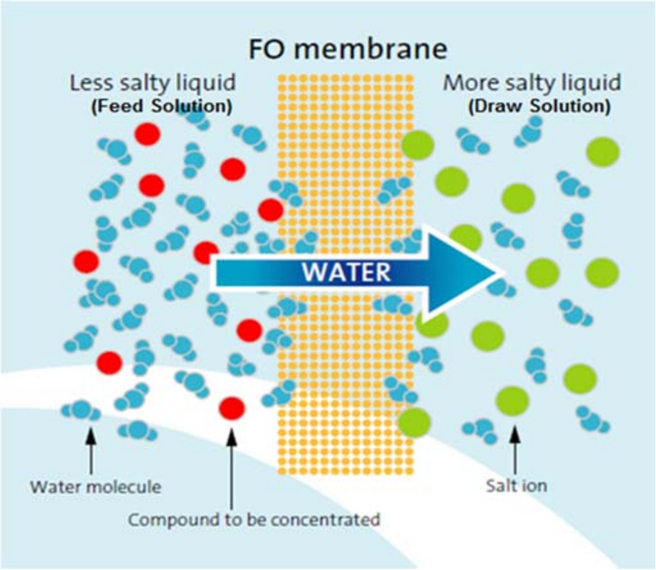


Figure 2.2: Mechanism of water flux through the membrane in Forward Osmosis

The viability of FO technology either in bench scale or pilot scale has been explored by many of academic institutes and commercial organisations. FO process has been involved in wide applications including water extraction applications, desalination, wastewater and sludge treatment, food concentration, pharmaceutical products dehydration, power generation, resource recovery and others (Nicoll 2013; Chung et al. 2012; Zhang et al. 2017).

2.3 FO Membranes- Structure/Morphology

Morphological characteristics of membrane affect strongly the performance of membranes. Membranes generally can be categorised into isotropic membranes and anisotropic membranes. The classification occurs based on the similarity of layers composition and structure, besides of size and distribution of the pores. Isotropic and anisotropic membranes are illustrated in Fig 2.2

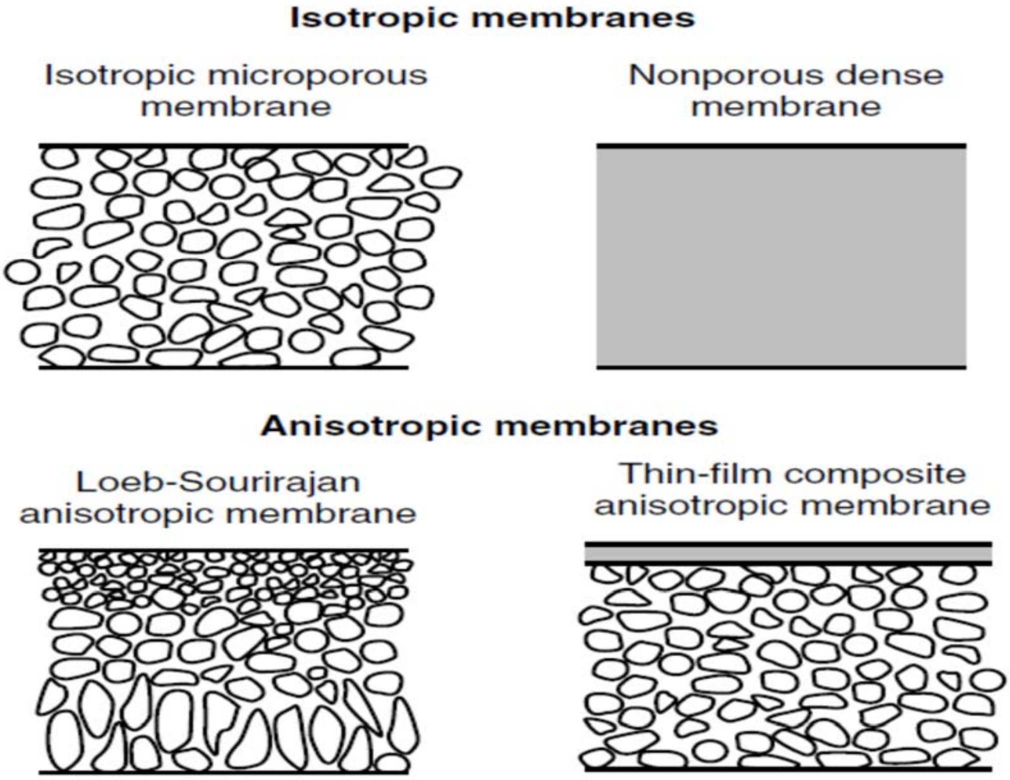


Figure 2.3: Schematic diagrams of the principal types of membranes (Baker 2012)

2.3.1 Isotropic Membranes

Isotropic membrane is a completely homogeneous thin membrane which is composed of one layer of similar molecules in the structure. It can be either microporous membrane or nonporous membrane.

2.3.1.1 Microporous Membrane

A microporous membrane is composed of a symmetric membrane which contains high percentage of pores as illustrated above in figure 2.2. These pores are randomly placed in a manner forming interconnected voids. The size of these pores ranges from 0.01 to 10 µm in diameter. The separation process using microporous membrane is a function of solute particles size and pore size distribution. Solute particles with diameter larger than 10 µm are completely hindered to cross the membrane, meanwhile the particles with diameter much smaller than 0.01 µm will pass unrestrictedly through the membrane. Particles with diameter larger than the smallest pores and smaller than the largest pores would be partially rejected as a result of the randomly distribution of the pore size (Baker 2012). Microporous membranes are also used effectively, besides FO process, in liquid separation applications by means of a sieving technique as in case of MF and UF processes (Jaffrin 2015).

2.3.1.2 Nonporous Membranes

A nonporous membrane is a symmetric dense film with relatively low permeant flux compared to the permeant flux in microporous membrane. The diffusion of the components of the mixture across the dense membrane require an external driving force. The driving force can be applied pressure, concentration gradient, thermal gradient, or electrical potential.

The mass transport through the membrane is a function of both the diffusivity ratio of the liquid and the solubility ratio in the membrane materials. In other words, the dense membrane can separate molecules of mixture which have the same size if their solubility ratio in the membrane material is significantly different. Usually this type of membrane is used as an active layer of the anisotropic composite membranes to enhance the permeate flux (Baker 2012). Nonporous Membranes are also used effectively for RO, NF, and gas separation processes (Jaffrin 2015).

2.3.2 Anisotropic Membranes

Serious steps have been taken for the development of the structure of membranes to produce a stable membrane with high mass transport. One of these steps was the manufacturing of anisotropic membrane which became later the widest type of membranes used in water separation industries.

An anisotropic membrane is composed of a multilayer barrier, usually two layers. The top one is called active layer or top skin layer, and the bottom one is called the support layer. The Active layer must be extremely thin dense layer to provide high flux. Meanwhile, the support layer must be porous sublayer and thicker to provide the mechanical strength to membrane thickness. The anisotropic membranes are divided to two types based on the homogeneity of the layers, namely integrally skinned asymmetric membranes and composite membranes. In the integrally skinned asymmetric membranes, the material of the active and the support layers are the same. In the composite membranes, the material of the active layer and support layer are different. Choosing the materials separately to prepare the layers of composite membrane can enhance the overall performance of the membrane. Enhancing the performance occurs by gaining the merits of various materials in one membrane (Baker 2012; Khulbe et al. 2008).

2.4 FO Membranes - Materials, Preparation

Both chemical and physical characteristics of membranes materials play an integral role in the performance of membrane processes. High performance of membranes can be obtained by considering significant characteristics during the materials manufacturing stage. These characteristics including membrane selectivity, chemical resistance, permeability, mechanical stability, and thermal stability. Membrane with high selectivity causes low permeability and low water flux; therefore, membrane surface area is needed to be increased to overcome this issue. In contrast, membrane with low selectivity causes high permeability. This option leads to combine multi units to achieve products with high quality results, which require more energy and cost. The manufacturing of the layers of FO membranes requires the use of either or both type of raw materials including modified natural products and synthetic products. The diversity of membrane materials with various characteristics assists in selecting the compatible materials for each layer based on the transport mechanism across it (American Water Works Association & James Edzwald 2011; Li et al. 2008).

Two generation of synthetic membrane types are used in FO applications. The early generation had started since 1960s with preparation the first asymmetric membrane by Loeb and Sourirajan. In this period the majority of studies have been used the pressure driven membranes, especially RO membranes, for FO application. In 2000s serious attempts were recorded in the development of a new generation of membranes especially for osmotically driven process. The structure of new generation of FO membranes is quietly different than pressure driven membrane for better performance and high efficiency. Zhao et al. (2012) categorised the membranes based on the preparation technique to three types, namely phase inversion membranes, thin film composite (TFC) membranes, and chemically modified membranes (Zhao et al. 2012).

2.4.1 Phase Inversion Membranes

Phase inversion process is the most commonly method used in manufacturing the cellulosic and polymeric membranes. It is utilised in the preparation of both isotropic and integrally skinned anisotropic membranes. Phase inversion process is feasible for polymers which can be dissolved in a proper solvent or a mixture of solvents at certain temperature and then be casted to form a solid phase. Forming solid phase of membranes can be done by many techniques including solvent evaporation, thermal precipitation, etc. (Mohanty & Purkait 2011); (Khulbe et al. 2008). Increasing the polymer concentration in the casting solution and accelerating the evaporation rate of solvent leads to increase the layer density. Increasing density of the layers occurs especially in the preparation of the active thin layers of anisotropic membranes (Khulbe et al. 2008).

Cellulose acetate is the first material used in manufacturing of the early generation RO membranes via phase inversion process (Khulbe et al. 2008). It was chosen by Loeb and Sourirajan to prepare the first asymmetric membrane after the observations of its merits by Reid and co-workers in 1959 (Zhao et al. 2012). They reported that cellulose acetate films have higher salt rejection feature than other polymeric materials. The hydrophilic nature of cellulose acetate provides for the FO membranes a high water flux and low ICP. Besides that, it has the mechanical strength and the degradation resistance caused by chlorine. These advantages of phase inversion cellulosic membranes grant it to be a good competitor compared to the osmotic driven membranes for FO application. Moreover, Thorsen (2004) has reported that cellulose acetate membranes have the lower natural organic matter fouling compared to other hydrophilic membranes such as Polysulfone (PSf) (Zhao et al. 2012); (Alsvik & Hägg 2013).

However, some limitations should be considered in using cellulose acetate before utilising it in FO process. It is hydrolysed easily compared with TFC polyamide RO membranes (Zhao et al. 2012). As early as 1966, Kenneth Vos and others studied the hydrolysis of RO membranes formed by cellulose acetate. Several types of different buffers over pH range of 2-10 were used in the study. The membranes were approximately 60.00% porous and the pores diameter less than 1µm. Water and acetic acid were observed as products of the hydrolysis reaction. To overcome this disadvantage, chemical stability of cellulose acetate and cellulose triacetate membranes should be achieved by adjusting pH of the draw and the feed solutions in 4-7 range. The temperature should be also less than 35C (Vos et al. 1966).

The first FO membrane was commercially available by Chung research group in 2007. It was NF hollow fibre membrane manufactured from Polybenzimidazole (PBI) via phase inversion process. PBI has good characteristics in terms of mechanical strength and chemical stability. However, it is poor in salt rejections when the inorganic salts used as a Draw Solution. Therefore, PBI NF hollow fibre membrane was modified by adding polyethersulfone (PES) and polyvinylpyrrolidone (PVP) into the casting solution during the phase inversion process to improve the salt rejection of FO membrane. The modified membrane is commercially used under the tradename of dual layer PBI-PES/PVP membrane.

Recently, Chung research group (2010) has introduced cellulose acetate material in manufacturing FO membranes via phase inversion. Formation double dense active layers has incorporated to reduce ICP in the support layer of cellulose acetate membrane. The modification of membrane structure was done by using a hot water annealing as separation technique during the phase inversion process (Zhao et al. 2012). Fig 2.3 shows the structural comparison between FO membrane and RO membrane both prepared from cellulose acetate. FO membrane is thinner with porous open structure.

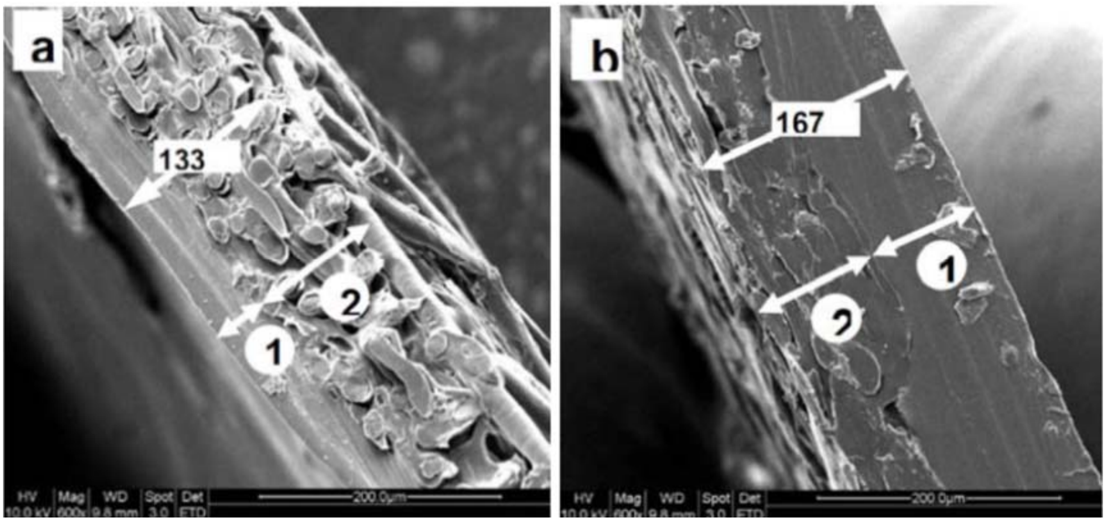


Figure 2.4: Cross sectional SEM images of (a) cellulose acetate FO membrane, (b) cellulose acetate RO membrane where 1 is active layer, 2 is support layer. adopted from (Nicoll 2013).

Currently, Hydration Technology Innovation HTI (Albany, Oregon, USA) provides for two commercial types of anisotropic CTA based membranes. Firstly, the integrally skinned asymmetric membrane with approximately 50 µm as overall thickness, and secondly the conventional TFC membrane with much thicker than 100 µm. These types are widely utilised nowadays in FO research especially the thin integrally skinned asymmetric one because it has high water flux compared with the thick conventional TFC membrane. Phase inversion process is utilised to prepare the support layer in both of these membranes using CTA material.

Other processes are used for preparation the active thin layer and manufacture a new FO composite membrane. Dip Coating and Interfacial Polymerization processes are used to achieve the purpose (Zhao et al. 2012; Khulbe et al. 2008).

2.4.2 Thin Film Composite Membranes

Same methods of manufacturing pressure driven composite membranes such as RO are followed in preparing the FO composite membranes. The porous support layers are prepared by phase inversion process and the selective thin layers by Dip Coating or Interfacial Polymerization (Zhao et al. 2012; Khulbe et al. 2008).

In **Dip coating process;** a dried porous support layer manufactured from appropriate polymer via phase inversion is dipped in bath of dilute solution of a different polymer. A thin layer of the latter polymer is deposited on the top of the support layer. After that the membrane is removed from the bath and the solvent is evaporated. Final product of the TFC membrane consists of porous support layer coated by thin dense polymeric layer is prepared (Khulbe et al. 2008). This method was used by Wang et al. (2005) in coating asymmetric membrane capsule utilised the FO technology to deliver poorly water-soluble drugs. The path consisted of a mixture of cellulose acetate, ethyl cellulose, and plasticizer dissolved in a mixture of acetone, alcohol, and glycerine solution (Wang et al. 2005). Same method was reported by Kumar et al. (2012) to coat the wall asymmetric membrane capsule and used it osmotic drug delivery mechanism (Kumar et al. 2012).

In **Interfacial Polymerization;** a porous support layer is coated on the top by a thin active layer of a polyamide via interfacial in *situ* polycondensation. It occurs when the porous support layer is dipped in an aqueous amine monomer solution (amine solution mixed with water). Then the pores on the surface are sealed with the same aqueous monomer solution. The extra solution should be removed from the top to adjust the level of polymerization. After that, the membrane is soaked in acid chloride monomer solution dissolved in hexane as an organic solvent. The amine monomer is easily dissolved in the organic solvent. However, the acid chloride is not soluble in the aqueous solution. Therefore, the polycondensation reaction of amine solution and acid chloride occurs at the boundary of the two phases to form a thin dense layer of polyamide. Preparation of TFC membranes by Interfacial Polymerization is illustrated in Fig 2.4 (Khulbe et al. 2008; Alsvik & Hägg 2013).

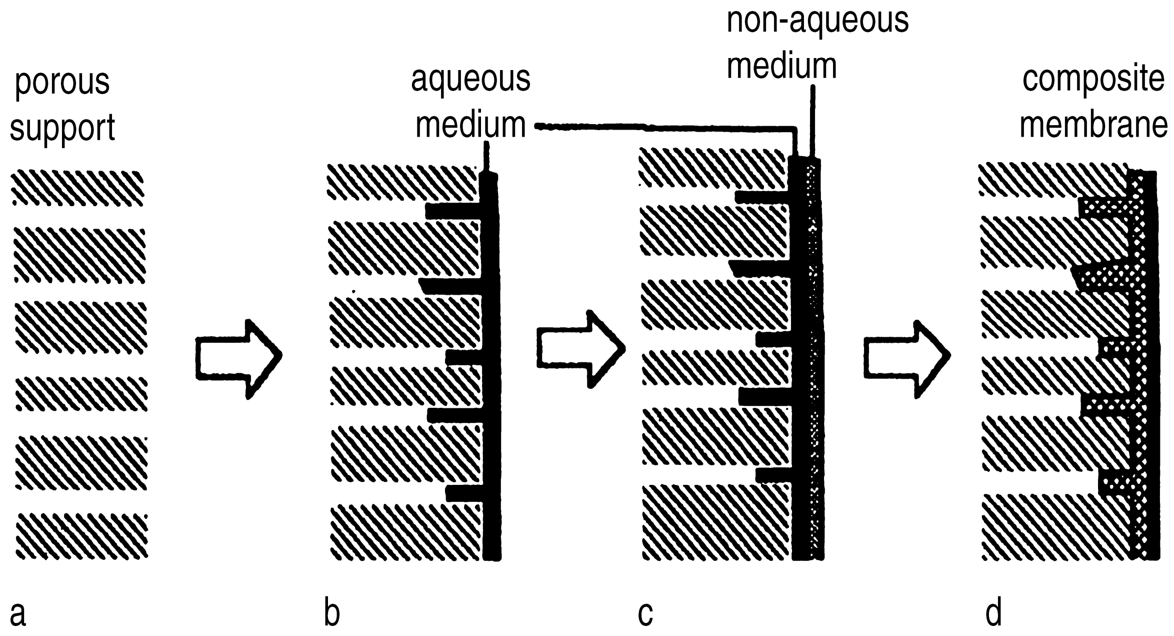


Figure 2.5: Step of thin film composite membrane formation via Interfacial polymerization. Adopted from (Khulbe et al. 2008)

Alsvik & Hägg (2013) have mentioned some of synthetic chemical materials which are involved widely in manufacturing the FO membranes such as CTA, PSf, PES, PBI, polyamide-imide (PAI), and polyamide. The PSf and PES have a quite same characteristics, yet the PSf has longer chain of aryl-SO_2-aryl units than the PES, as illustrated in Fig 2.5. Both of these polymers are used to prepare the porous support layer in the TFC membranes because of its suitable properties. It has high resistance of hydrolysis and thermal oxidative besides the good mechanical strengthen to reinforce the thin active layers.

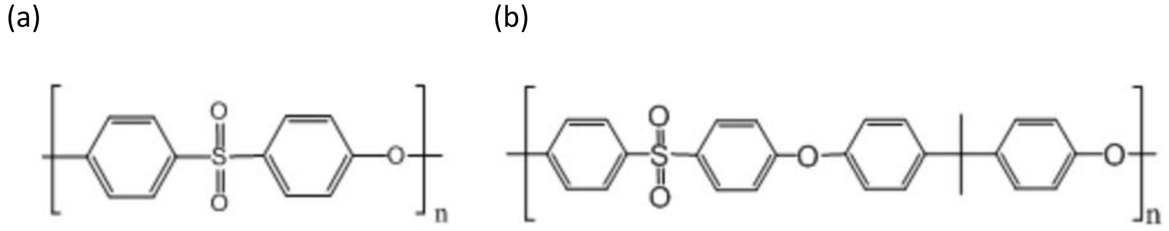
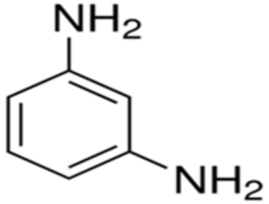
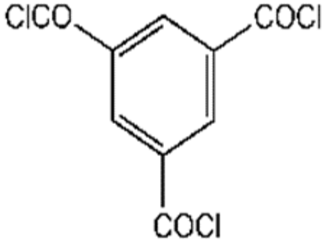
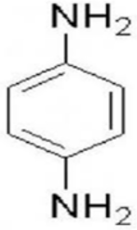
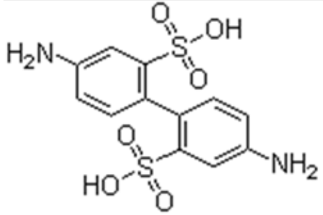
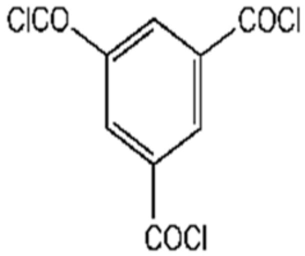


Figure 2.6: Chemical structure of (a) Polyethersulfone, (b) Polysulfone

Moreover, polyamides are the final products of the reaction between an amine monomer and an acid chloride monomer. It widely used to coat the porous support layer in the TFC membranes to display good performance. Deposit a thin active layer of polyamides based on the concept of Interfacial Polymerization was reported firstly by Cadotte. The process of Interfacial Polymerization described later. Another polymer PAI is commercially used under the trade name of Torlon®4000T. It is preferred to add it with other polymers during the manufacturing process of the membranes to enhance the membrane resistance against strong chemicals. Table 2.2 illustrates the amine-acid chloride combinations used in FO membrane preparation via Interfacial Polymerization process (Alsvik & Hägg 2013).

Table 2.2: Amine-acid chloride combinations used in FO membrane preparation via Interfacial Polymerization process.

Literature	**Active layer**	
	Amine	**Acid Chloride**
Tiraferri et al. (2011) has prepared thin active TMC-MPD layer via Interfacial Polymerization. This polyamide is commonly used in FO and Pressure Retarded Osmosis (PRO) applications. It provides high solute rejection and excellent water flux (Alsvik & Hägg 2013; Tiraferri et al. 2011). The porous support layer was prepared from the PSf casted on polyester nonwoven. It has been observed that changing the concentrations of the components affects the characteristics of the active layer. Water permeability through the layer increases by increasing the concentration of the acid chloride (TMC) or reducing the concentration of the Amine (MPD). However, negative impacts on the solute rejection have been observed in this case (Zhao et al. 2012).	 m-Phenylene diamine (MPD)	
Juhn Roh (2003) studied the effluence of physicochemical properties of the TFC membranes on the permeation performance. He used Interfacial Polymerization process but replaced MPD with PPD which has similar chemical composition but different structure. The final polyamide TMC-PPD product has lower molecular chain compared to TMC-MPD. It has been demonstrated that TMC-PPD provides lower water flux and higher solute rejection. This behaviour attributed to the high hydrophilicity of TMC-MPD membrane and low solubility of TMC-PPD, respectively (Roh 2003).	 p-Phenylene diamine (PPD)	

<table>
<tr><th rowspan="2">Literature</th><th colspan="2">Active layer</th></tr>
<tr><th>Amine</th><th>Acid Chloride</th></tr>
<tr><td>Garry Baroña et al. (2012) enhanced the water flux and solute rejection of RO membrane by adding 2,2’-Benzidinedisulfonic acid (BDSA) monomer to TMC-MPD to prepare the thin active polyamide layer on the top of a PSf porous support layer. The rejection of NaCl and $MgCl_2$ solutes were studied. The results showed the morphology of the active layer surface becomes more smooth and hydrophilic by increasing the concentration of BDSA which increases the water flux. The rejection of solutes also increases by increasing the content of BDSA until 5.00%, then the rejection decreases because of reduced the reactive activity of BDSA with TMC (Baroña et al. 2012).</td><td>
2,2’-Benzidinedisulfonic acid (BDSA)</td><td>
Trimesoyl chloride (TMC)</td></tr>
</table>

In previous studies, a conventional Interfacial Polymerization process was applied to prepare the TFC membranes. The conventional Interfacial Polymerization process was based on the adhesive forces to combine the polymers of both active and support layers. However, the conventional process is not suitable for manufacturing the TFC membranes which consisted of a thin active layer bonded to a hydrophilic cellulose acetate /CTA support layer. The challenge in this method is that, the thin active layer easily peeled off from the support base in case of using the conventional Interfacial Polymerization process. Alsvik and Hägg (2013) succeeded in coating the hydrophilic cellulose acetate /CTA support layer by thin polyamide layer by modification Interfacial Polymerization method. The modified Interfacial Polymerization method works by linking the hydrolysed CTA support layer with the molecules of TMC in the thin active polyamide layer. The molecules of both active and support layers bonded by covalent bonds instead of adhesion force, as illustrated in Fig 2.6. This combination between hydrophilic cellulose acetate/CTA support layer and thin active polyamide layer has provided for promising TFC membranes for osmotically driven applications. It has integrated the hydrophilic feature of the CTA layer with the high water permeability of thin polyamide layer resulted in reducing the ICP in the support layer and increasing the water flux cross the active layer (Alsvik & Hägg, 2013).

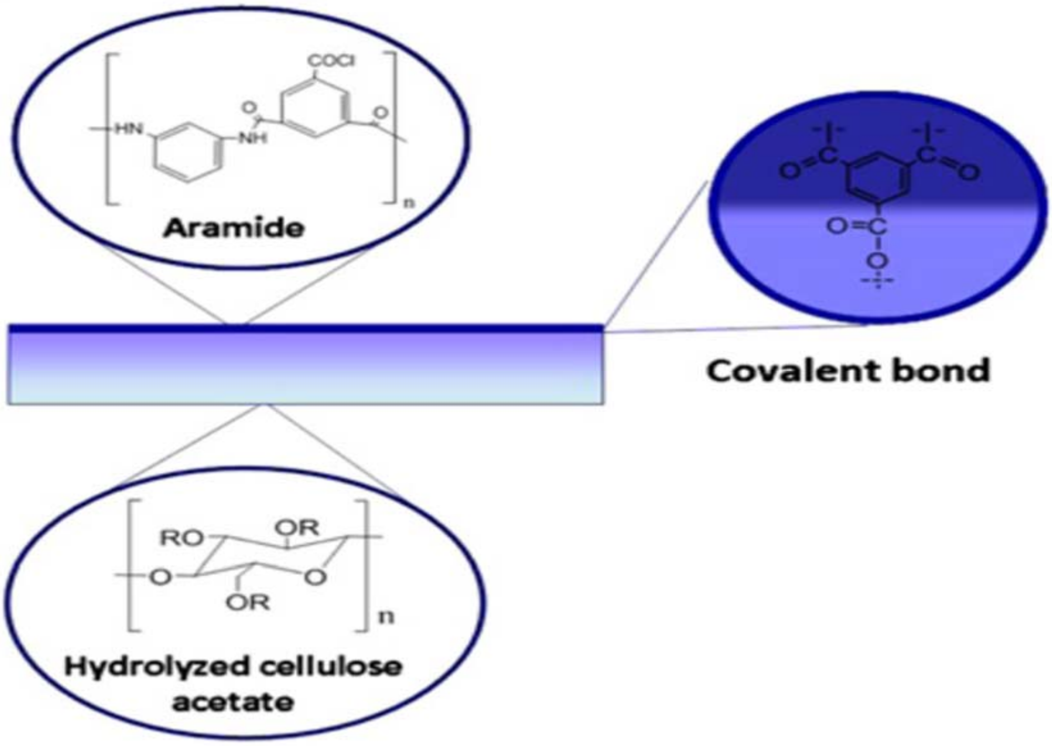


Figure 2.7: Modified Interfacial Polymerization process, where membrane layers are linked via covalent bond, (Alsvik & Hägg 2013)

Sterlitech Corporation has developed one brand of FO membranes based on incorporating the aquaporin protein water channels in the commercial TFC membranes. The TFC active layer is prepared through Interfacial Polymerization in which an additional aquaporin water channels component has been integrated. This new component has been added to the aqueous amine solution before the Interfacial Polymerization reaction occurred. The thin active layer is formed by dipping the porous support layer of the PES in MPD aqueous solution contains the aquaporin water channels. Then the membrane is soaked in TMC solution dissolved in organic solvent. A highly crosslinked polyamide TMC-MPD active thin layer comprising embedded aquaporin water channels is formed on the top of the PES porous support layer. The thickness of active layer becomes approximately 100-700 nm. The integration of aquaporin water channels creates narrow passages with a diameter of only 2.4 nm in the nonporous active layer. These narrow passages improve performance of the TFC membranes. They stimulate water transport which results in high water flux. Nonetheless, high rejection of solutes and organic molecules joined with low fouling tendency have been observed (Petrinić & Hélix-Nielsen, 2014; Mentzel, Perry, Vogel, Braekevelt, Geschke, Larsen, 2016).

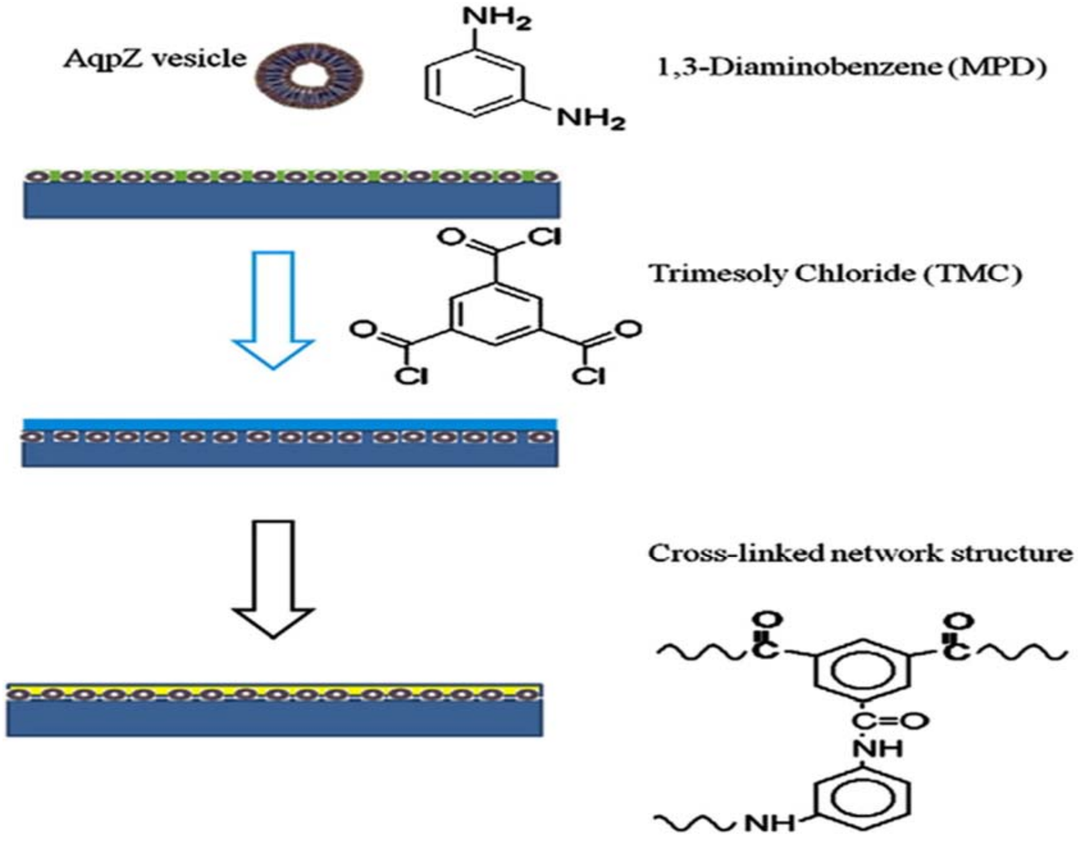


Figure 2.8: Preparation of TFC aquaporin protein membrane by Interfacial Polymerization, adopted from (Shenvi et al. 2015)

2.4.3 Chemically Modified Membranes

Operating FO process for a long time can cause water flux decline due to the contaminants deposition on the active layer of membranes. Membrane surface modification has been done to prevent the contaminants deposition and enhance the water flux. The polyamide active layer surface of composite membrane can be chemically modified by exposure it to strong solution of hydrofluoric acid. A chemical reaction occurs and results in a slight decrease in the polyamide active layer thickness. Consequently, water flux increases; meanwhile the NaCl solute rejection remains without change or slightly improved (Khulbe et al. 2008).

Setiawan et al. (2011) reported that the chemical modification of the PAI porous layer can be used to add a positive charged active layer. The chemical modification resulted from the reaction between the porous layer and a cationic polyethylene mine. At a later stage, the group of Setiawan et al. developed a FO flat sheet membrane consisted of this positive charged layer embedded with woven fabric, which result in reduction of the membrane thickness to 55µm (Setiawan et al. 2011; Zhao et al. 2012).

Tang and co-workers have produced a novel FO membrane via layer-by-layer assembly technique (Qiu et al. 2011). The support layer of polyacrylonitrile (PAN) was prepared by phase inversion process and exported to sodium hydroxide to modify the surface in order to increase both the hydrophilicity and the negative charge density. The requirement to add double charged layers which are chemically crosslinked with negative PAN support layer prevails. This was done by a chemical reaction between three layers, namely the negative PAN support layer, polyanion layer and polycation layer. As Fig 2.8 illustrates, the support layer is coated first by positive layer via soaking it in positive Poly (allylamine hydrochloride) (PAH) solution. Then, the negative Poly (sodium 4-styrene sulfonate) (PSS) is also coated by the same method to add a negative layer. Between the coating steps, the membrane was rinsed by deionised water to remove the extra polyelectrolytes. The desired number of polyelectrolytes layers on the top of negative PAN support layer can be acquired by repeating the coating steps (Zhao et al. 2012).

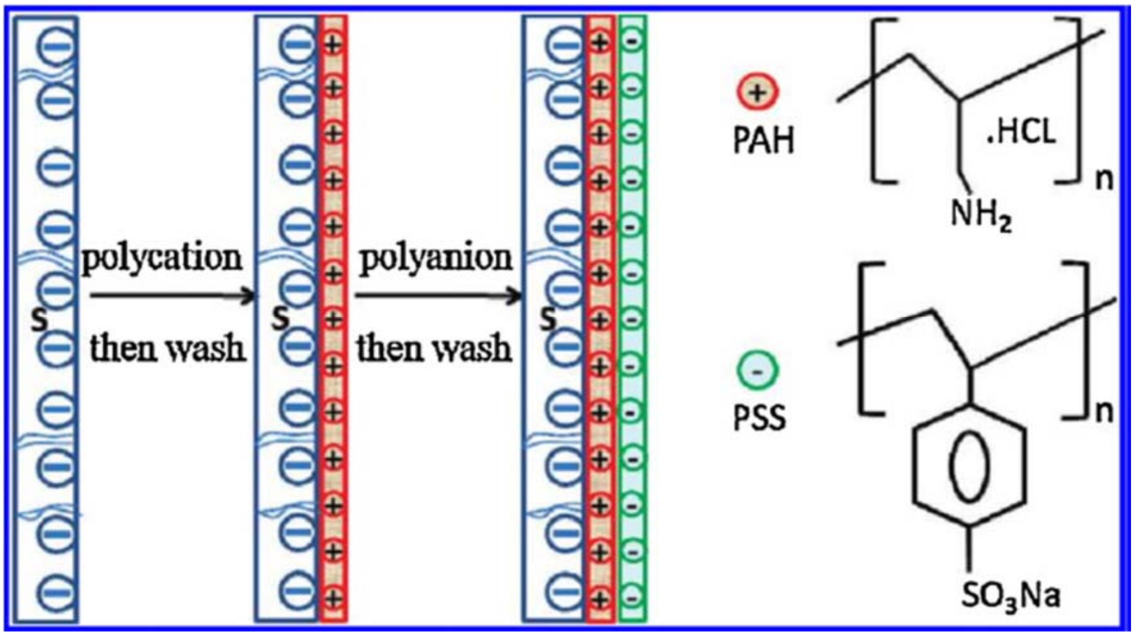


Figure 2.9: Layer-by-layer assembly method of PAH and PSS, adopted from (Zhao et al. 2012).

2.5 Draw Solutions

The viability of using FO processes in principle does not only depends on the membrane materials, but also depends critically on the type of the Draw Solution. However, the lack of the optimal Draw Solution still poses challenges to operate efficient large scale applications of FO. The selection of appropriate Draw Solution will improve the performance of FO process and save money regarding the regeneration process. Cai and Hu (2016) stated four main criteria of the appropriate Draw Solution i.e. (i) Draw Solution which has relatively good solubility in water, (ii) Draw Solution which has a high osmotic pressure leading to a positive water flux across the membrane, (iii) Draw Solution which is easily reconcentrated by effective and commercial processes to reuse it again, and (ix) Draw Solution which has a proper physicochemical characteristics such as small molecular weight and low viscosity to minimize ICP. Ge et al (2013) added another criterion to the selection process of the Draw Solution relating to the reverse solute diffusion, which must be minimal. The Draw Solution should also have other noble properties such as zero toxicity, the absence of any damage effects on the membranes structure, and has chemical stability.

Various materials and components are proposed as an ideal Draw Solution for FO process. However, researches are ongoing to investigate new materials for this purpose. Scientists and researchers have differed in the classification of the Draw Solution. On the one hand, Ge et al.

(2013) categorised the draw solutes, the components which dissolved or used to prepare the Draw Solutions, into two groups including commercially available components and synthetic components. The commercially available components are divided based on their physicochemical into four categories; inorganic solutes, organic solutes, nutrients components and volatile components. Synthetic draw solutes such as hydrophilic magnetic nanoparticles are presented as promising draw agents which have a high amount of interest recently (Ge et al. 2013).

On the other hands, Cai and Hu (2016) classified the draw solutes based on their response to the external environmental factors into two categories; responsive draw solutes and non-responsive draw solutes. Both draw solutes are exposed to external factors such as temperature, light, pH and electromagnetic. In the non-responsive draw solutions, the solute-solvent intermolecular forces are not affected significantly by the external factors. However, in the responsive draw solutions, these intermolecular forces are affected by the exposure to the previous external environmental factors. This response causes a significant changes in the state and characteristics of solutions. Investigating the influence of the external environmental factors on the Draw Solutions gives an indicator of the ability of reconcentrate and reuse them. Therefore, this classification provides an intrinsic assessment for the selection of the proposed draw agents of FO proses in the future (Cai & Hu 2016).

2.5.1 Non-Responsive Draw Solutes

2.5.1.1 Inorganic Solutes

The usage of sugar as a Draw Solution to desalinate the seawater was only tested in 1970s, however; the intention of using inorganic solutes for industrial applications started in the late 1990s (Cai & Hu 2016; Ge et al. 2013). Mainly, NaCl solute has been utilised in the majority of FO applications because of its benign characteristics. It is nontoxic, inexpensive, high soluble, generate high osmotic pressure as well as easy to reconcentrate by available processes like RO. However, NaCl has a relatively high reverse solute diffusion which is considered a weakness (Achilli et al. 2010).

Various inorganic draw solutes have been tasted in FO applications. In 2010, Andrea Achilli et al. established a protocol for selection an ideal inorganic Draw Solution. The composition of the protocol includes three steps, namely initial screen process, laboratory evaluation and finally explore the viability of reconcentration the Draw Solutions. Among 500 inorganic solutes were initially considered, 14 compounds were passed the screaming process to the second stage of the protocol. The selected compounds were then tested in the laboratory to determine their water flux, reverse solute diffusion, as well as the efficacy of the reconcentration using Reverse Osmosis System Analysis (ROSA) software. Ultrapure water as a Feed Solution and a negatively charged flat sheet membrane of CTA were used in all the experiments.

The study of Andrea Achilli has demonstrated that various Draw Solutions with the same osmotic pressure achieve different values of water flux and reverse solute diffusion due to the influence of ICP. Moreover, it has been observed that the highest water flux of 10.9 LMH was achieved by KCl solution with osmotic pressure 28 atm. The reverse solute diffusion of solutions containing large hydrated anions such as $MgSO_4$, $KHCO_3$, $NaHCO_3$, Na_2SO_4, $(NH_4)_2SO_4$, K_2SO_4 was the lowest comparing with other compounds.

Table 2.3 lists the properties, water flux and reverse solute diffusion of the 14 draw inorganic solutions finally selected by Andrea Achilli et al.

Table 2.3: Draw inorganic solutions - properties, water flux and reverse solute diffusion.

Draw solutes	Solubility at 25°C, g/L	Concentration g/L	Osmotic pressure (atm)	Water flux (LMH)	Reverse solute diffusion,(GMH)
KCl	313	47.0	28	10.9	12.3
NH_4Cl	305	32.6	28	10.4	7.6
KBr	536	71.3	28	10.2	22
NaCl	315	35.2	28	9.6	7.2
$CaCl_2$	821	43.8	28	9.5	7.9
K_2SO_4	105	101.4	28	9.1	3.7
$NaHCO_3$	101	63.9	28	8.9	1.7
$Ca(NO_3)_2$	1209	87.2	28	8.9	6.0
$MgCl_2$	466	33.8	28	8.4	4.8
$(NH_4)_2SO_4$	542	74.3	28	8.2	3.3
$KHCO_3$	200	65.5	28	8.1	1.4
Na_2SO_4	256	84.7	28	7.7	2.7
NH_4HCO_3	232	52.8	28	7.3	18.2
$MgSO_4$	342	141.3	28	5.5	1.2

Chekli et al. (2017) investigated nine inorganic fertilisers including NH_4NO_3, $(NH_4)_2SO_4$, NH_4Cl, $Ca(NO_3)_2$, KCl, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, KNO_3, and KH_2PO_4. These fertilisers were used to prepare Draw Solutions with high osmotic pressure and utilise it to extract the water from wastewater. The diluted Draw Solutions with nutrients compounds were used directly for irrigation purpose. Therefore, reconcentration of diluted Draw Solution step was unnecessary. The efficiency of fertiliser Draw Solution was determined based on their water flux, reverse solute diffusion, and water recovery percentage values. Chekli et al. (2017) used a commercial FO membrane prepared from TFC-polyamide to overcome the hydrolysis issue which is a real problem for cellulose acetate /CTA FO membranes as it is explained before.

2.5.1.2 Polymers

Recently, few studies have been conducted on utilising polymers compounds as draw agents compared to inorganic solutes. Often, soluble polymeric organic compounds meet the requirements to be appropriate draw agents. They have high molecular weight which make them easy to reconcentrate using low pressure driven processes. Large molecular weights grant the Draw Solution to reduce the reverse solute diffusion back to the Feed Solution side (Cai & Hu 2016).

These properties encouraged Ge et al. (2012) to explore the performance of an anionic polyelectrolyte polyacrylic acid sodium salts (PAA-NA) with various molecular weights as a Draw Solution in FO process. Investigating the performance of PAA-NA with molecular weights of 1200, 1800, and 5000 was based on water flux, reverse solute diffusion and the ability of reconcentration the diluted Draw Solutions (Ge et al. 2012).

Ge et al (2012) reasoned the choice of PAA-NA (1800) instead of PAA (1800) as a Draw Solution as follows: Firstly, NaCl solute was added to adjust the acidity degree of polyacrylic acid to reach the neutral range of 6.9-7.3. Neutral solution would skip the hydrolysis issue therefore be safe on the cellulose acetate/CTA membranes structure which was used in the study. Secondly, PAA-NA (1800) has higher dissociation degree than PAA (1800) which causes the increase in ionization of solution by 89.00% compared to 0.6.00% in PAA solution. Increasing ionization degree comes accompanied with increasing electrical conductivity and osmotic pressure of the Draw Solution which is required to achieve high water flux. However, water fluxes are limited by the sharp increasing of the viscosity due to increasing the molecular wright of the polyelectrolyte.

Table 2.4 represents the properties and the comparison of PAA-NA with various concentrations in osmotic pressure, water flux, and reverse solutes diffusion via cellulose acetate hollow fibre membrane, PRO mode (Ge et al. 2012).

Table 2.4: PAA-NA solutions - properties, water fluxes and reverse solute diffusions.

Draw solute	Concentration (g/mL)	Relative viscosity	Osmotic pressure (atm)	Feed solution	Water Flux (LMH)	Reverse solute diffusion (GMH)
PAA-Na, 1200 Da	0.48	~ 13	36.6	DI water	16.7	1.2
	0.48	~ 13	36.6	Seawater	3.6	Unmeasured
	0.72	~ 80	44.0	DI water	21.6	1.7
	0.72	~ 80	44.0	Seawater	6.5	Unmeasured
PAA-Na, 1800 Da	0.48	~ 14	33.5	DI water	15	1.4
	0.72	~ 120	39.5	DI water	18.7	1.7
PAA-Na, 5000 Da	0.48	~ 30	21.8	DI water	11.3	1.2
	0.72	~ 320	25.8	DI water	13.7	1.5

Besides that, PSS was studied as another anionic polyelectrolyte draw solute by Enling Tian et al. (2015). Various concentrations of different molecular weight solute were investigated. It was highlighted that the diluted Draw Solution of strong polyelectrolyte PSS needs less hydraulic pressure via ultrafiltration membrane process to reconcentrate than PAA-NA. The PSS achieved water flux better than that of PAA-Na at the same concentration. The best water flux produces by 0.24 g/mL PSS (70.000 Da) is 18.2 LMH and higher than that of 0.24 g/mL PAA-Na (1800 Da) which is approximately 12 LMH. In contrast, the reverse diffusion of 0.24 g/mL PSS (70.000 Da) solute is higher than that of 0.24 g/mL PAA-Na (1800 Da) by 7 times due to the strong and intensive charged ions presented in the solution. The intensive charged ions lead to high osmotic pressure, high water flux, and high reverse solute diffusion. The effect of increasing the viscosity of PSS solutions was also studied. Increasing the viscosity causes a severe concentration polarization near the surface of the membrane, which causes a high reverse solute diffusion and low water flux (Tian et al. 2015).

2.5.1.3 Organic Solutes and Organic-Based Compounds

Organic solute is an electrolyte compound results from reaction between organic acid (anion) and organic or inorganic base (cation) (Ge et al. 2013). Organic electrolytes have molecular weights approximately from 100 to 1000 g/mol, higher than the molecular weights of inorganic solutes and lower than that of polyelectrolyte. They have lower viscosities than their polymers counterparts, while they generate higher water flux (Cai & Hu 2016). Bowden et al. (2012) investigated the viability of using various organic solutes as draw agents in osmotic membrane bioreactors to treat wastewater. Ten organic solutes result of the reaction between inorganic cations of Na^+ and Mg^+ and organic anions of acetate, formate, propionate, and fumarate/maleate were initially proposed. Only four organic salts were finally selected and evaluated based on a modified protocol build on the Achillie's protocol (Bowden et al. 2012).

The selection of the Draw Solution for osmotic membrane bioreactors was according to two criteria. Firstly, the organic anion part of draw solute must be biodegradable to prevent the solutes accumulation inside the bioreactors. It must also act as a carbon resource which is required for removing the nutrients by denitrification of the ammonium compound. Secondly, it should be commercially available and has benign properties. Organic Draw Solution should have a reasonable relationship between the concentration and its osmotic pressure. Water flux, reverse solute diffusion, reconcentration the diluted draw solutions, and the biodegradation potential of each organic solutes were measured. Table 2.5 shows the properties, concentrations, water flux, and reverse solute diffusion of each draw solution using the CTA flat sheet membrane, FO mode.

Table 2.5: Draw organic solutions - properties, water flux and reverse solute diffusion.

Draw solutes	Concentration g/L	Osmotic pressure (atm.)	Water flux (LMH)	Reverse solute diffusion (GMH)
Sodium formate $HCOONa$	46	28	9.36	6.04
Sodium acetate CH_3COONa	91	28	9.00	2.73
Sodium propionate CH_3CH_2COONa	66	28	8.68	1.47
Magnesium acetate $(CH_3COO)_2Mg$	166	28	8.10	1.07

The aforementioned table illustrates, on the one hands, the water flux generated at 28 atm range from 8.10 LMH for magnesium acetate to 9.36 LMH for sodium formate. The change in water flux occurs due to the effect of ICP inside the support layer of the membrane. Solutes with high diffusion coefficient have high ability to diffuse inside the support layer than that of have low diffusion coefficient. It causes increasing the concentration of the Draw Solution within support layer and less ICP effluence. Sodium formate with high diffusion coefficient ($1.59 \times 10^{-9}\ \mathrm{m^2/S}$) at 28 atm was less influenced by ICP than magnesium acetate with low diffusion coefficient ($1.14 \times 10^{-9}\ \mathrm{m^2/S}$). Therefore, sodium formate generated water flux higher than magnesium acetate (Bowden et al. 2012). More explanation of ICP is demonstrated in section 2.6.1.2.

On the other hands, by comparing the reverse solute diffusion of two organic solutes have the same anions; sodium acetate and magnesium acetate, it is observed that the reverse diffusion of sodium acetate is double of magnesium acetate. In explaining this phenomenon, Achillie et al. (2010) stated that the charge of the membrane surface plays a role of changing the reverse solute diffusion. The increase of the cations concentration in the Draw Solution leads to decrease the reverse solute diffusion through the negative charged CTA membrane.

Akther et al. (2015) reported another group of non-electrolytes organic draw solutions were used for various FO applications. These draw solutions are shown in table 2.6

Table 2.6: Non-electrolytes organic draw solutions - properties, water flux and application.

Draw solutions	Concentration g/L	Osmotic pressure (atm)	pH at given concentration	Water flux (LMH)	Application
Fructose	360	55.02	7.01	7.50	Desalination
Glucose	360	55.03	7.01	0.24	Desalination
Sucrose	684	56.81	6.18	0.35	Food industry
Ethanol	92	43.93	7	N/A	Desalination

2.5.2 Responsive Draw Solutes

The osmotic pressure of Draw Solutions prepared by smart responsive draw solutes can change significantly due to the exposure to external environmental factors. Temperature, magnetic field, electric field, light, and pH changing are environmental factors which able to affect the osmotic pressure of the Draw Solutions. Therefore, choosing appropriate responsive draw solutes for FO can mitigate prevailing challenges, difficulties pertaining to reconcentration of the non-responsive Draw Solutions. Cai and Hu (2016) reported different types of responsive draw solutes suitable for FO applications such as nanoparticles, hydrogels, and volatile components. Some of these are practically used and others are in the development stage (Cai & Hu 2016).

2.5.2.1 Nanoparticles

Nanoparticles are defined as ultrafine particles with size ranges from 1 nm to 100 nm. Nanoparticles such as carbon quantum dots and magnetic Fe_3O_4 have been used as Draw Solutions for FO applications. In this case, Draw solutions are prepared by dispersing these nanoparticles in water. The osmotic pressure of the Draw Solution can be increased by adding ionic compounds to the solution such as Na^+ which pairs the carbon quantum dots and then increase the surface charge of particles.

Number of advantages can be derived from the use of nanoparticles in FO applications. For example, low reverse solute diffusion can be obtained since the size of nanoparticles is much larger than the pore size of the FO membranes. Paramagnetic nanoparticles can be regenerated readily from Draw Solutions by using external magnetic field (Cai & Hu 2016), and pressure membrane processes such as UF process. As it is illustrated in Fig 2.9, a responsive Fe_3O_4 nanoparticle Draw Solution was utilised to generate osmotic pressure to extract water from saline and meanwhile it can easily be separated via magnetic field.

However, water flux produced by the nanoparticles Draw Solution is still very low compared to the non-responsive Draw Solutions. Water flux of approximately 2 LMH was achieved against seawater feed solution. Other drawbacks were also stated of using nanoparticles by Kim et al (2011). They investigated that the separation of nanoparticles with less than 11 nm is difficult even by using strong magnetic fields. In the same time, it is not easy to separate those which have a size bigger than 20 nm from the magnetic column. To overcome this problem, nanoparticles with uniform dimensions can be effectively recovered by membrane processes such as NF process. It was also observed that nanoparticles can agglomerate during the separation stage due to the magnetic force. This issue can be alleviated by replacing the magnetic field with electrical field or using weaker magnetic field during the regeneration stage (Cai & Hu 2016; Kim et al. 2011).

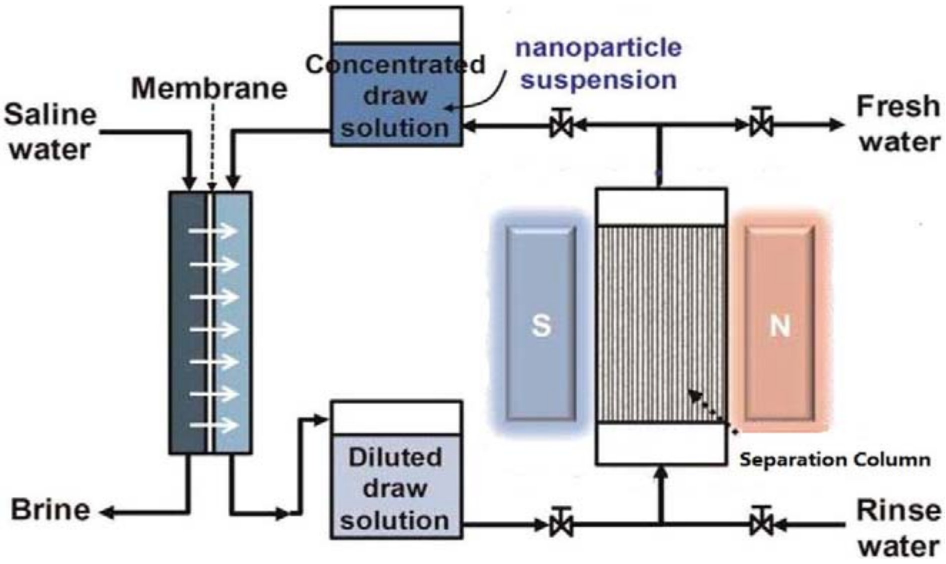


Figure 2.10: Schematic demonstrates the utilisation of magnetic nanoparticles as draw solutes in FO desalination. Adopted from (Cai & Hu 2016)

2.5.2.2 Hydrogels

Hydrogel is another responsive compound has been developed and used as a draw agent. It is defined as a hydrophilic polymer composed by a network of cross-linked polymer chains. Hydrogel polymers have the ability of absorbing water and releasing it easily by exposure to hydraulic pressure, temperature or via light-absorbing carbon particles. Using the hydrogel polymers in desalination process was explored by directly sinking and swelling it in a feed saline solution.

No reverse solute diffusion occurs and capable to be used again since the networks of hydrogel do not dissolve in water. However, it was reported that hydrogel polymers give poor results at room temperate. Hydrogel polymers also require a high hydraulic pressure of 30 bars to dewater and reuse it. Hartanto et al. reported that new dry hydrogels can achieve high water flux reaching up to 20 LMH, but this water flux became lower when the same hydrogels were dewatered and reused again. Hydrogel polymers still contain significant amount of water even after the de-swelling process. This obstacle of regeneration the hydrogel reduces the total performance of FO process. Literatures enumerated various types of hydrogels were investigated as draw agents such as thermally responsive PNIPAm hydrogels, cross-linked PSA polyelectrolyte, thermally responsive polyionic liquids, and semi-interpenetrating network hydrogels (Cai & Hu 2016; Ge et al. 2013).

2.5.2.3 Volatile Compounds or Soluble-Gases

Draw Solutions with a proper osmotic pressure can be prepared by dissolving soluble-gases in water. Since 1960s, group of soluble gases have been proposed by early studies to be used as a Draw Solution for FO desalination process. A mixture of two highly soluble gases carbon dioxide $\mathrm{CO_2}$ and ammonia $\mathrm{NH_3}$ were involved by Neff (1964) in preparing a promising Draw Solution for FO desalination. The concentrated Draw Solution was prepared by dissolving ammonium bicarbonate $\mathrm{NH_4HCO_3}$ salt in freshwater. However, poor solubility of $\mathrm{NH_4HCO_3}$ salt in water limited the osmotic pressure of the Draw Solution. Therefore; McCutchoen et al. (2007) were able to improve the solubility by adding ammonium hydroxide $\mathrm{NH_4OH}$ to $\mathrm{NH_4HCO_3}$ salt. The new Draw Solution with much high osmotic pressure due to improvement of the solubility became a very good agent for FO desalination process, see Fig 2.10. The laboratory results of water flux, reverse solute diffusion and salt rejection were given to evaluate the efficiency of $\mathrm{NH_4OH}$+$\mathrm{NH_4HCO_3}$ as a Draw Solution. These results demonstrate a high reverse solute diffusion and membrane scale formation can be attributed to the alkalinity of the Draw Solution where the carbonate ions are existed. Controlling the stability of the soluble-gas $\mathrm{NH_4HCO_3}$ Draw Solution concentration after the regeneration was an obstacle because of the undesirable water evaporation. Moreover, removing the residue of high soluble ammonia from the final water product is still a drawback of using $\mathrm{NH_3-CO_2}$ draw agent system to produce a drinking water via FO application (Cai & Hu 2016; Ge et al. 2013).

Recently in 2015, Boo et al. (2015) proposed thermolytic trimethylamine carbon dioxide $(\mathrm{TMA-CO_2})$ as a Draw Solution and compared the experimental results with the $\mathrm{NH_3-CO_2}$ Draw Solution system. The reverse solute diffusion of $\mathrm{TMA-CO_2}$ was lower than $\mathrm{NH_3-CO_2}$. However, water flux produced by $\mathrm{TMA-CO_2}$ was not improved because $\mathrm{TMA-CO_2}$ was affected by CP more than $\mathrm{NH_3-CO_2}$ due to its lower diffusivity (Boo et al. 2015).

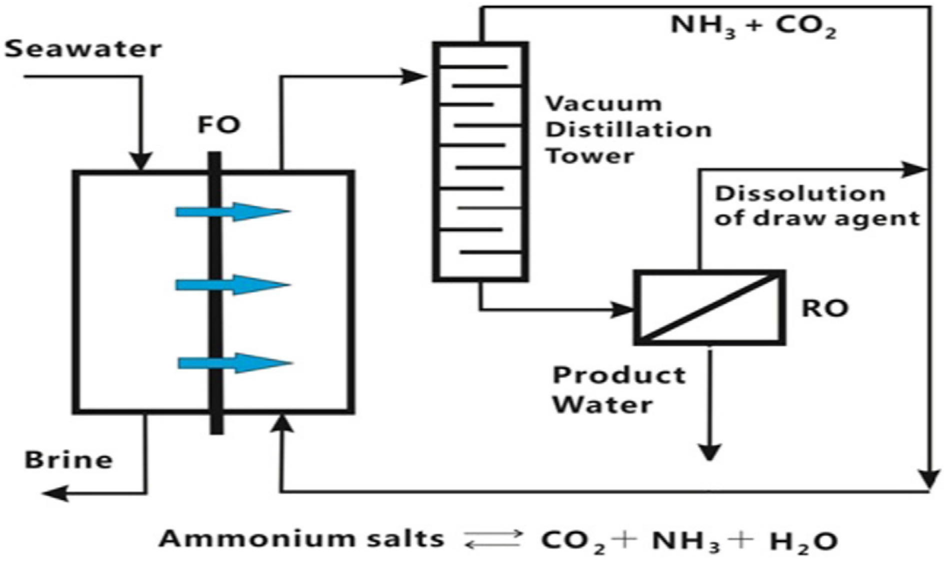


Figure 2.11: Schematic demonstrates the utilisation of ammonium salts as draw solutes in FO desalination. Adopted from (Cai & Hu 2016)

Sulphur dioxide SO_2 was investigated as a draw agent by Batchelder (1965). In his experiments, two Draw Solutions were utilised in FO process to extract water from seawater. The first one was prepared by dissolving SO_2 in freshwater and the second was in seawater. Positive water fluxes were reported, however; no experimental results of water flux or salt rejection were given. The separation of the soluble gas was done by evaporation or air stripping. In another study, Glew (1965) prepared his Draw Solution by dissolving SO_2 in aliphatic alcohols instead of water to increase the osmotic pressure. Distillation process was chosen to recover the water and SO_2. Recovered soluble gas was reused by dissolving it again in water or another liquid. In 2002, McGinnis used saturated SO_2 solution to reconcentrate a diluted potassium nitrated KNO_2 solution. The saturated KNO_2 solution was used as a draw agent to extract water from heated seawater in FO desalination unit. In this regards, good care should be considered when SO_2 is used because of its special properties. It is corrosive, volatile and its solution behaves like unstable acid (Cai & Hu 2016; Ge et al. 2013).

2.6 Limitations of Forward Osmosis

Water flux across the membrane can be generally governed by equation 2.2

$$J_W = A\sigma\Delta\pi \qquad \text{Eq. 2.2}$$

where $A, \sigma, and\ \Delta\pi$ are the water permeability coefficient, the reflection coefficient, the osmotic pressure difference between the bulk Draw and Feed solutions, respectively.

The results of effective water flux which come from the laboratory show lower values than the theoretical value comes from equation 2.2 (Mattia Stefani 2014). This declination of water flux can be attributed to various phenomena occurred during the FO process such as CP, reverse solute diffusion, and membrane fouling. These phenomena consequently limit the efficacy of the utilisation of FO technology at a large scale. The effect of these phenomena varies according to several factors including changing temperature of solutions, concentration and type of the Draw Solution, membrane structure, and membrane orientation (Akther et al. 2015). Fig 2.11 illustrates the concentration polarisation types in both pressure driven and osmotically driven membrane processes. Each phenomenon is described more below.

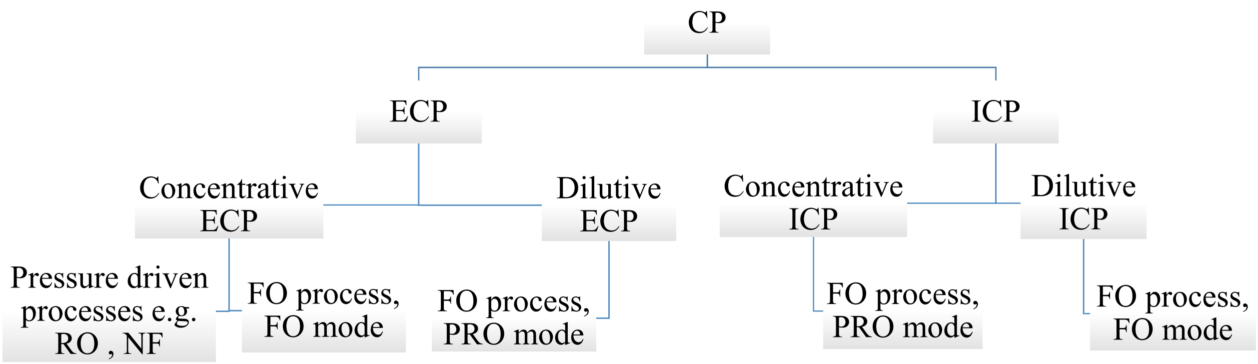


Figure 2.12: Concentration polarisation types in both pressure driven and osmotically driven membrane processes.

2.6.1 Concentration Polarisation CP

Concentration polarisation (CP) is a phenomenon which can hit both types of membrane separation processes whether governed by hydraulic pressure or osmotic pressure. It is classified as an External Concentration Polarisation (ECP) and Internal Concentration Polarisation (ICP). ECP occurs on the membrane surface meanwhile ICP occurs inside the porous layer. ECP affects both FO osmotic pressure driven and hydraulic pressure driven membrane processes. However, ICP only affects FO process significantly causing the main reason of reducing the water flux (Zhao et al. 2012; Mattia Stefani 2014).

2.6.1.1 External Polarisation Concentration

The ECP takes place close to the active layer of membranes and it can be whether concentrative ECP or dilutive ECP. The concentrative ECP occurs in both hydraulic pressure driven process and FO mode of osmotic pressure driven process where the active layer faces the Feed Solution. Due to the effect of applied hydraulic or osmotic pressure, water molecules cross the active layer of the membrane and leave the solutes behind it. The cumulative solutes create a layer with high concentration functions as a barrier which separates the bulk solution from the active layer. The cumulative solute layer causes a reduction of the driving force which results in declination of the flux through the membrane (Zhao et al. 2012; Abdulwahab et al. 2013). This phenomenon could be minimized by producing a suitable turbulence close to the active layer in order to disperse the cumulative solute layer (Mattia Stefani 2014).

Conversely, the dilutive ECP occurs only on the active layer side in PRO mode of osmotic pressure driven process where the active layer faces the Draw Solution. Water molecules enter the membrane layers from the Feed Solution side to the Draw Solution side due to osmotic driven force of the Draw Solution. The water flux forces the dissolved draw solute away from the active layer and thereby creating a diluted layer between the bulk Draw Solution and the active layer of membrane which leads to decrease the effective driving force of the Draw Solution (Abdulwahab et al. 2013). The effluence of the dilutive ECP can be reduced during a high water flux. Decreasing the effect of the diluted layer between the bulk Draw Solution and the active layer can be done by increasing the water flux which produces continuous mixing of the Draw Solution, consequently limiting the opportunity of creating this layer. (Akther et al. 2015).

2.6.1.2 Internal Concentration Polarisation

The ICP takes place in both modes of FO process and it is difficult to be eliminated. Unlike the ECP, the ICP occurs inside the porous support layer. Earliest literature demonstrated that the ICP can be responsible of the declining water flux by higher than 80.00%. Fig. 2.12 illustrates that the ICP phenomenon appears as a result of the concentration gradient between the Feed Solution and the Draw Solution (Akther et al. 2015; Mattia Stefani 2014; Zhao et al. 2012). It is also categorised into two types either concentrative ICP which happens in PRO mode, or dilutive ICP which happens in FO mode (Nicoll 2013; Phuntsho et al. 2013).

In the concentrative ICP case, water passes the porous support layer and diffuses easily through the active layer to the Draw Solution side by means of the osmotic pressure gradient. The solute molecules in the saline Feed Solution can also pass through the open structure of the porous layer but cannot diffuse through the active layer. The solute molecules accumulate and then increase the solute concentration inside the porous support layer.

In the dilutive ICP case, which occurs in FO mode where the porous support layer faces the Draw Solution, water molecules diffuse through the active layer and reach to support layer due to the driving force of the Draw Solution. The permeate will dilute the Draw Solution which occupies the open structure of the porous layer and decrease the diving force. A severe dilutive ICP occurs when solutes with large molecular weight is used. Literatures state that the ICP in FO mode is more severe than PRO mode, consequently reduces the effective driving force (Abdulwahab et al. 2013; Alsvik & Hägg 2013; Nicoll 2013; Phuntsho et al. 2013). This is clearly illustrated in Fig 2.12 where the effective osmotic pressure in case of FO mode is less than that of PRO mode.

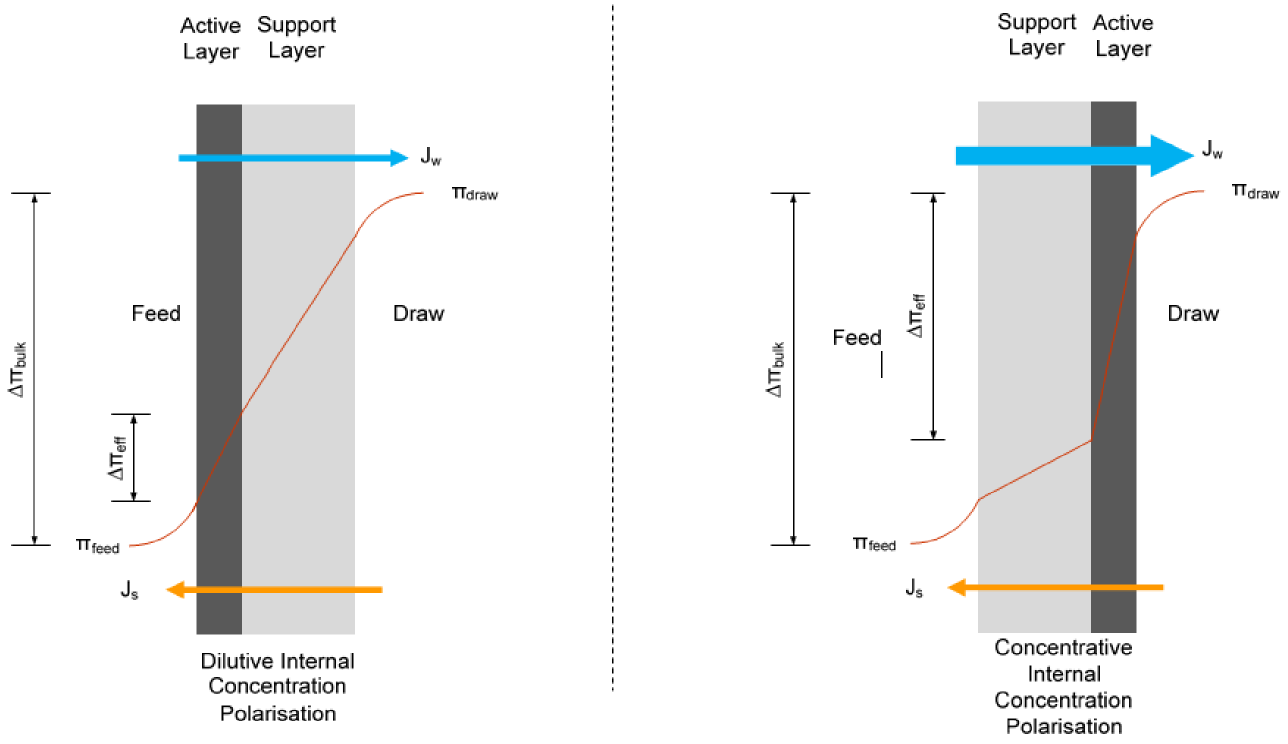


Figure 2.13: Driving force and internal concentration polarisation of FO mode (left) and PRO Mode (right), adopted from (P. Nicoll, 2013)

2.6.2 Reverse Draw Solute Diffusion

Reducing the concentration difference between the Draw and the Feed Solutions occurs due to the dilution of the Draw Solution and also due to increasing the Feed Solution concentration. The increase in the Feed Solution concentration occurs by the reverse diffusion of draw solutes. In FO process, solutes diffuse reversely through the membrane from the Draw Solution side with high solute concentration to the Feed Solution side with low solute concentration. The reverse solute diffusion is governed by Fick's Law:

$$J_s = B\Delta C \qquad \text{Eq. 2.6}$$

where, B and ΔC are the solute permeability coefficient and the solute concentration difference, respectively (Nicoll 2013; Mattia Stefani 2014)

The reverse draw solute diffusion is considered an inevitable challenge which causes a limitation in the efficiency of FO process. A new term named specific reverse solute flux $\left({}^{J_W}/_{J_s}\right)$ has provided by Hancock and Cath (2009). This term expresses the ratio between the forward water flux to the reverse draw solute flux across the semi permeable membrane. It is used to evaluate the selectivity of FO membrane which is needed to understand the solute transport between the membrane layers. Philip et al. (2010) illustrated that specific reverse solute flux is not affected by the porous support layer structure and the concentration of the Draw Solution. It is only affected by the selectivity feature of the thin active layer. Therefore, manufacturing a promising FO membrane with high selectivity active layer is needed to minimize the reverse solute diffusion. The hydration radius and the ions charge can also play a role in reducing the reverse solute diffusion. It has been observed that cations with divalent such as Ca^{2+}, Mg^{2+} and Ba^{2+} have less reverse diffusion rate than the monovalent ions. However, multivalent ions could cause high ICP (Akther et al. 2015; Phillip et al. 2010; Zhang et al. 2017).

Many studies have been conducted to investigate the effect of membrane orientation on reverse solute diffusion. It shows that the reverse solute diffusion in FO mode is lower than of PRO mode. The studies also illustrate that the reverse solute diffusion increases proportionally by the increasing of the Draw Solution concentration in both modes (Mattia Stefani 2014; Akther et al. 2015; Zhao et al. 2012).

The reverse solute diffusion phenomenon has negative impacts on environment. For example, the reverse diffusion of Draw Solutions containing nitrogen such as $NH_3 - CO_2$ could cause contamination of the Feed Solution and consequently forming eutrophication. In this case, post treatment processes and high energy are needed to treat the Feed Solution. The reverse solute diffusion phenomenon can be reduced by taking three approaches into consideration; seeking a competent draw solution, improving the selectivity of FO membranes, and choosing optimal operation parameters (Cai & Hu 2016).

2.6.3 Membrane Fouling

Membrane fouling is another limitation which occurs in both type of membrane separation processes including pressure driven processes and FO process. Membrane fouling causes a performance declination of aforementioned processes. In pressure driven membrane process, the fouling is formed on the surface facing the applied hydraulic pressure. In FO process it happens on or inside the open structure of the porous support layer when PRO mode is used, and on the active layer surface when the FO mode is used. Fouling can be categorised into organic fouling, inorganic fouling (scaling), biofouling, and colloidal fouling (Mattia Stefani 2014; Alsvik & Hägg 2013; Zhang et al. 2017). Number of studies have been conducted by Cornelissen et al., Lee et al., Holloway et al., Thompson and Nicoll to compare between the fouling under the FO process and pressure driven process (Nicoll 2013). It was concluded that the fouling in case of FO process has smaller impacts than pressure driven which grants it the merit of low maintenance and consequently longer membrane life. In driven pressure membrane process the fouling layer on membrane surface is irreversible and compacted due to the high applied hydraulic pressure. While, in FO process which operated without external hydraulic pressure, the fouling layer is loose and reversible (Zhao et al. 2012; Nicoll 2013), see Fig 2.13.

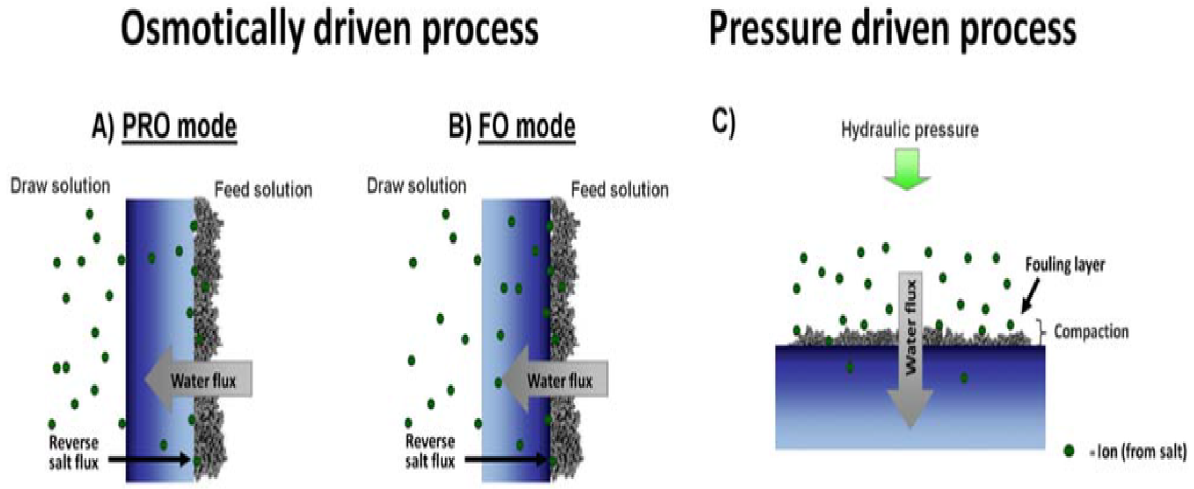


Figure 2.14: Fouling membrane mechanisms in osmotically driven and pressure driven processes, adopted from (Alsvik & Hägg 2013).

The loose fouling deposition on the active layer of FO membranes can impede the reverse diffused draw solute ions and held it. Impeding the draw solutes leads to increase the local osmotic pressure of the strip which is close to the membrane surface consequently increase the negative effects of the ECP. This phenomenon is known as a Cake Enhanced Concentration Polarisation (CECP) and reduces the net driving force which adversely affects the performance of FO process. Solutes with high reverse solute diffusion can easily cause the CECP which is more than the solutes with low reverse solute diffusion. This investigation stated by Lee et al. (2010) during their study using NaCl as a small hydrated radius solute with high reverse solute diffusion, and dextrose as a larger hydrated radius solute with low reverse solute diffusion. The conclusion of Lee et al. study besides of many studies also show that the type of a Draw Solution has strong effect on forming the fouling during FO process (Zhao et al. 2012; Mattia Stefani 2014; Lee et al. 2010).

The majority of FO membrane can be cleaned readily from inorganic and organic fouling by low pressure backwash flush and no need to use chemicals (Akther et al. 2015). Achilli et al. (2009) reported in their study of treating domestic wastewater using submerged OMBR, that approximately 90.00% of the initial water flux value was recovered by backwashing flush process (Zhao et al. 2012; Achilli et al. 2009). On the contrary, this physical cleaning does not work efficiently in case of biofouling formation. The chemical cleaning process becomes necessary to remove foulants and sticky substance produced by the bacteria which is strongly agglutinated on the membrane surface (Akther et al. 2015). Main factors including the nature of the draw solute, appropriate material choices, and membrane surface modification should be taken into considerations to avoid the fouling (Mattia Stefani 2014).

2.7 Summary

FO is an emerging technology with good potential in water and wastewater treatment as well as separation and purification of the valuable components from the industrial downstream. The advantages of FO membrane process make it favourable compared to other separation processes such as driven pressure membrane processes, crystallization and ion exchange. It is more energy efficient, and easy to operate, less prone to membrane fouling, and works at ambient temperature. The concept of FO process is placing a semi-permeable membrane between Feed Solution and Draw Solution with high osmotic pressure. Water is driven to the Draw Solution side due to the osmotic pressure gradient between both solutions. The efficiency of FO performance depends on both Draw Solution and composition of the membrane. Developing the composition of FO membranes and finding an efficient Draw Solution are essentials to overcome the inherent limitations occur during the FO process such as concentration polarisation, reverse solute diffusion and membrane fouling. On the one hand, the important criteria to be considered in development of the FO membrane composition are the ability of achieving high water flux by reducing the membrane thickness, meanwhile; improvement the selectivity of the active layer to reduce the reverse solute diffusion. Interfacial Polymerization as an advanced technique has been used to manufacture the thin selective layer of the FO polymeric membranes. Furthermore, recent studies have been conducted to incorporate the aquaporin protein water channels in the manufacturing of FO membranes to enhance the water flux. On the other hand, the viability of utilising FO technology does also depends on the type of the Draw Solution. A competent Draw Solution with high osmotic pressure and proper characteristics can improve the performance of FO, meanwhile; save money regarding its regeneration process. The lack of the competent Draw Solution limits the utilisation of FO technology in large scale applications. Several types of responsive draw solutes and non-responsive draw solutes have been investigated either in laboratory scale or industry. However, finding the optimal Draw Solution is still searchable issue. This valorises the current study at hand which is intended to contribute to the knowledge pertaining to the appropriateness of organic cationic solutions to be draw agents and use them to recover water from industrial fermentation Feed Solution.

CHAPTER 3

Materials and Methods

3.1 Experimental Plan

The experiments were planned so as to obtain the optimum operating conditions of both FO and reconcentration systems and utilise them for concentrating fumaric acid produced by a fermentation process as a Feed Solution. Three main phases were conducted in sequence to achieve the previous objective. Firstly, determination of the optimum operating conditions for FO system. Secondly, determination of the optimum operating conditions for the reconcentration system. Thirdly, implementation of those optimum operating conditions for water recovery from both solutions of a synthesis fumaric acid and fumaric acid solution produced by an industrial fermentation process.

I. **Determination of the optimum operating conditions for FO system:** In this section a set of series of experiments were conducted using distilled water as a Feed Solution to investigate the influence of various operating conditions on water flux rate and reverse solute diffusion through FO membranes. Draw Solution type, Draw Solution concentration, membrane type, and membrane orientation are the targeted conditions which were tested in this phase. The following matrix clarifies that.

Operating conditions	Draw Solution type	Membrane sheet type	Membrane orientation	Draw Solution concentration
Variables	$\begin{bmatrix} \text{L} - \text{Alanine} \\ \text{DADMAC} \\ \text{PolyDADMAC} \end{bmatrix}$	$\begin{bmatrix} \text{CTA} \\ \text{Aquaporin protein} \end{bmatrix}$	$\begin{bmatrix} \text{FO mode} \\ \text{PRO mode} \end{bmatrix}$	$\begin{bmatrix} 0.035\ \text{g/mL} \\ 0.085\ \text{g/mL} \\ 0.120\ \text{g/mL} \\ 0.155\ \text{g/mL} \end{bmatrix}$

II. **Determination of the optimum operating conditions for the regeneration system**: A NF system was chosen to regenerate the diluted Draw Solution produced in the FO system. A NF90- Nanofiltration membrane with a stirred dead end filtration cell was chosen to achieve the reconcentration.

III. **Implementation of the optimum operating conditions of the FO system for water recovery from a fumaric acid solution produced by industrial fermentation**

process: The results obtained from the experiments conducted in phase I were used in the extraction of water from fumaric acid produced by fermentation process and from synthesis fumaric acid. The results of the experiments in both phase II and phase III produced also product streams such as clean water and concentrated fumaric acid solution as a useful industrial product.

The experimental plan establishes that the efficiency of FO system can be determined by comparing water flux rate, and reverse solute diffusion in each experiments under the various operating conditions. The efficiency of NF system was also explored through comparing the rejection ions percentage of each Draw Solution with NF90- Nanofiltration membrane.

3.2 Experimental Setup

Two separated bench-scale of FO and NF systems were set up and operated at a temperature of $(22℃ \pm 1℃)$. The FO system was utilised to extract the water molecules from the Feed Solution, which resulted in the dilution of the Draw Solution. This occurs with decreasing the weight of Feed Solution and concurrently increasing its concentration. The NF system was used to reconcentrate the diluted Draw Solutions via a stirred dead end filtration cell to reuse it again in FO experiments.

3.2.1 Forward Osmosis System

The core element of the FO set up is the cross-flow membrane cell with two different sized cavities for the Draw Solution and the Feed Solution flows. The channels were separated by flat sheet FO membranes. Both Cavities have the same surface area with the following dimensions of 200 mm in length and 40 mm in width. However, the depth of the Feed Solution cavity (10 mm) is more than the depth of the Draw Solution cavity (3 mm) as it illustrated in figure 3.1 and 3.2.

The schematic diagram of the FO setup is illustrated in figures 3.3 and 3.4. The diagram also includes auxiliary components, namely two pre-calibrated peristaltic pumps (Masterflex L/S, Model 77201-60, Korai) were used to pump the Draw Solution in counter clockwise loop and the Feed Solution in clockwise loop across the two channels of the membrane cell. The flow of both Draw Solution and Feed Solution was pumped by the same flow rate 1 L/min (60 L/hr) and the Feed Solution was mixed continuously using magnetic stirrer. The increase in the weight of the Draw Solution was recorded by an electronic balance (Radwag Model PS

4500/C/2, Poland), and these measurements were used to calculate the water flux. A conductivity meter was linked to the Feed Solution tank to determine the electrical conductivity to calculate the reverse diffusion of the solute.

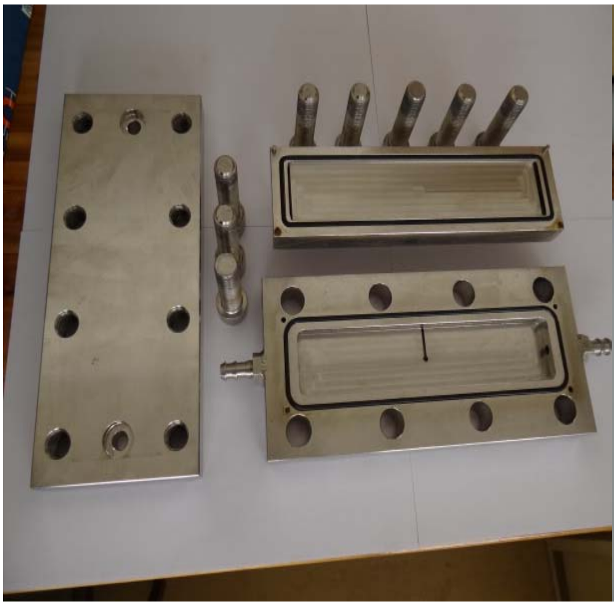


Figure 3.1: Channels of FO cell in details

Figure 3.2: FO cell

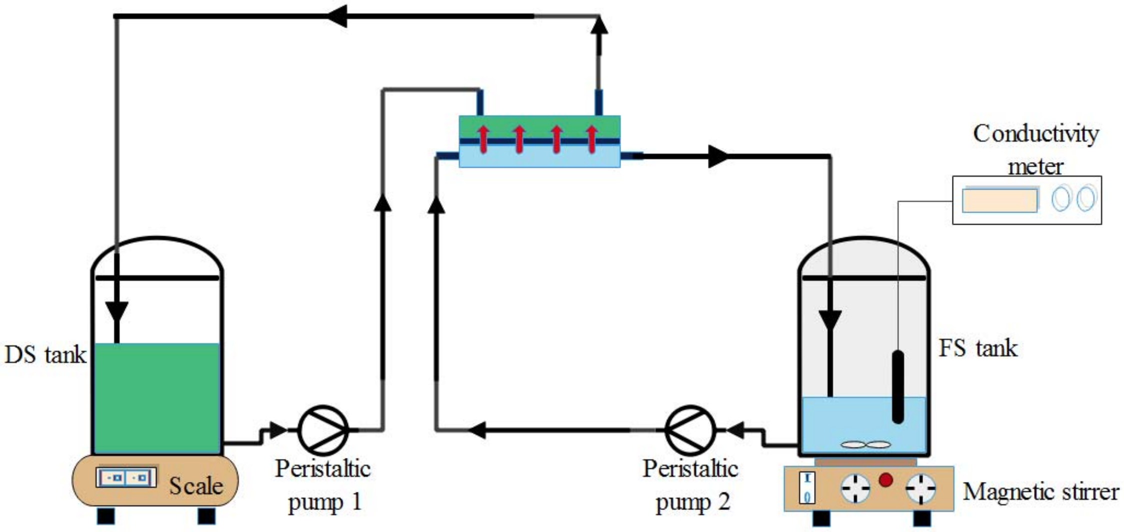


Figure 3.3: Schematic diagram of the bench-scale FO system

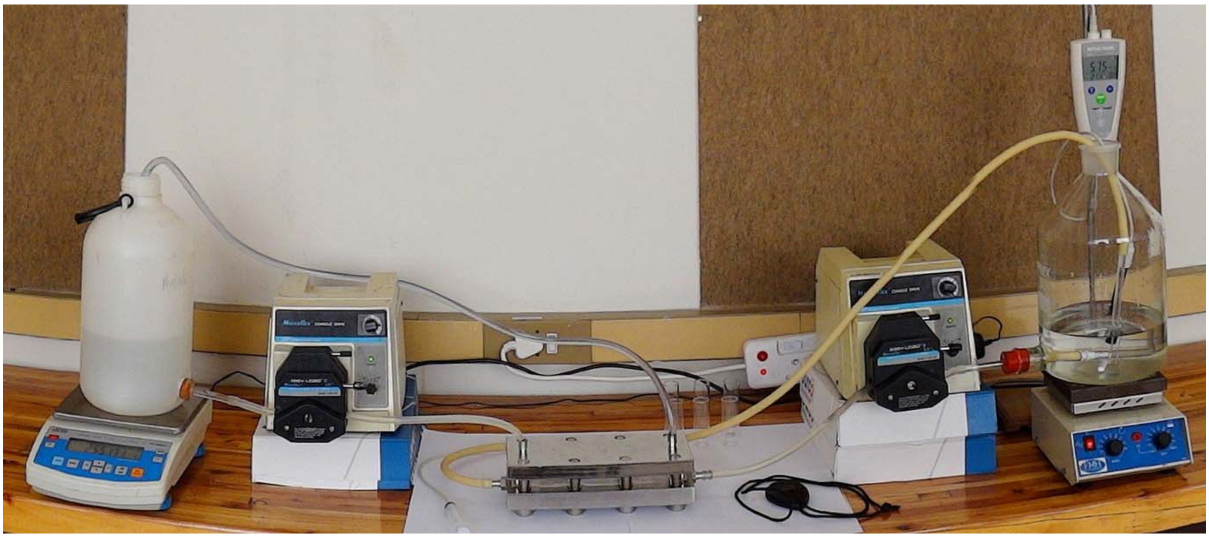


Figure 3.4: The bench-scale FO system

3.2.2 Nanofiltration System

A Stirred stainless steel dead-end cell was supplied by Memcom Pty. Ltd (Newlands, Johannesburg, South Africa) and was utilised for reconcentration of the diluted Draw Solutions. As shown in figures 3.5 and 3.6, the stirred dead-end cell consists of three main parts; bottom plate with sintered stainless steel plate, cylindrical container with magnetic stirrer bar, and top plate with pressure gauge. The Stirred dead-end cell was connected to a pressurized nitrogen gas cylinder acted as an applied pressure source.

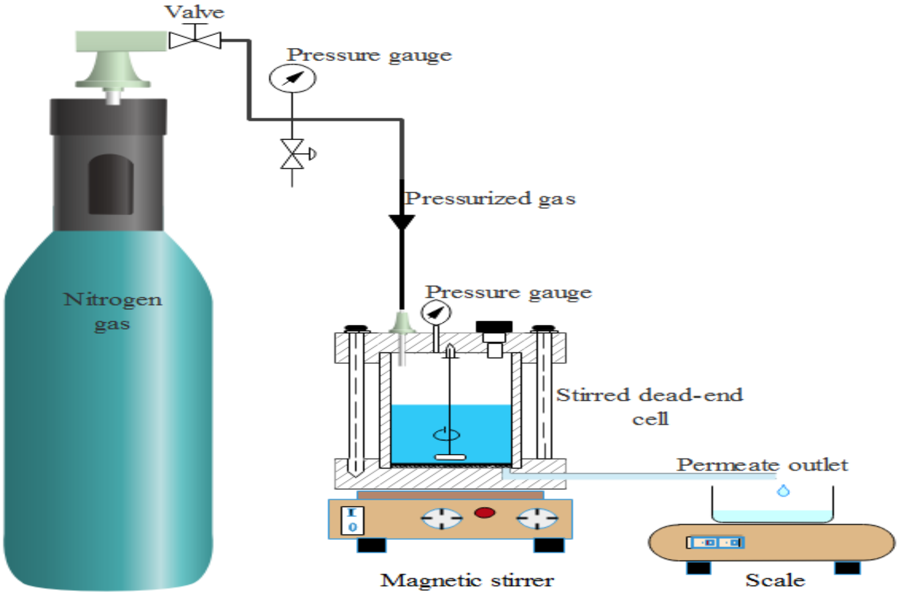


Figure 3.5: Schematic diagram of reconcentration system

Figure 3.6: Stirred stainless steel dead-end cell

During the experiments, the pressure was adjusted every two hours to keep the pressure difference between external applied pressure and osmotic pressure of the Draw Solution constant as illustrated is table 3.1

Table 3.1: Initial and increasing rate of applied pressure per two hours.

Draw Solution	Initial concentration, Initial osmotic pressure	Initial applied pressure	Constant increase per 2 hr
L-Alanine	0.035 g/mL, 11.0 atm	14.80 atm	3.80 atm
DADMAC	0.035 g/mL, 11.0 atm	14.80 atm	3.80 atm
PolyDADMAC	0.035 g/mL, 3.58 atm	06.91 atm	3.33 atm

3.3 Experimental Protocols

3.3.1 Experimental Protocols for FO Experiments Represented by the Following Steps

1- Preparation and Assembly of the Cell

I. Feed spacer was inserted into the cavity of cell bottom. The feed spacer as required to be flat and fitted the area of cavity. Note: the cell bottom is the part of cell body which has four holes.

II. Wetted O-rings were inserted into the grooves on the cell bottom and cell top to avoid the leakage.
III. Pre-cut membrane sheet was placed over the cavity using the four holes to put the sheet in right position.
IV. Two parts of the cell body were combined by fitting the alignment pins in the cell top snugly into the alignment holes in the cell bottom.
V. Solid plate was placed onto the cell top and the assembly of the membrane cell was completed by combining the bolts and nuts tightly.

2- Operation of the System

I. Feed and draw tanks were filled with 2 L solutions.
II. Two pumps and pipes were connected with the membrane cell as shown in schematic Fig 3.3. Cross flow rates of the Draw Solution and the Feed Solution were 1 L/min (60 L/hr).
III. Firstly, the Feed Solution was pumped into the Feed Solution channel for 5 min without pumping the Draw Solution to remove the air babbles.
IV. After 5 min, the Draw Solution was pumped into the Draw Solution channel and be directly in touch with the surface of the membrane.

The system was run for 24 hours and the changes of the weight of the Draw Solution was recorded by the electronic balance every 2 hours except the first two hours was taken every 30 minutes. The process was stopped after 24 hours and the new volume of both Draw Solution and Feed Solution were collected and measured. Changing of the osmotic pressure of the both solutions occurred as a result of transmission water molecules across the membrane sheet.

The aforementioned procedures were repeated using new variables according to the matrix in section 3.1 of this chapter till obtaining the optimum operating conditions.

3.3.2 Experimental Protocols for Reconcentration Experiments Using Nanofiltration System Represented by the Following Steps

1- Preparation and Assembly of the Stirred Dead-End Cell

I. Pre-cut membrane sheet was rinsed by distilled water to remove the preservative materials.
II. Membrane sheet was fitted on the top of the sintered stainless plate which occupies the cavity of bottom plate.

III. Wetted O-rings were inserted into the groove in bottom and top plates to avoid the solution leakage and releasing of pressurized gas.

IV. Cylindrical container with magnetic stirrer bar and top plate were combined the bottom plate by locking bolts and nuts tightly.

V. Pressurized nitrogen gas cylinder was connected to pressure gauge at the top plate.

2- Operation of the System

I. The cylindrical container was filled with 1 L of the Draw Solution at 0.035 g/mL and then the blind plug was closed tightly.

II. The stirred dead- end cell was placed on a magnetic stirrer and speed increased slowly from zero to 450 rpm.

III. Nitrogen gas was pressurized gently through the pressure gauge to reach the required pressure and then it was adjusted every two hrs according to table 3.1.

IV. Permeate volume was measured by electronic scale, whereas its osmotic pressure was measured by Osmomat 030 device.

V. Osmotic pressure of the concentrate Draw Solution inside the cylindrical container was calculated by the mass equation.

VI. The experiments were stopped when the concentration of the Draw Solution inside the cylindrical container raised to 0.085 g/mL.

VII. After the experiments was run completely, pressurized nitrogen gas gauge was closed and the cell was depressurized by opening the blind plug till the pressure gauge indicates 0.

VIII. The reconcentrated Draw Solution was collected and then the cell was prepared for a new experiment.

3.4 Characterisation of Membranes

3.4.1 FO Membranes

FO membranes used in the experiments are of two types, namely CTA-FO flat sheet membrane and TFC aquaporin flat sheet membrane:

- CTA-FO, supplied by Hydration Technology Innovation (Albany, Oregon, USA), is an anisotropic membrane with thickness less than 50 µm. The structure of the membrane consists of CTA active layer casted over embedded polyester mesh layer forming a two-layer membrane. Unlike the RO membranes structure which have thick porous support layer, the usage of the mesh layer is intended to reduce the thickness of the support layer

- TFC aquaporin inside^{TM} membrane, supplied by Sterlitech Corporation (Kent, Washington, USA), is a thin film composite membrane with thickness equals 110 μm (±15μm). It consists of thin dense polyamide active layer comprising aquaporin water channels deposited on porous PES support layer.

3.4.2 Nanofiltration Membrane

NF90 flat sheet Nanofiltration membrane, supplied by Dow FilmTec, USA, was chosen to reconcentrate the diluted Draw Solutions. NF90 membrane is a commercial and industrial TFC polyamide membrane with high chemical stability and durability. It is described by the manufacturer as a low net driving pressure membrane which allows it to operate effectively under low pressure and low energy. The maximum operating pressure and the maximum operating temperature are 41bar 45°C, respectively.

Table 3.2: Characteristics of NF90 Nanofiltration membrane.

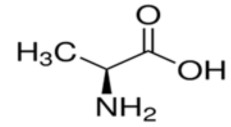
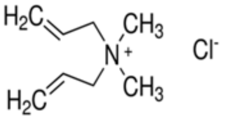
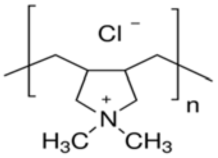
Membrane	Flux LMH/bar	Rejection %	MWCO Daltons	pH range	Pore size nm	Surface charge
NF90	78.2-102/8.96	99.00% $MgSO_4$	~200-400	2-11	0.73/0.68	Negative

3.5 Characterisation of Draw and Feed Solutions

3.5.1 Draw Solution

L-Alanine, DADMAC, and PolyDADMAC were purchased from Sigma-Aldrich Pty. Ltd, (Kempton Park, Johannesburg, South Africa). They were used to prepare the Draw Solutions of FO process. DADMAC and PolyDADMAC stock solutions were diluted by using distilled water to prepare 4 diluted Draw Solutions from each one at concentrations 0.035, 0.085, 0.120 and 0.155 g/mL. In the case of the L-Alanine, the solubility limit of L-Alanine is approximately 0.120 g/mL at the operation temperature. Therefore, only three Draw Solutions at 0.035, 0.085, and 0.120 g/mL concentrations were prepared. This will be detailed in section 3.6.1 of this chapter.

Table 3.3: Characteristics of the three Draw Solutions used in the research.

Common Name	Appearance	Formula	MW (g/mol)	Stock solution Concentration	Chemical Structure
A-Alanine	Powder	$C_3H_7NO_2$	89.09	≥ 98 % Purity (TLC)	
DADMAC	Liquid	$C_8H_{16}Cl\,N$	161.67	65 wt. % in H_2O	
Poly-DADMAC	Liquid	$C_8H_{16}Cl\,N$	< 100,000	35 wt. % in H_2O	

3.5.2 Feed Solution

Three Feed Solutions were investigated for the purpose of this dissertation: distilled water, synthesis fumaric acid, and fumaric acid produced by fermentation process. Firstly, distilled water was used in entire of the experiments during phase I, where the optical operation conditions for FO system were determined. Secondly, synthesis fumaric acid $C_4H_4O_4$ was purchased from Merck Pty. Ltd, (Merck Schuchardt OHG, Germany) and was used to prepare solution with concentration of 5 g/L. Synthesis fumaric acid solution was explored as a Feed Solution to investigate the efficiency of both CTA and TFC aquaporin protein membranes in rejection the molecules of fumaric acid. Thirdly, fumaric acid produced by fermentation process.

Fumaric acid was produced by microbial fermentation process using Rhizopus oryzae microorganism. It was collected as a final downstream of the current project of Bioreaction Engineering group at University of Pretoria. Rhizopus oryzae bioconverts glucose used as a source of carbon for producing fumaric acid. The downstream was processed through filter paper with 2.5 µm pore size (Whatman, 1442-110 Ashless, Grade 42) to produce filtrated downstream. This downstream consists of fumaric acid as a major product besides of other organic acids (succinic acid, lactic acid, citric acid, and acetic acid). Glucose, ethanol and mineral salts were also found in the downstream as by-products.

3.6 Measurements and Analytical Methods

3.6.1 Preparation the Draw Solution

Dilution process was used to prepare the desired Draw Solution from concentrated stock solution. The concentration of stock solutions were reduced by mixing it with distilled water that functions as a solvent. This entailed the application of the mass equation, to calculate the ratio between the required stock solution volume and the required amount of distilled water. The mass equation is expressed as follows

$$C_i X\, V_i = C_f\, X\, V_f \qquad \text{Eq 3.1}$$

where C_i is the stock solution concentration (g/mL). V_i is the required stock solution volume (mL). C_f is the final solution concentration (g/mL). And V_f is the final solution volume after the dilution (mL).

DADMAD stock solution with 65 wt.% in H_2O, and PolyDADMAC stock solution with 35 wt.% in H_2O were used to prepare 4 diluted solutions from each stock solution at concentrations of 0.035 g/mL, 0.085 g/mL, 0.120 g/mL, and 0.155 g/mL. L-Alanine powder with ≥ 98% purity was used to prepare 3 diluted solutions with concentrations of 0.035 g/mL, 0.085 g/mL, and 0.120 g/mL. Each diluted solution was 2000 mL.

For instance, preparation a diluted DADMAC solution with final concentration equal 0.035 g/mL from stock DADMAC solution 65 wt.% in H_2O was calculated according to the following equation

$$\left[\left(65\ {}^{\mathrm{g}}/_{100\ \mathrm{g\ H_2O}}\right) \mathrm{X}\ 1.04\ {}^{\mathrm{g}}/_{\mathrm{mL}}\right] \mathrm{X}\ \mathrm{V_i} = 0.035\ {}^{\mathrm{g}}/_{\mathrm{mL}}\ \mathrm{X}\ 2000\ \mathrm{mL}$$

$$\mathrm{V_i(mL)} = \frac{0.035\ \mathrm{X}\ 250.0}{0.676}$$

Then, V_i = 103.55 mL.

This means, to prepare 2000 mL of diluted DADMAC solution with concentration of 0.035 g/mL, a 103.55 mL was taken from stock solution and then a distilled water was added to the level of 2000 mL. The same procedure was applied to calculate the required volumes of the other concentrations. The following table summarises the required volumes to prepare 2000 mL of the Draw Solutions with various concentrations.

Table 3.4: Required volumes to prepare 2000 mL of the Draw Solutions with various concentrations

Final required concentration g/mL	Required mass of L-Alanine g	Required volume of stock DADMAC mL	Required volume of stock PolyDADMAC mL
0.035	70	103.55	183.49
0.085	170	251.48	445.61
0.120	240	355.03	629.10
0.155	----	458.58	812.58

3.6.2 Determination of Osmotic Pressure

Freezing point depression osmometer (Osmomat 030, cryoscopic osmometer, Gonotec, Berlin, Germany) was used to measure the osmolality of the solutions ($\mathrm{Osmol\,.\,kg^{-1}}$).

Figure 3.7: Osmomat 030, cryoscopic osmometer

Figure 3.8: Pipette and tubes

A 50 μL of the Draw Solution was pipetted into 0.5 mL centrifuge tube (Eppendorf AG, Hamburg, Germany) and ran it on the Osmometer. The readings of three samples were taken at zero time of experiments and then every two hours successively for 24 hours. However, the first two hours are marked by high drop in the readings. Therefore readings were taken every 30 minutes. The average of these three readings was taken to represent the osmolality. Then, osmotic pressure was calculated by converting the osmolality measurements to osmotic pressure in atm using the following equation

$$OP = RTc \qquad \text{Eq 3.2}$$

where OP is the osmotic pressure in atm. RT = 24.22 kg . atm . mol^{-1} at 22 °C. And

c is the osmolality in moles. kg^{-1}

The instrument was calibrated with distilled water and NaCl calibration solution of 1000 mosmol. Kg^{-1}.

3.6.3 Determination of Draw Solution Viscosity

Dynamic viscosity of the Draw Solutions was measured by Anton Paar MCR301 rheometer attached with Rheoplus 3.0X software, as illustrated in figure 3.9.

Figure 3.9: Anton Paar MCR301 rheometer

An enough amount of the Draw Solution was settled on the instrument base and then 50 mm parallel plate spindle descended toward the sample to push excess amount away. The sample would occupy the gab setting between parallel plate and the base. The gap was set up at 1 mm. Shear rate was applied on the sample and increased from 0.1 S^{-1} to 100 S^{-1} on logarithmic scale. The dynamic viscosity results were measured by Rheoplus 3.0X software. The rotational shear movement of the spindle depends on air bearing instead of mechanical bearing. This mechanism functions as an agent in the reduction of friction and therefore enhancing the instrument sensitivity during viscoelastic measurements (Ramjee 2015).

3.6.4 Determination of Water Flux

Water flux through the effective membrane area of 0.008 m^2 was calculated from the observation of the Draw Solution weight change. The balance reading was taken at zero time of experiments and then every two hours successively for 24 hours; except the first two hours the readings were taken every 30 minutes. Water flux was calculated by the following formula every two hours. (This formula assumes only the water flux)

$$J_{w_{i+2}} = \frac{W_{i+2} - W_i}{\rho_{water} \times A \times (t_{i+2} - t_i)} \qquad \text{Eq 3.3}$$

where $J_{w_{i+2}}$ is the water flux on the top of every two hours, $\mathrm{L/m^2.hr}$

$W_{i+2} - W_i$ is the change of the Draw Solution weight between every two hours, g

ρ_{water} is the water density, $\mathrm{g/L}$

A is the effective membrane area, m^2. And $t_{i+2} - t_i$ is the change of time, hour.

3.6.5 Determination of Ion Rejection by Nanofiltration Membrane

A certain percentage of solute molecules passed easily the membrane during the Draw Solution reconcentration due to the effect of external applied pressure, meanwhile other molecules were rejected. The dead-end stirred cell, which was used to reconcentrate the diluted Draw Solutions, works as a batch system. The ion rejection percentage by the dead-end stirred cell is defined as the reduction percentage of solute concentration in permeate at any time related to the initial solute concentration of the diluted Draw Solution and it is expressed as follows

$$R = (1 - {}^{C_P}/_{C_F}) \times 100 \qquad \text{Eq 3.4}$$

where C_P is the solute concentration in cumulative permeate, $\mathrm{g/mL}$. And C_F is the initial solute concentration of the diluted Draw Solution, $\mathrm{g/mL}$

The samples of the cumulative permeate were collected every 2 hours to measure the osmolality of permeate by OSMOMAT unit. Thus, the solute concentration in concentrate at any time was calculated by mass balance equation as follows

$$C_C = \frac{C_F V_F - C_P V_P}{(V_F - V_P)} \qquad \text{Eq 3.5}$$

where V_F & V_P are the initial volume of the diluted Draw Solution (was 1 L), and the volume of cumulative permeate at any time, respectively.

C_F &C_P are the initial solute concentration of the diluted Draw Solution (was 0.035 $\mathrm{g/mL}$), and the solute concentration in cumulative permeate at any time,$\mathrm{mg/L}$, respectively.

The experiment was run till the concentration of concentrate inside the cell reached the desirable concentration, which was 0.085 g/mL.

3.6.6 Determination of Reverse Solute Diffusion

Reverse Solute Diffusion of the Draw Solutions across the membrane into the Feed Solution side was calculated by measuring the Total Dissolved Solids (TDS) inside the Feed Solution. TDS was taken at zero time of experiments and then every two hours successively for 24 hours; except the first two hours the readings were taken every 30 minutes. The following formula was used to calculate the RSD

$$J_s = \frac{(C_t \times V_t - C_0 \times V_0)}{A \times t \times 1000} \qquad \text{Eq 3.6}$$

where; J_s is the reverse Solute Diffusion, $\mathrm{g/m^2.hr}$

C_0 & V_0 are the initial TDS, $\mathrm{mg/L}$, and the volume of Feed Solution, L, respectively

C_t & V_t are the TDS, $\mathrm{mg/L}$, and the volume of Feed Solution at time t, respectively

A is the effective membrane area, $\mathrm{m^2}$. And t is the time, hours.

The TDS was measured by using handheld conductivity meter (FG3-FIVEGO, METTLER TOLEDO) connected with LE703 robust conductivity probe. The TSD measuring range of this probe is 0.1 mg/L to 199.9 g/L.

3.6.7 HPLC Analysis

Samples from the Draw Solution and the Feed Solution tanks were collected after each experiment of phase III and analysed by the Agilent 1260 Infinity HPLC with refractive index RI detector (Agilent Technologies, USA). The amount of fumaric acid, glucose, succinic acid, lactic acid, ethanol and others, see the appendix, were separated and determined in a single injection by Aminex HPX-87H column (Bio-Rad Laboratories, USA). A 0.3 $\mathrm{mL/L}$ H_2SO_4 aqueous solution was utilised as mobile phase with flow rate started at 0.2 $\mathrm{mL/min}$ increased in gradual increments to 0.6 $\mathrm{mL/min}$ at a column temperature of $60°\mathrm{C}$.

CHAPTER 4

Forward Osmosis Performance Evaluation

The chapter summarizes the findings of the experiments conducted to evaluate the performance of the FO system. The chapter is presented under three main themes i.e., findings and discussions of FO system, findings and discussions of reconcentration system, and findings and discussions of the potential application.

Under the first theme results from the preliminary studies on the Draw Solution characteristics are reported. The change over time, the effect of osmotic pressure, membrane orientation, and flow direction parameters on water flux and reverse solute diffusion were evaluated. Secondly, findings on NF reconcentration system are also discussed. The third theme, a specific investigation of the viability of utilisation the FO process to recover water from both solutions of synthesis fumaric acid and fumaric acid produced by fermentation process was conducted.

4.1 The FO System

4.1.1 Preliminary Study on Draw Solutions Characteristics

Preliminary studies on the Draw Solutions characteristics were conducted before the bench-scale FO system was setup and FO experiments was started. Two characteristics including osmotic pressure and viscosity for each concentration were investigated. Knowing these characteristics assists in the performance exploration of the Draw Solutions and their influence on water flux and reverse solute diffusion studies.

Preparation of the Draw Solutions and determination of osmotic pressure were carried out according to methods described in chapter three, section 3.6.1 and 3.6.2. The osmotic pressure gradient versus concentrations of the three Draw Solutions L-Alanine, DADMAC, and PolyDADMAC are illustrated in Figure 4.1. It shows that the osmotic pressure of the three Draw Solutions increased linearly with increasing the Draw Solution concentration. Osmotic pressure values of L-Alanine and DADMAC were almost the same and higher than the osmotic pressure of PolyDADMAC.

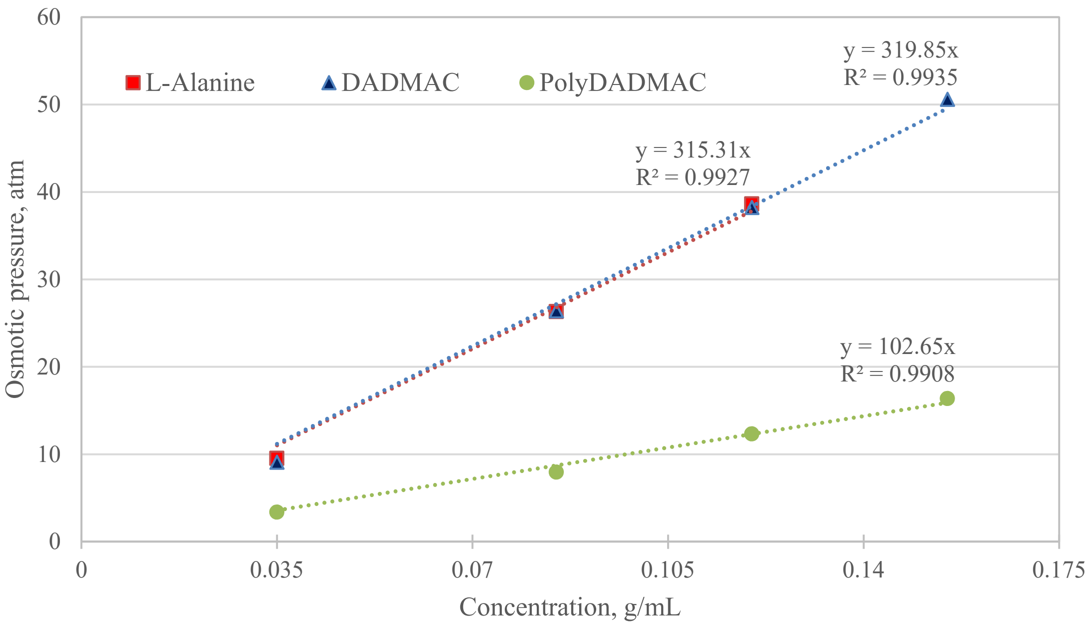


Figure 4.1: Osmotic pressure of L-Alanine, DADMAC, and PolyDADMAC solutions.

The dynamic viscosity results were measured by the Rheoplus 3.0X software as explained in chapter three, section 3.6.3. Figure 4.2 shows the dynamic viscosity versus the concentrations of the three Draw Solutions. The y-axis starts with 9.8×10^{-4} Pa. s which indicates at the dynamic viscosity of distilled water.

Figure 4.2 demonstrates that the dynamic viscosity of both L-Alanine and DADMAC with different concentrations are quite similar and close to the dynamic viscosity of distilled water. For example, the dynamic viscosity values of L-Alanine and DADMAC at 0.035 g/mL are 10.04×10^{-4} Pa. s and 9.19×10^{-4} Pa. s, respectively. The dynamic viscosity increased slightly by increasing the concentration of the Draw Solution. However, the dynamic viscosity of PolyDADMAC increased significantly from 20.74×10^{-4} Pa. s to 72.15×10^{-4} Pa. s with increasing the concentration of the Draw Solution from 0.035 g/mL to 0.155 g/mL. L-Alanine and DADMAC Draw Solutions with Low dynamic viscosity gave better performance than the high dynamic viscosity PolyDADMAC Draw Solution.

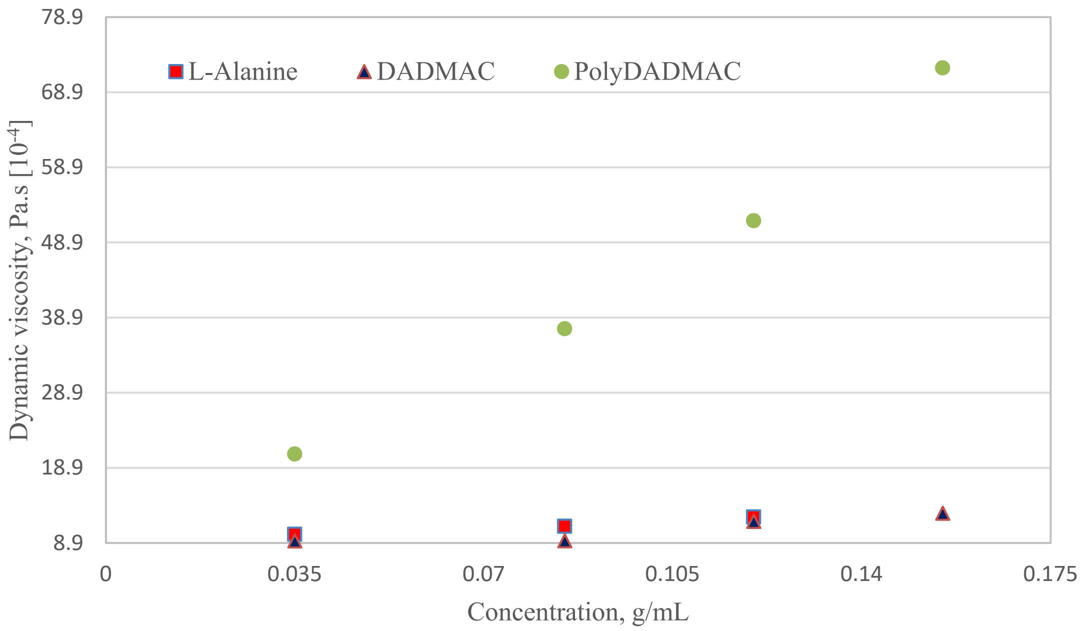


Figure 4.2: Dynamic viscosity of L-Alanine, DADMAC, and PolyDADMAC solutions

4.1.2 Water Flux and Reverse Solute Diffusion Studies

This section reports on the effect of varying osmotic pressure, flow direction, and membrane orientation on the flux output and reverse solute diffusion through CTA and TFC aquaporin protein membranes. The time of operation for each experiment was kept constant at 24 hr for each experiment. Distilled water was used as the Feed Solution for these experiments.

4.1.2.1 Variation of Water Flux and Reverse Solute Diffusion over Operation Time

In order to identify the values of water flux and reverse solute diffusion a series of experiments were conducted. On the one hand, CTA and TFC aquaporin protein membranes were used under FO mode during the set up experiments of water flux identification. Distilled water as a Feed Solution was pumped first into the membrane cell with flow rate 1 L/min (60 L/hr) and then the Draw Solution was pumped with same rate. The following figures were plotted by using water flux calculations based on the change in the Draw Solution weight as it is explained in chapter three, section 3.6.4.

Figure 4.3 represents the water flux produced by L-Alanine, DADAMAC, and PolyDADMAC with different concentrations of each one using the CTA flat sheet membrane. While figure 4.4 represents the water flux of same components and under similar conditions using the TFC aquaporin protein flat sheet membrane. Figures 4.3 and 4.4 show similar water flux behaviour of the three Draw Solutions with different concentrations through both CTA and TFC aquaporin protein membrane. The water flux decreased dramatically during the first four hours of the experiments. Afterward, the water flux decreased relatively slowly over the remaining time of the experiment. However, in the case of using PolyDADMAC as a Draw Solution with the TFC aquaporin protein membrane (Fig 4.4-c), the water flux decreased slightly from the beginning of experiments to the end. Figure 4.3 also illustrates that the highest water flux was achieved by using 0.085 g/mL L-Alanine (Fig 4.3-a) and 0.155 g/mL DADMAC (Fig 4.3-b) through the CTA flat sheet membrane with initial water Flux 22 LMH and 20 LMH, respectively. Water flux of 0.085 g/mL L-Alanine dropped to 9.63 LMH after four hours then decreased slowly with time to 4.75 LMH after 24 hours.

The water flux of 0.155 g/mL DADMAC dropped to 12.69 LMH after four hours then decreased to 4.31 LMH after 24 hours. Whereas, the lowest initial water flux occurred through the CTA flat membrane when 0.035 g/mL PolyDADMAC was used as a Draw Solution. It fell from 4 LMH to 0.075 LMH at the end of experiment (Fig 4.3-c). Water flux demonstrated similar behaviour through the TFC aquaporin protein flat sheet membrane as it is illustrated in figure 4.4. However, it was observed in the figures 4.3 and 4.4 that water flux through the CTA flat sheet membrane were higher than water flux through the TFC aquaporin protein flat sheet membrane. L-Alanine at concentration 0.085 g/mL (Fig 4.4-a) and DADMAC at concentration 0.155 g/mL (Fig 4.4-b) maintained the highest water flux. Water flux of L-Alanine at concentration 0.085 g/mL started at 17 LMH as an initial value and reached to 4.50 LMH at the end of experiment. While, water flux of DADMAC at concentration 0.155 g/mL declined from 11.50 LMH as an initial to 3.50 LMH at the end of experiment.

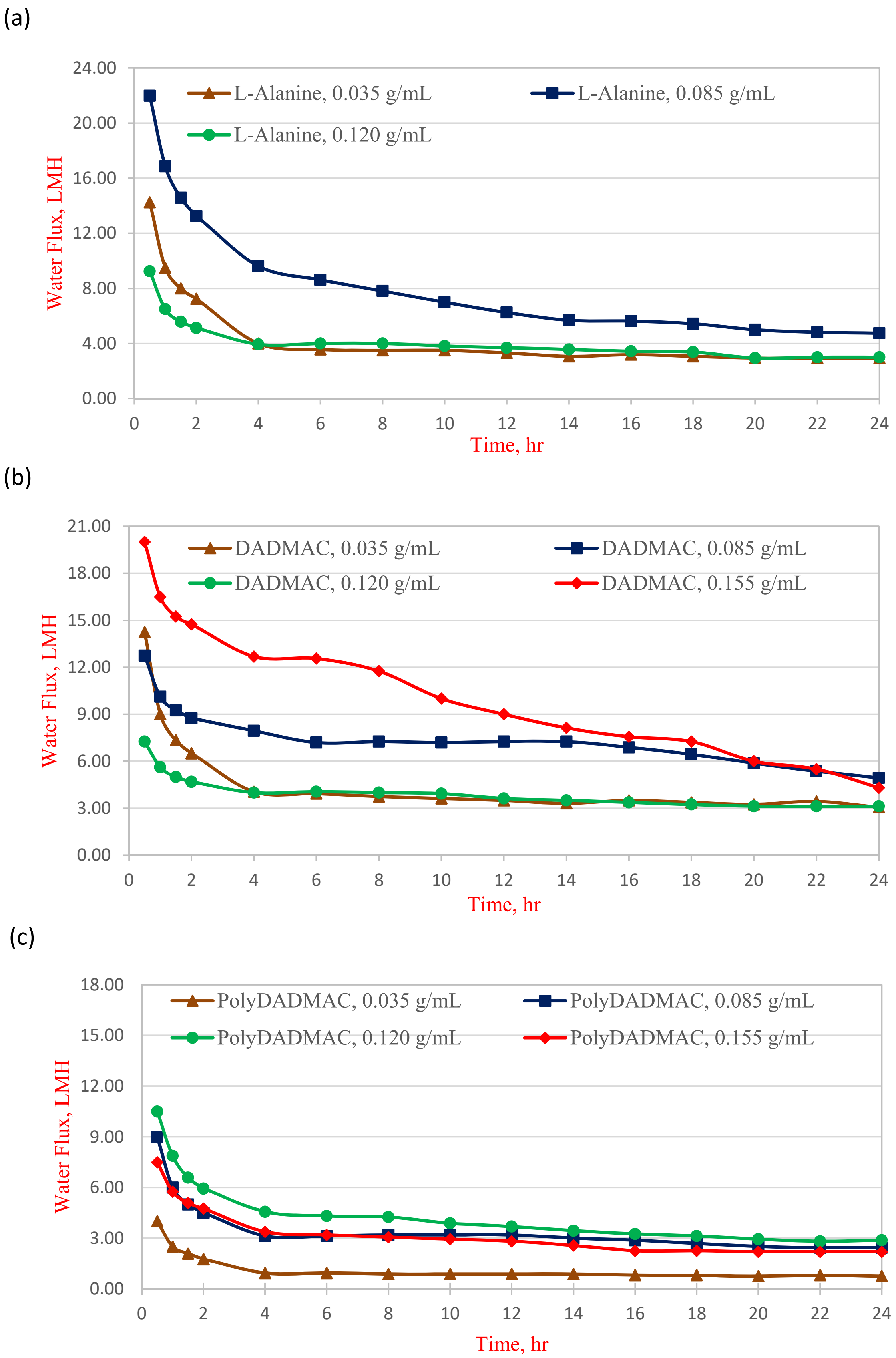


Figure 4.3: Variation of water flux by L-Alanine, DADMAC and PolyDADMAC using CTA flat sheet membrane over the operation time

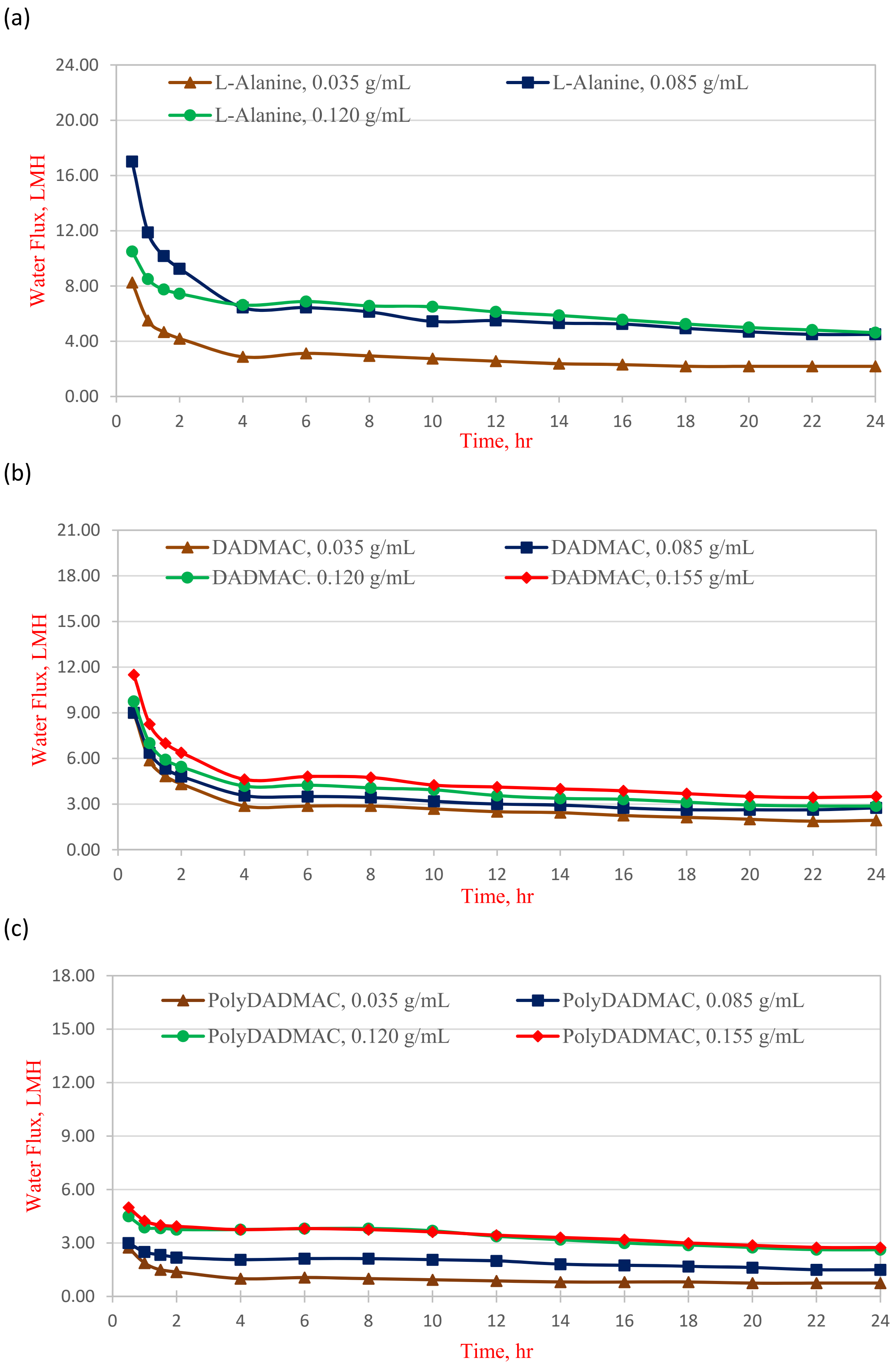


Figure 4.4: Variation of water flux by L-Alanine, DADMAC and PolyDADMAC using TFC aquaporin protein flat sheet membrane over the operation time

The features of both membranes including structure, thickness and hydrophilic nature influenced the water flux. Both of CTA and TFC aquaporin protein are anisotropic membranes. The support layer of the CTA is polyester mesh meanwhile the one of the TFC aquaporin protein membrane is porous PES layer combined with water channels. The porous support layer of CTA and TFC aquaporin protein membrane enhances water flux by allowing water molecules to diffuse easily through it. However, the high water flux through the CTA membrane compared with the TFC aquaporin protein membrane can be explained regarding to the thickness and the material of the membranes. The open structure of mesh layer in the CTA is more loose than that of the PES support layer. The thinner CTA flat sheet membrane with thickness of about 50 µm achieved high water flux than the thicker TFC aquaporin protein flat sheet membrane with thickness of about 110 µm. The hydrophilic property of CTA material also resulted in a high water flux.

On the other hand, figures 4.5 and 4.6 were plotted based on the measurements of the reverse solute diffusion. The measurements were taken intensively every 30 minutes during the first two hours, after that every two hours till the end of the experiments. The method of measuring reverse solute diffusion is explained in chapter 3, section 3.6.6. Figure 4.5 displays the magnitude of reverse solute diffusion of L-Alanine, DADMAC, and PolyDADMAC with different concentrations of each one through the CTA flat sheet membrane versus operation time. Figure 4.6 shows the magnitude of reverse solute diffusion of the same components and the same period of time through the TFC aquaporin protein flat sheet membrane.

By studying both figures 4.5 and 4.6, it was demonstrated generally that the reverse diffusion of all Draw Solutions through the TFC aquaporin protein membrane was less than that through the CTA membrane. Figure 4.6 shows that the reverse solute diffusion through the TFC aquaporin protein membrane was nearly constant from the beginning to the end of experiments regardless of the variety in the Draw Solution concentration. Nevertheless, figure 4.5 shows the reverse solute diffusion through the CTA membrane changed gradually with time especially reverse diffusion of DADMAC at high concentration 0.155 g/mL (Fig 4.5-b). It was observed that the lowest reverse solute diffusion was the reverse diffusion of 0.085 g/mL of L-Alanine through both used membranes. It fell from 0.05 GMH to 0.00 GMH through the CTA membrane (Fig 4.5-a) and from 0.05 GMH to 0.01 GMH through the TFC aquaporin protein membrane (Fig 4.6-a). On the contrary, the highest reverse solute diffusion was the reverse diffusion of DADMAC at 0.155 g/mL of through the CTA membrane (Fig 4.5-b). The magnitude started from 16.77 GMH and reached gradually after 24 hours to 8.83 GMH.

The reverse diffusion of 0.155 g/mL of DADMAC through TFC aquaporin protein membrane was nearly constant (Fig 4.6-b). It started from 7.98 GMH to 7.40 GMH at the end of experiment. In case of using PolyDADMAC as a Draw Solution (Fig. 4.5-c), it was observed that the reverse diffusion of PolyDADMAC increased by increasing the viscosity of the Draw Solution. Increasing the viscosity of the Draw Solution due to concentration incline caused a severe concentration polarization near membrane surface and then increasing in reverse solute diffusion.

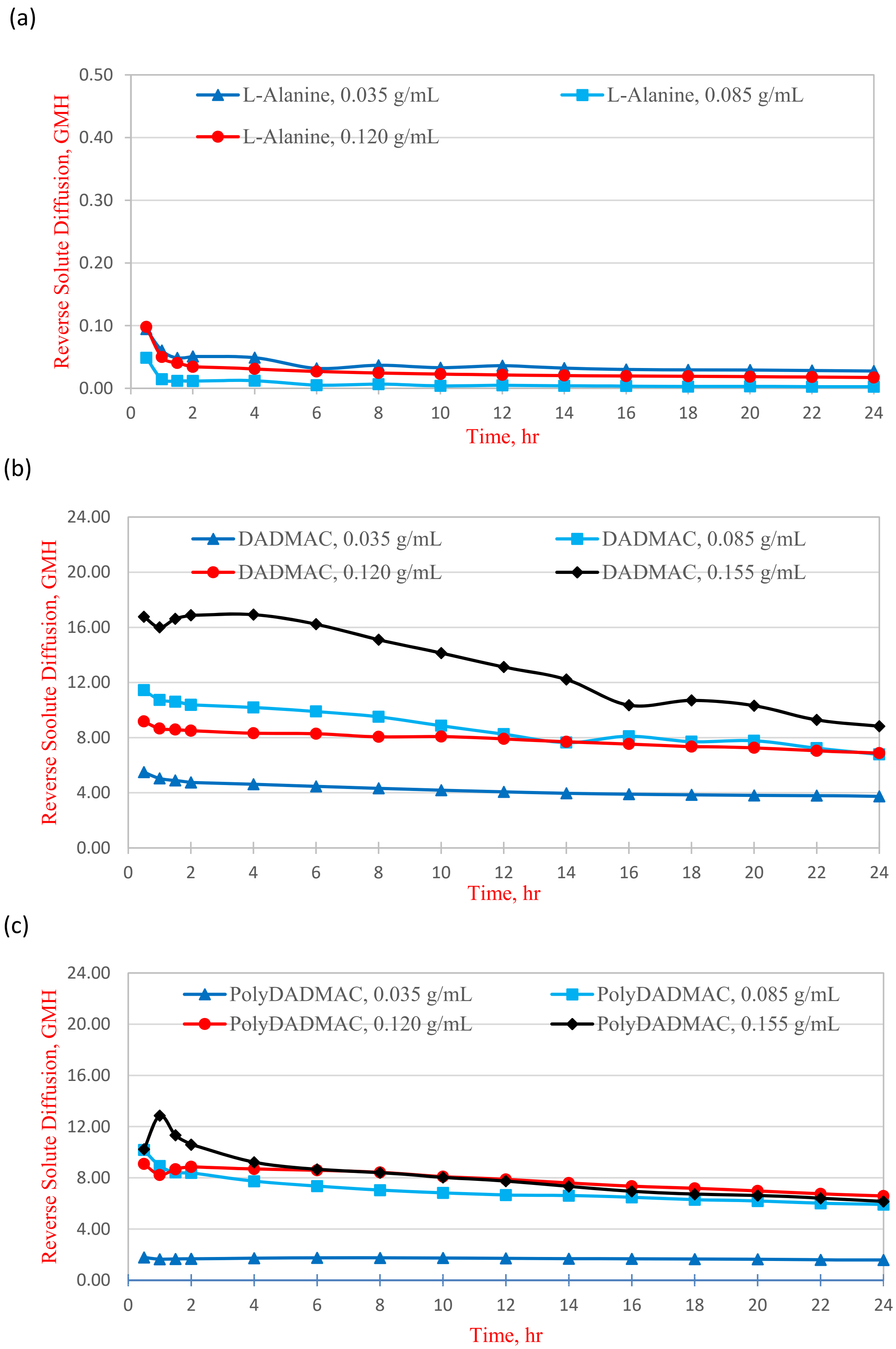


Figure 4.5: Reverse solute diffusion of L-Alanine, DADMAC and PolyDADMAC using CTA flat sheet membrane over the operation time

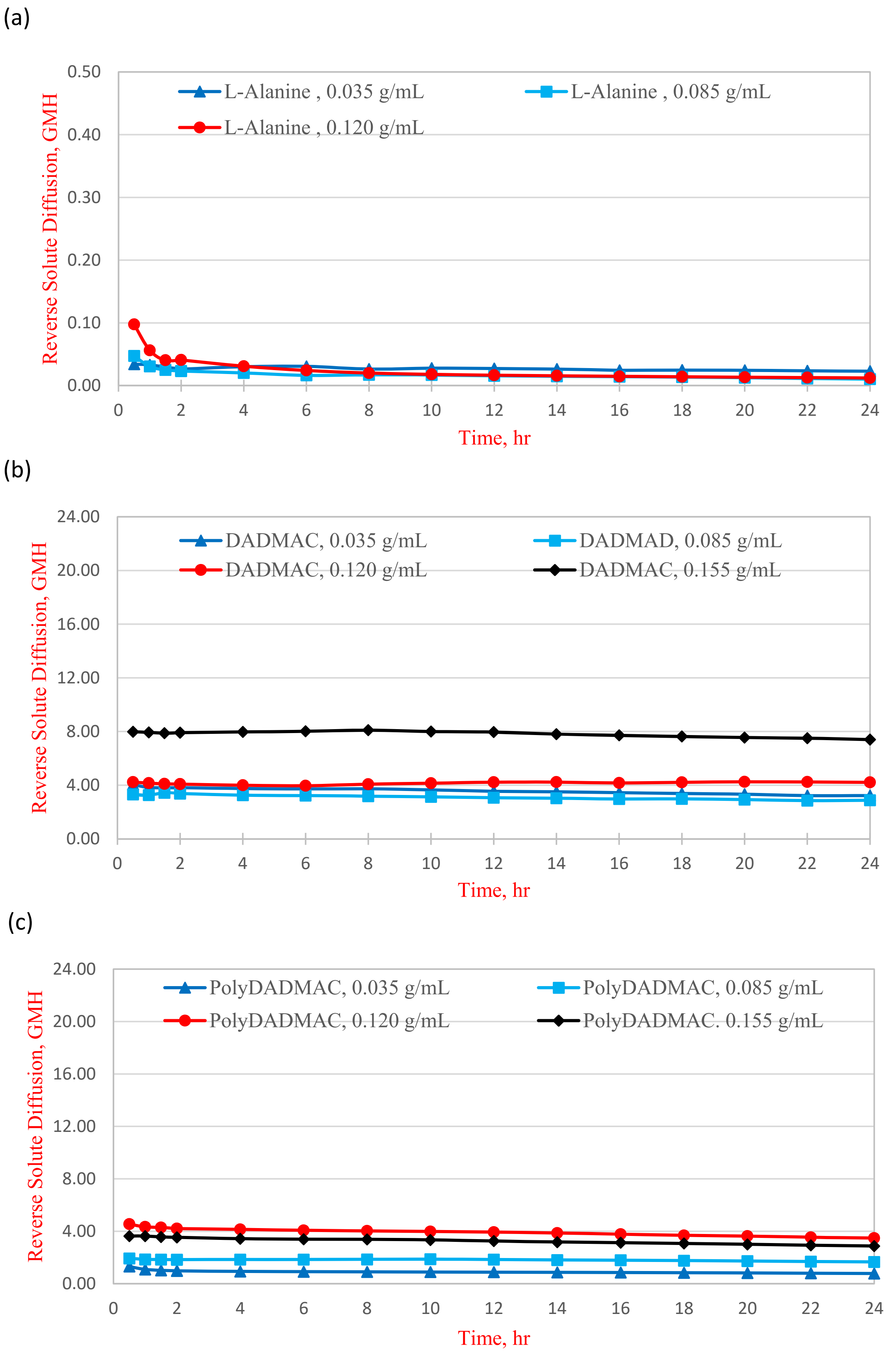


Figure 4.6: Reverse solute diffusion of L-Alanine, DADMAC and PolyDADMAC using TFC aquaporin protein flat sheet membrane over the operation time

4.1.2.2 The Effect of the Draw Solutions Osmotic Pressure on Water Flux

The decline of osmotic pressure of the Draw Solutions over the experiment time affected the water flux significantly. This declination was attributed to the dilution effects in the Draw Solutions. Water molecules cross the membranes from the Feed Solution side to the Draw Solution side due to the driving force of the Draw Solution. Figure 4.7 shows that water flux trends of L-Alanine, DADAMAC, and PolyDADMAC at various concentrations through the CTA flat sheet membrane versus the changing of osmotic pressure during the experiments. Figure 4.8 represents the water flux trends of same components versus the changing of osmotic pressure using the TFC aquaporin protein flat sheet membrane.

These trends showed similar behaviour to the previous observation which was the change in water flux over operation time. In case of using the CTA membrane, water flux produced by the Draw Solutions with osmotic pressure less than 15 atm dropped dramatically within 2 hrs after commencing the experiments while the osmotic pressure decreased faintly. However, after the first 2 hrs the water flux declined slightly while the decrease of osmotic pressure was more apparent. Similar behaviour of the water flux drop was observed when the TFC aquaporin protein membrane was used as shown in figure 4.8. Besides that, Figure 4.7 illustrates that the majority of water flux cross CTA membrane reached approximately the same level at the end of experiments irrespective of the initial values of the water flux. For example, (Fig 4.7-a) and (Fig 4.7-b) show that water flux was much closer to 4 LMH when L-Alanine and DADMAC with different concentrations and different initial water flux values were used. The same was observed when the TFC aquaporin protein membranes were used as shown in figure 4.8.

As a general rule, the magnitude of water flux depends on the osmotic pressure of the Draw Solution. Solutions with high solute concentration should have high osmotic pressure resulting in high water flux. However, in the course of the experiments conducted, I noticed that some of the Draw Solutions at low concentration produced a higher water flux than the same Draw Solutions at higher concentration. For instance, L-Alanine and DADMAC with 0.120 g/mL achieved the lowest water flux through the CTA membrane compared to other concentrations as shown in (Fig 4.7-a) and (Fig 4.7-b). The same was also observed through the TFC aquaporin protein membrane when L-Alanine at the same concentration was used as a Draw Solution. Water flux produced by L-Alanine at 0.120 g/mL concentration was lower than water flux when 0.085 g/mL of L-Alanine was used as displayed in (Fig 4.8-a).

At this point I submit that the unexpected behaviour of the L-Alanine and DADMAC at 0.120 g/mL has no reference in the literatures pertaining to FO. I forward a simple explanation which is based on the interaction between the ions of the Draw Solution and the charged FO membrane surface. The number of ions presented in the Draw Solution at certain concentration could have serious impacts on the FO membrane surface consequently affects the performance of the membrane. It was observed in this research that the low water flux behaviour occurred when L-Alanine and DADMAC with exactly concentration of 0.120 g/ml among other concentrations were used as draw agents. In this regards, an intensive studies are recommended to take a place in the future focusing the interaction between Draw Solutions with different concentrations and the charged FO membrane surface.

In case of using PolyDADMAC as a Draw Solution (Fig 4.7-c), water flux produced by 0.155 g/mL concentration through the CTA membrane was lower than 0.120 g/mL. This declination of water flux occurred due to the sharp increasing in PolyDADMAC viscosity with increasing the concentration. High viscosity of PolyDADMAC causes severe concentration polarization near membrane surface and causes decrease in water flux. Similar results were observed in the literatures of Ge et al. (2013) and Tian et al. (2015) when anionic polyelectrolytes of PAA-NA and PSS were used as a Draw Solution with high viscosity (Ge et al. 2013; Tian et al. 2015). The performance of high viscosity polymer solutions was less than that of lower viscosity. However, the effect of viscosity did not appear when L-Alanine and DADMAC were used with various concentrations because of their viscosity is quite similar to water viscosity.

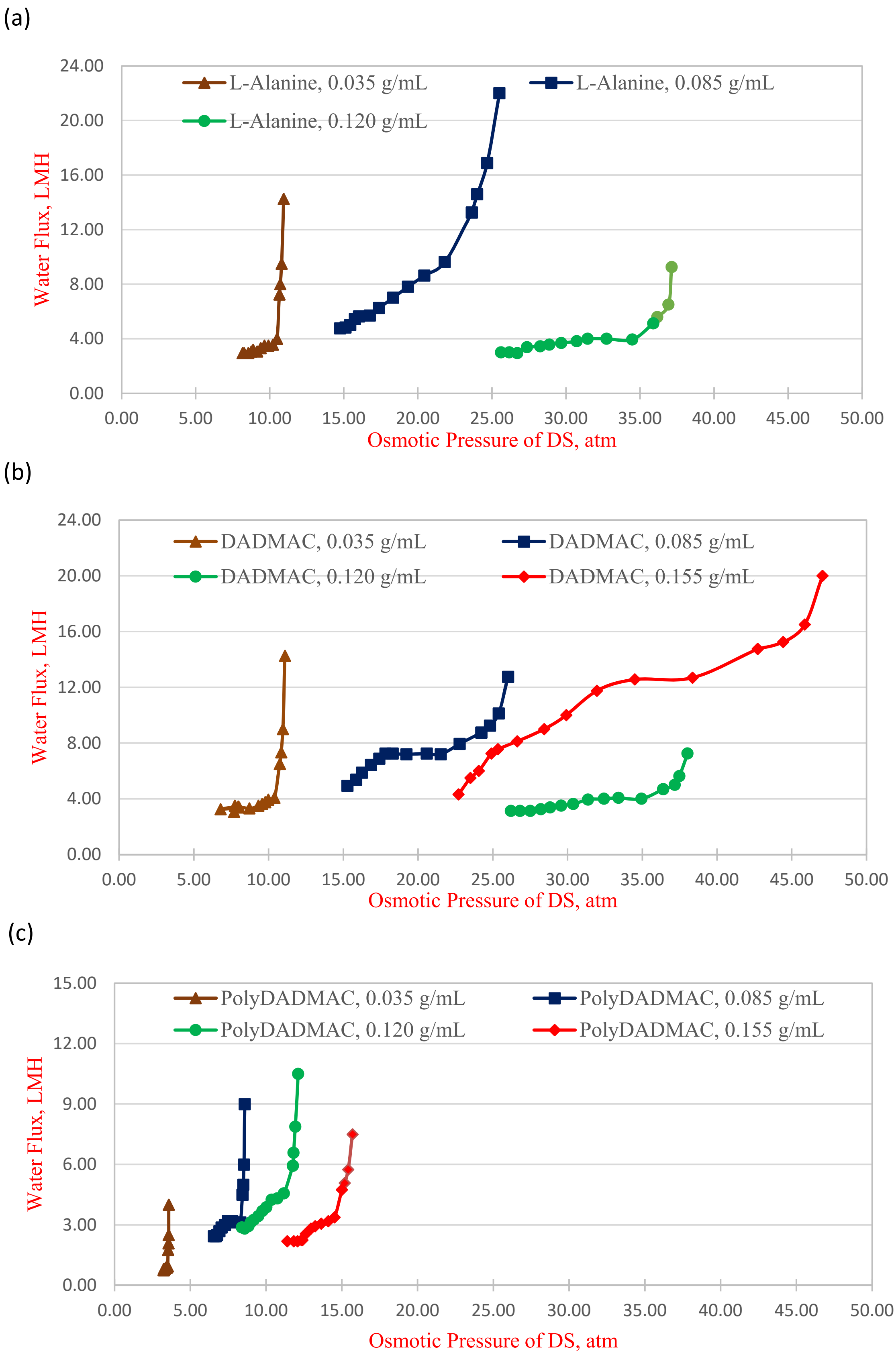


Figure 4.7: Water flux by L-Alanine, DADMAC and PolyDADMAC using CTA flat sheet membrane under osmotic pressure variable.

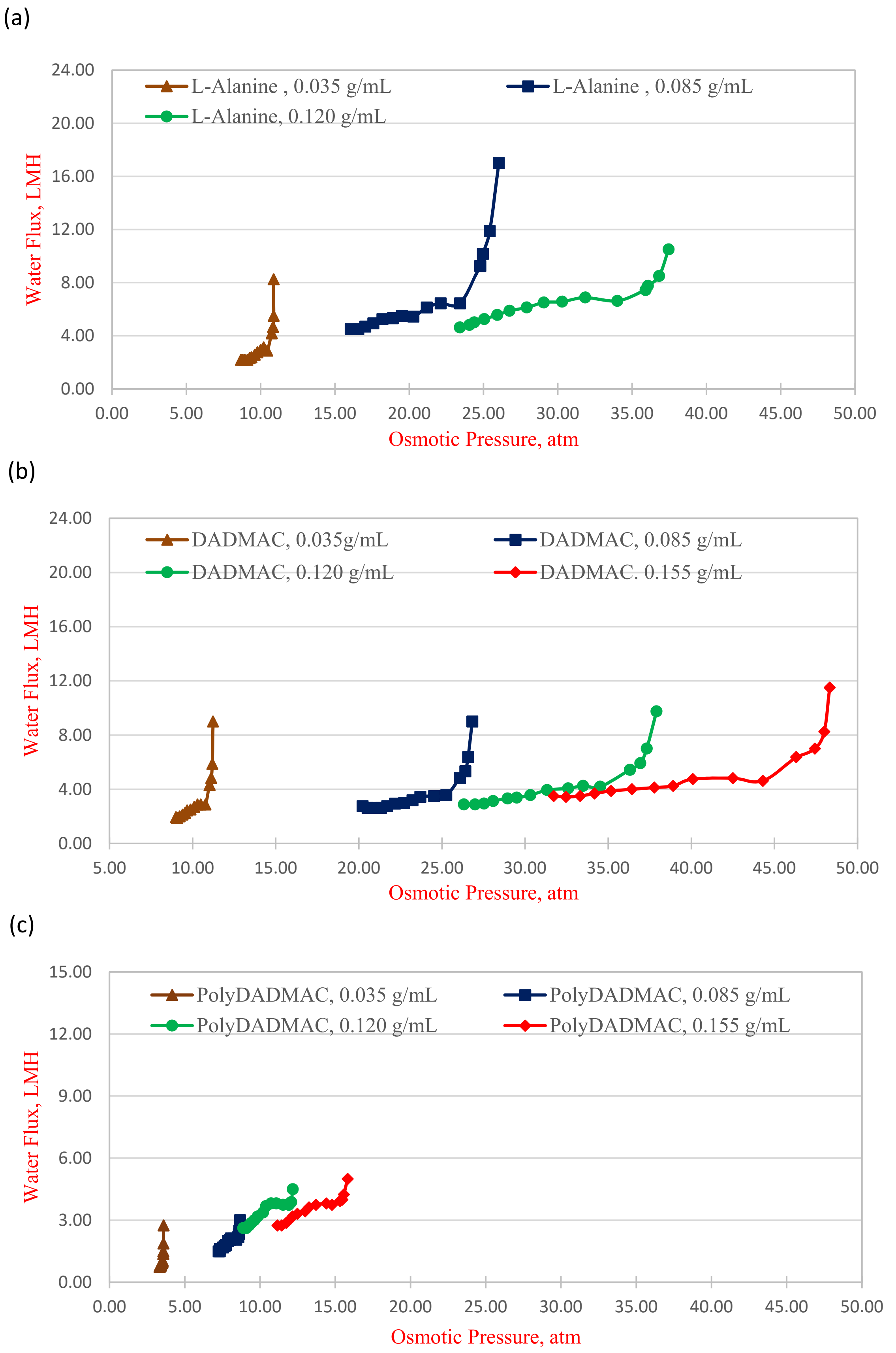


Figure 4.8: Water flux by L-Alanine, DADMAC and PolyDADMAC using TFC aquaporin protein flat sheet membrane under the osmotic pressure variable.

4.1.2.3 The Effect of Membrane Orientation on Water Flux and Reverse Solute Diffusion

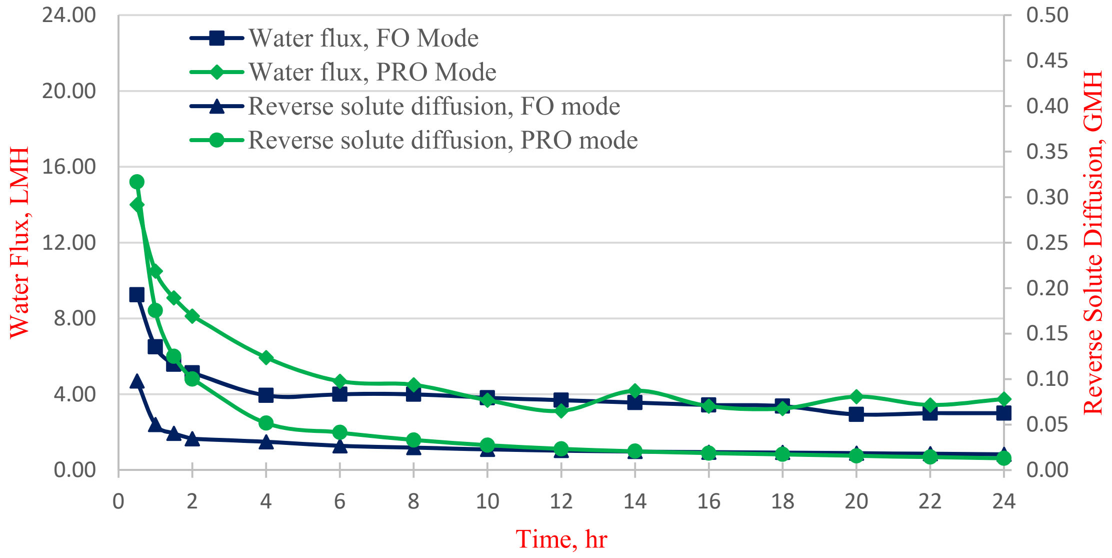
The effect of changing the orientation of the CTA and TFC aquaporin protein flat sheet membranes on water flux and reverse solute diffusion were tested. L-Alanine and DADMAC at concentration 0.120 g/mL were used. Meanwhile distilled water was used as the Feed Solution.

Figure 4.9 shows the comparison between water flux and reverse solute diffusion L-Alanine at 0.120 g/mL and DADMAC at 0.120 g/mL using the CTA flat sheet membrane under FO and PRO modes. Figure 4.10 demonstrates the comparison between water flux and reverse solute diffusion of both Draw Solutions using the TFC aquaporin protein flat sheet membrane under both modes. As observed in figures 4.9 and 4.10, water flux through both CTA and TFC aquaporin protein membranes under PRO mode was higher than water flux under FO mode. The observed behaviour was expected in line with the previous results of the literatures (Ge et al. 2012; Chen 2013; Mattia Stefani 2014; Cai & Hu 2016). The explanation of achieving higher water flux under PRO mode is due to the asymmetric structure of membranes which leads to increase the effect of the ICP inside the support layer under FO mode compared to PRO mode and then decline the water flux.

In case of using the CTA membrane under PRO mode, the declination of water flux produced by L-Alanine over the experiment time was 10.25 LMH (Fig 4.9-a). Similar magnitude of water flux declination from the initial time to the end of the experiment was also observed when DADMAC was used as a Draw Solution (Fig 4.9-b). In Contrast, the magnitude of the water flux declination became less in case of using the TFC aquaporin protein membrane under PRO mode. The declination of water flux trend through the CTA membrane under PRO mode was sharper than that of through the TFC aquaporin protein membrane. This declination is attributed to the membrane structure that affects the ICP of membranes. The concentration of reverse solute diffusion inside the loose open structure of the CTA membrane support layer would be higher than that in PES layer of the TFC aquaporin protein membrane. High magnitude of the ICP inside the CTA membrane occurred with time which caused fast drop in water flux. (Fig 4.10-a) illustrates that water flux of L-Alanine dropped by 6.5 LMH from the initial time to the end of the experiment. In the same way (Fig 4.10-b) demonstrates water flux of DADMAC dropped by 5.94 LMH.

The reverse solute diffusion of L-Alanine through both CTA (Fig. 4.9-a) and TFC aquaporin protein (Fig. 4.10-a) membranes was higher in PRO mode than that in FO mode in the first 12 hours of the experiment. Thereafter, the two trends started matching each other and demonstrating same values. In case of using DADMAC as a Draw Solution, the reverse solute diffusion through the TFC aquaporin protein membrane in PRO mode was also higher than that in FO mode in first 12 hours of the experiment (Fig. 4.10-b). However, reverse solute diffusion of DADMAC through the CTA membrane manifested exact opposite behaviour (Fig. 4.9-b). The reverse solute diffusion of DADMAC through the CTA membrane was in FO mode higher than that in PRO mode in the first half time of the experiment. The observed results were in line with previous results of the literatures (Ge et al. 2012; Chen 2013; Mattia Stefani 2014; Cai & Hu 2016). The literatures demonstrate that the reverse solute diffusion in FO mode is lower than in PRO mode. These behaviours are also attributed to the asymmetric structure of membranes where the combination of CP and orientation impacts affect the reverse solute diffusion.

(a)



(b)

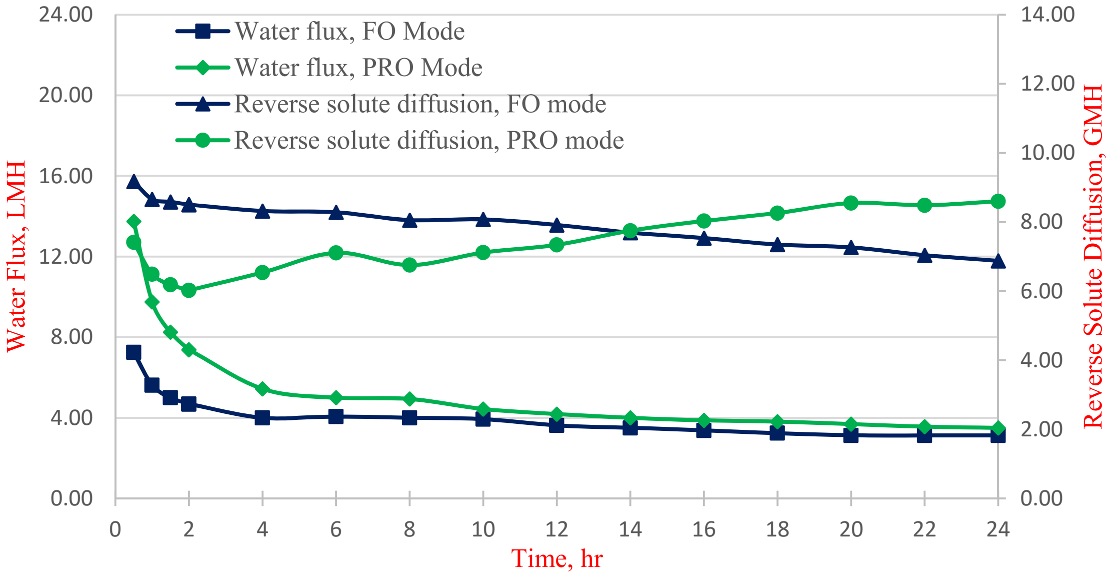
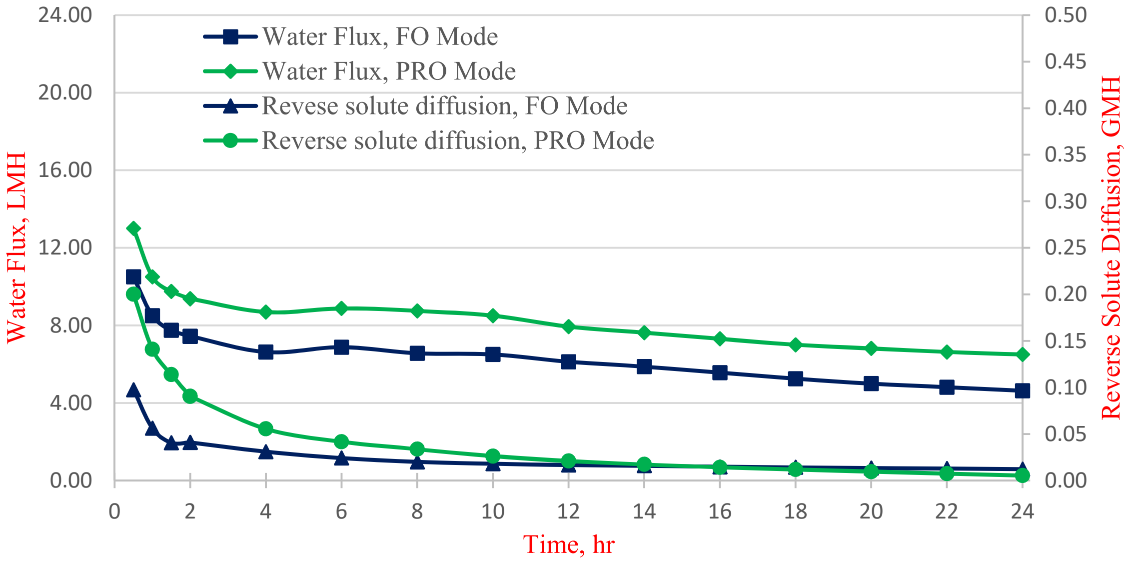


Figure 4.9: Comparison between water flux and reverse solute diffusion of L-Alanine at 0.120 g/mL and DADMAC at 0.120 g/mL using CTA flat sheet membrane under FO mode and PRO mode.

(a)



(b)

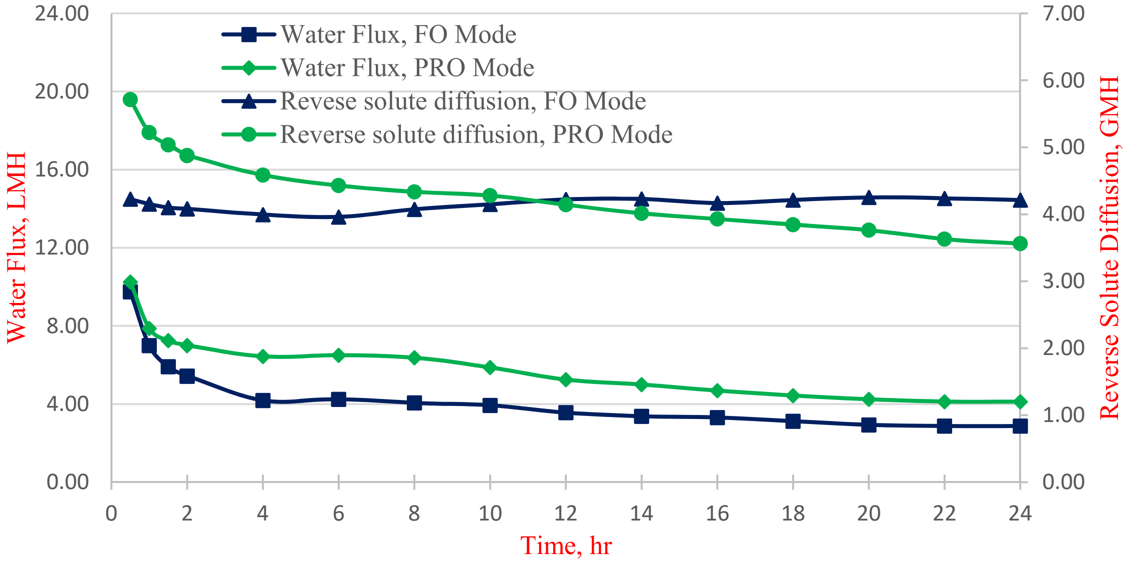


Figure 4.10: Comparison between water flux and reverse solute diffusions of L-Alanine at 0.120 g/mL and DADMAC at 0.120 g/mL using TFC aquaporin protein flat sheet membrane under FO mode and PRO mode.

4.1.2.4 The Effect of Changing the Pumping Scheme of the Draw Solution and Feed Solution on Water Flux and Reverse Solute Diffusion

In the previous experiments, the Feed Solution was pumped firstly for 5 minutes into the Feed Solution channel then the Draw Solution was pumped into the Draw Solution channel. However, a series of experiments were intended to examine the effect of reversing the pattern of pumping the solutions. The reversing of pumping pattern was applied to study the effect of that on water flux and reverse solute diffusion through membranes. Hence, the Draw Solution was pumped into its channel then by 5 minutes later the Feed Solution was pumped into its channel. Membranes were also operated in this section under FO mode. L-Alanine at 0.085 g/mL and DADMAC at 0.085 g/mL were used as Draw Solutions. The flow rate of the Draw Solutions and the distilled water, which the latter was used as a Feed Solution, was 1 L/min (60 L/hr). Figure 4.11 displays water flux and reverse solute diffusion through the CTA flat sheet membrane of 0.085 g/mL L-Alanine and 0.085 g/mL DADMAC under two patterns of pumping the solutions. While, figure 4.12 shows water flux and the reverse solute diffusion of same Draw Solutions but using the TFC aquaporin protein flat sheet membrane.

Pumping the Draw Solution first into the membrane has affected the integrity of the membrane structure especially the support layer during the operation under FO mode. The support layer was fully saturated by the Draw Solution for sometimes before the Feed Solution was ready to be pumped. Consequently, a severe ICP inside the support layer occurred when the Feed Solution was pumped. Low water flux and high reverse solute diffusion through membranes were manifested. Figure 4.11 illustrates that water flux through the CTA membrane in case of pumping both L-Alanine and DADMAC first was clearly lower than the case of pumping the Feed Solution first. In case of pumping 0.085 g/mL DADMAC solution first, the water flux through the CTA membrane collapsed dramatically from 15.75 LMH to 0.25 LMH within the first 10 hours of the experiment time. A massive amount of DADMAC solute was reversely diffused to the Feed Solution side through the structure of the CTA membrane when the Draw Solution was pumped first (Fig. 4.11-b).The declination of water flux can be attributed to a severe ICP occurred inside the support layer. However, this dramatic collapse of the water flux can be attributed to the possibility DADMAC with 0.085 g/mL concentration empoisoned the membrane structure and affected seriously the integrity of the membrane.

Figure 4.12 shows a slight difference in water flux through the TFC aquaporin protein membrane between the two pumping cases. However, a low water flux was observed in case of pumping both L-Alanine and DADMAC before the Feed Solution. Additionally, the reverse diffusion of each Draw Solutions was quite similar in both cases. This indicates that the TFC aquaporin protein membrane was more stable than the CTA membrane. The TFC aquaporin protein membrane was not significantly affected by the changes in the pumping scheme of the solutions compared to the CTA membrane.

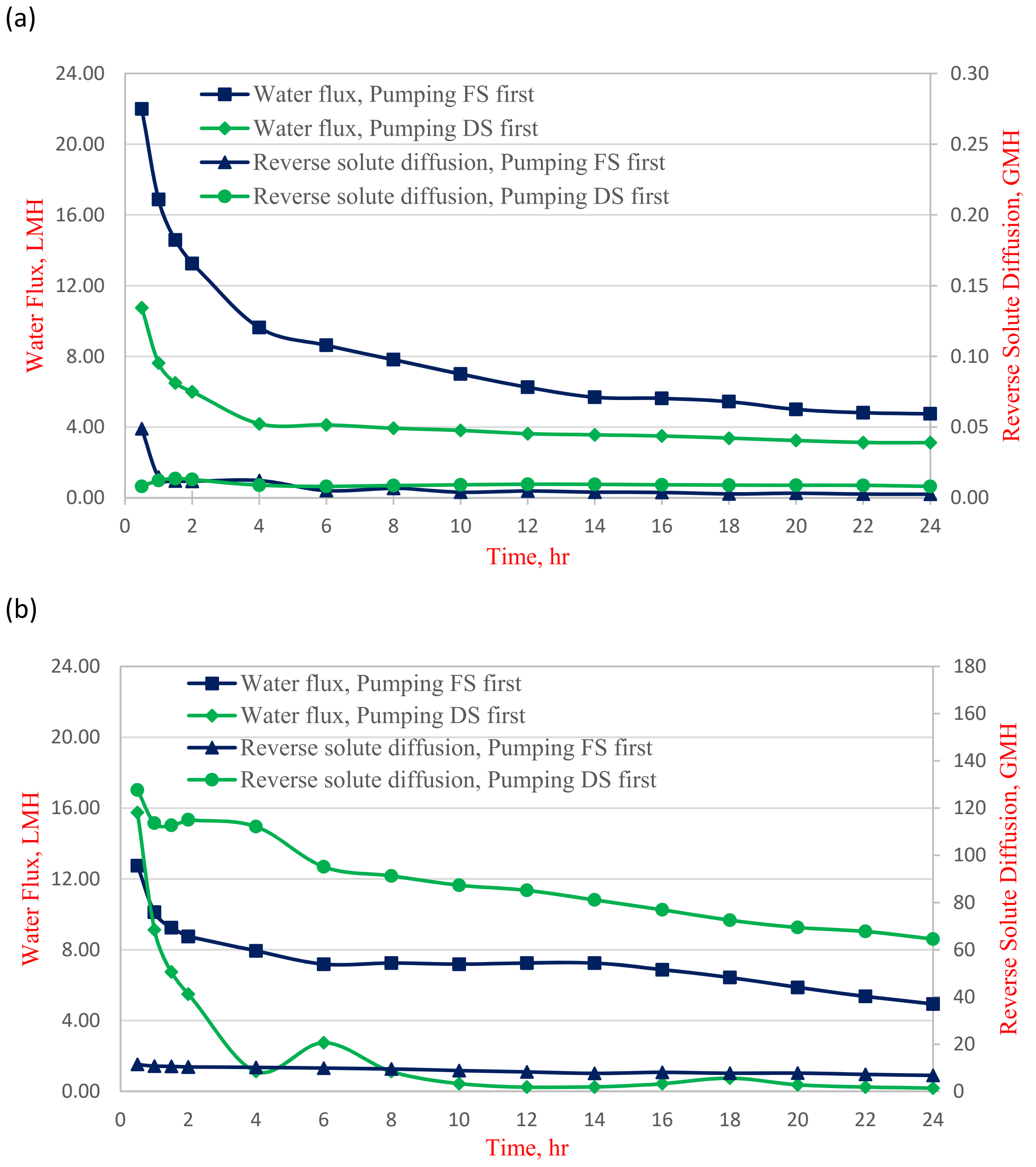


Figure 4.11: Comparison between water flux and reverse solute diffusion of L-Alanine at 0.085 g/mL and DADMAC at 0.085 g/mL using CTA flat sheet membrane under two ways of pumping scheme.

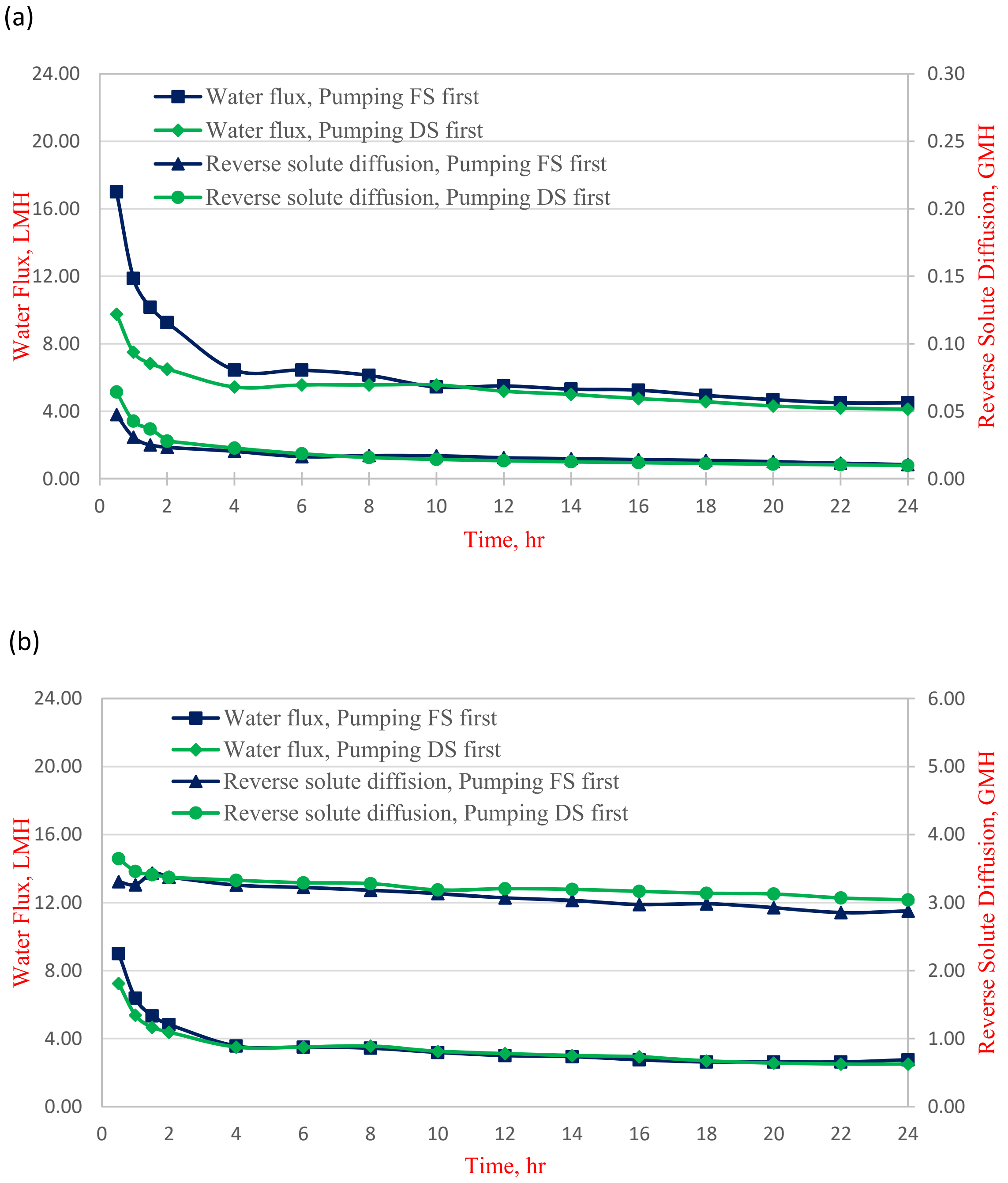


Figure 4.12: Comparison between water flux and reverse solute diffusion of L-Alanine at 0.085 g/mL and DADMAC at 0.085 g/mL using TFC aquaporin protein membrane flat sheet membrane under two ways of pumping scheme.

4.2 The Reconcentration System

The findings and discussions of the phase II of the experimental plan, which determines the optimum operating conditions for the regeneration system, are provided in this section. Diluted Draw Solutions of L-Alanine, DADMAC, and PolyDADMAC were produced at the end of the FO experiments. NF system was chosen to accomplish the mission of reconcentration them. The findings provided in this section demonstrates that the NF system is an effectual technique to reconcentrate the diluted Draw Solutions. The experimental procedures were conducted based on the experimental protocol of reconcentration the Draw Solutions using NF system as explained in chapter 3, section 3.3.2.

Tables 4.2, 4.3, and 4.4 show the results from the reconcentration experiments of L-Alanine, DADMAC, and PolyDADMAC, respectively. The tables indicate at the results of (i) the volume of cumulative permeate every 2 hrs, (ii) the osmolality and concentration of cumulative permeate, (iii) the concentration of cumulative concentrate, (iv) the ion rejection results. The concentration of cumulative concentrate and ion rejection results were calculated according to the mass balance and ion rejection equations illustrated in chapter 3, section 3.6.5 above.

The results demonstrated that the ion rejection percentage of the three Draw Solutions decreased by increasing the concentration of cumulative concentrate inside the dead end stirred cell. It was observed that the average ion rejection percentage of both L-Alanine and DADMAC was 96.00% and higher that the average ion rejection percentage of PolyDADMAC which was 85.00%. The big ions of PolyDADMAC were supposed to be trapped behind the membrane more than the small ions of L-Alanine and DADMAC. However, the observation of low ion rejection of PolyDADMAC can be attributed to the effect of high density of positive charged ions in PolyDADMAC solution. The poor rejection of high cationic PolyDADMAC ions was attributed to the interaction with the negative charge surface of the NF90 membrane.

Several studies have been conducted on the efficiency of Nanofiltration membrane in rejection the ions of high charge density solutions (Nguyen et al. 2015; Agboola et al. 2014; Cathie Lee et al. 2014; Mullett et al. 2014). The high charge density solution affects the pore size of the Nanofiltration membrane deforming the mechanism of the size exclusion ion rejection (Mullett et al. 2014). In this dissertation, the results demonstrated that PolyDADMAC, which is high charge cationic polymer, negatively affected the efficiency of the NF membrane surface in preventing the solute flux. The deformation of membrane pore size causing in high water flux and poor ionic rejection.

Table 4.1: Results of L-Alanine solution reconcentration under varying concentration of permeate and concentrate, and rejection percentage.

Time Hr.	Volume of cumulative permeate L	Osmolality of cumulative permeate Osmol/Kg	Concentration of cumulative permeate, C_p g/mL	Concentration of cumulative concentrate g/mL	Rejection $\left(1 - {C_p}/{C_f}\right) \times 100$ %
0				0.035, (C_f)	
2	0.083	0.0130	0.00099	0.038	97
4	0.159	0.0130	0.00099	0.041	97
6	0.232	0.0120	0.00092	0.045	97
8	0.303	0.0150	0.00115	0.050	97
10	0.37	0.0153	0.00115	0.055	97
12	0.432	0.0260	0.00200	0.060	94
14	0.485	0.0270	0.00207	0.066	94
16	0.532	0.0270	0.00207	0.072	94
18	0.579	0.0270	0.00207	0.080	94
20	0.625	0.0270	0.00207	0.090	94

Table 4.2: Results of DADMAC solution reconcentration under varying concentration of permeate and concentrate, and rejection percentage.

Time Hr.	Volume of cumulative permeate L	Osmolality of cumulative permeate Osmol/Kg	Concentration of cumulative permeate C_p g/mL	Concentration of cumulative concentrate g/mL	Rejection $\left(1 - {C_p}/{C_f}\right) \times 100$ %
0				0.035, (C_f)	
2	0.117	0.0120	0.00091	0.040	97
4	0.207	0.0140	0.00106	0.044	97
6	0.304	0.0150	0.00135	0.050	96
8	0.392	0.0157	0.00119	0.057	97
10	0.461	0.0160	0.00121	0.064	97
12	0.528	0.0180	0.00136	0.073	96
14	0.582	0.0190	0.00144	0.082	96
16	0.630	0.0190	0.00144	0.092	96

Table 4.3: Results of PolyDADMAC solution reconcentration under varying concentration of permeate and concentrate, and rejection percentage.

Time Hr.	Volume of cumulative permeate L	Osmolality of cumulative permeate Osmol/Kg	Concentration of cumulative permeate C_p g/mL	Concentration of cumulative concentrate g/mL	Rejection $\left(1 - {C_p}/{C_f}\right) \times 100$ %
0				0.035, (C_f)	
2	0.172	0.0170	0.0040	0.041	89
4	0.334	0.0190	0.0045	0.050	87
6	0.47	0.0220	0.0052	0.061	85
8	0.583	0.0250	0.0059	0.076	83
10	0.666	0.0270	0.0064	0.092	82

The effects of the variation of external applied pressure and internal osmotic pressure over the reconcentration experiments of the three Draw Solutions are presented in Figure 4.13. The external applied pressure was needed to oppose and overcome the osmotic pressure of solutions, consequently; water molecules crossed the membrane and left the reconcentrated solutions inside the dead-end stirred cell. Figure 4.13 illustrates that the external applied pressure in case of reconcentration of L-Alanine, and DADMAC solutions seem to be similar. The similarity of the external applied pressures was a result of the similarity of their internal osmotic pressures. However, PolyDADMAC which is the third Draw Solution needed less external applied pressure as a result of its low internal osmotic pressure.

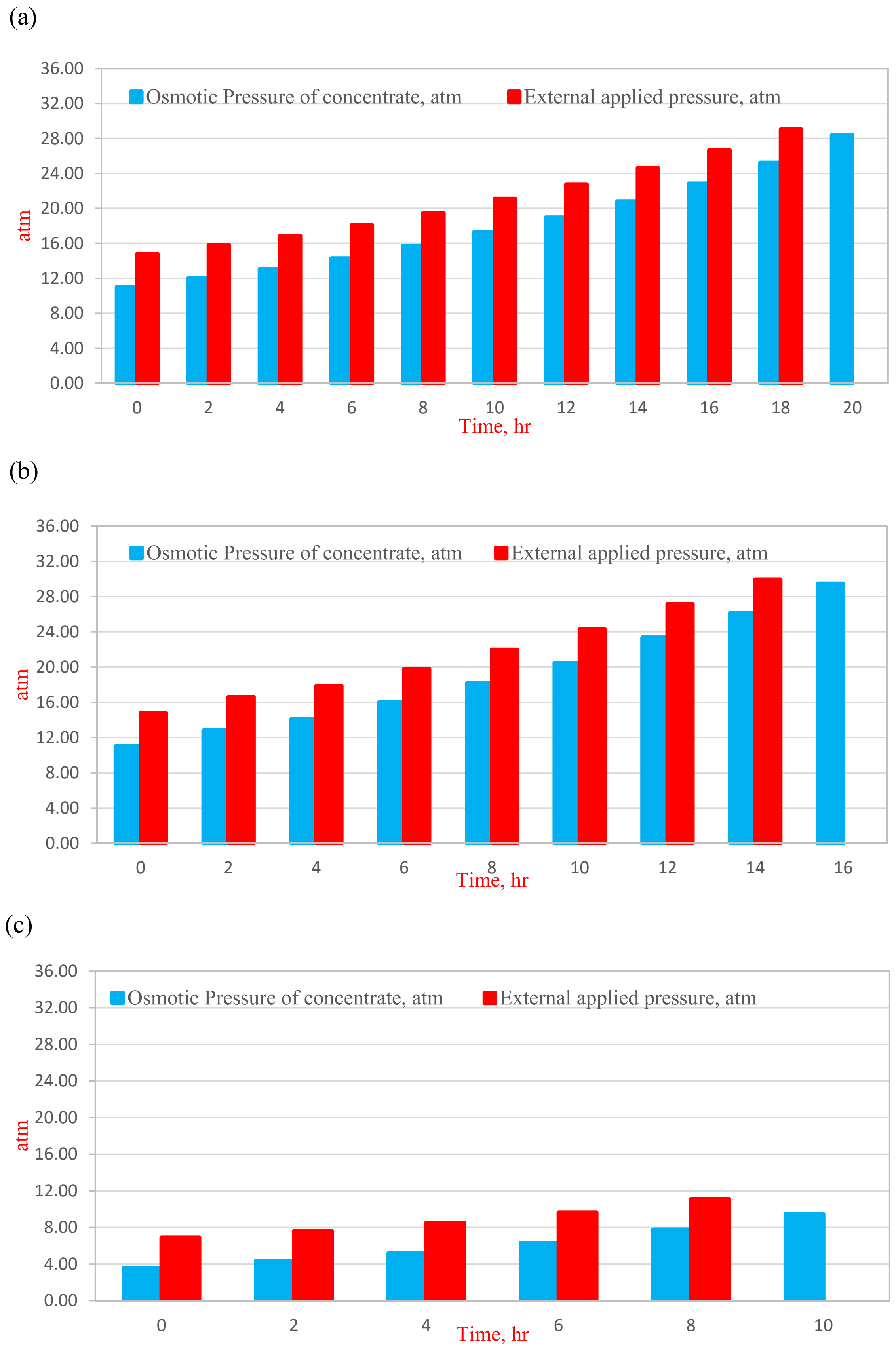


Figure 4.13: Change in the external applied pressure and the osmotic pressure of L-Alanine, DADMAC, and PolyDADMAC during reconcentration experiments.

The cumulative water flux across Nanofiltration membrane and the changing in the three solutions concentration during reconcentration experiments are displayed in Figure 4.14. Initial water flux with 4.79, 6.76 and 9.93 LMH were achieved after 2 hrs of reconcentration experiments of L-Alanine, DADMAC, and PolyDADMAC, respectively. A Quick reconcentration of the diluted Draw Solutions can be achieved by increasing the water flux where a high amount of water can be drawn from the diluted solution. Therefore, the diluted solution of PolyDADMAC with high initial water flux was reconcentrated faster than L-Alanine and DADMAC. Figure 4.14 demonstrates that the desired concentration, which was 0.085 g/mL, of L-Alanine, DADMAC, and PolyDADMAC was obtained after 19, 15, and 9 hours, respectively.

The difference between the external applied pressure and the osmotic pressure of diluted solution was monitored to be constant over the experiment time. However, a declination of water flux was observed. The drop of water flux is attributed to the ECP, membrane compaction, and scale formation:

Firstly, the ECP occurred due to the increase in the concentration of dissolved or colloidal solute near or atop of Nanofiltration membrane surface. The solutes accumulated behind the membrane and then created concentrated layer with high osmotic pressure. This layer with high osmotic pressure worked against the external applied pressure and contributed to the decrease in the water flux. Therefore, the stirred cell membrane was used to minimize the effect of the ECP.

Secondly, membrane compaction can also contribute the decreasing of water flux with time. It happened when the external pressure was applied on the polymeric driving force membrane. Under this compression force, the membrane structure deformed and became denser. The pore size decreased and hydraulic resistance increased.

Thirdly, the scale formation contributed to the declination of the water flux. In driven pressure membrane processes such as NF, some of solute molecules became non-dissolved due to solubility limits and the continuous drawing of the solvent through the membrane. Non-dissolved solute molecules then precipitated on the membrane surface. In the related experiments, the components which have relatively low solubility level leaded to reduction of water flux. Therefore, it was observed that L-Alanine took more time than DADMAC and PolyDADMAC to reach the same concentration due to its limited solubility.

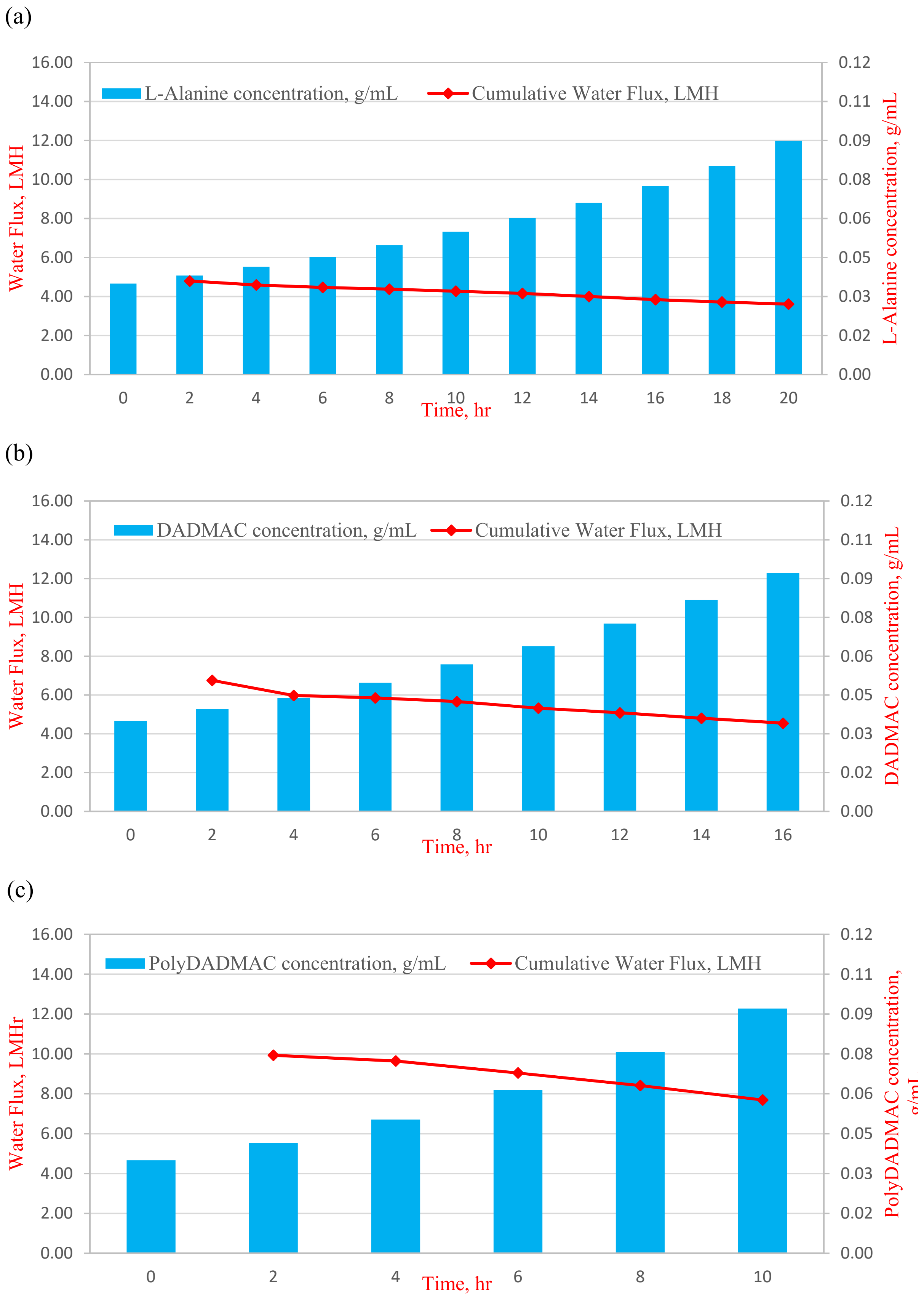


Figure 4.14: Cumulative water flux across Nanofiltration flat sheet membrane and concentration L-Alanine, DADMAC, and PolyDADMAC during reconcentration experiments.

4.3 The Potential Application

One of the main objectives of this dissertation is to investigate the viability of the utilisation of the FO for water recovery from fumaric acid produced by fermentation process in laboratory scale experiments. FO process was involved to minimize the water content and thus concentrate fumaric acid produced by fermentation process. The osmotic pressure of the Draw Solution was implemented to draw only the water molecules through membrane meanwhile the membrane prevented the fumaric acid solution components to shift to the Draw Solution tank.

The results obtained from the experiments conducted in phase I of the experimental plan were used in the recovery water experiments from both synthesis fumaric acid and fumaric acid produced by Fermentation process. A combination among the best Draw Solution, the efficient concentration and the best membrane type, which provided the highest water flux and lowest reverse solute diffusion were chosen. The viability of the regeneration of the Draw Solution was also considered. Membranes were operated under FO mode to minimize the effect of fouling.

As a result, the selected operating conditions were L-Alanine as a Draw Solution at 0.085 g/mL and CTA flat sheet membrane, which operated under FO mode, as shown in the following matrix.

Factors	Draw Solution type	Membrane sheet type	Membrane orientation	Draw Solution concentration.
Variables	$\begin{bmatrix} \mathbf{L-Alanine} \\ \text{DADMAC} \\ \text{PolyDADMAC} \end{bmatrix}$	$\begin{bmatrix} \mathbf{CTA} \\ \text{Aquaporin protein} \end{bmatrix}$	$\begin{bmatrix} \mathbf{FO\ mode} \\ \text{PRO mode} \end{bmatrix}$	$\begin{bmatrix} 0.035\ \text{g/mL} \\ \mathbf{0.085\ g/mL} \\ 0.120\ \text{g/mL} \\ 0.155\ \text{g/mL} \end{bmatrix}$

4.3.1 Findings and Discussions of Using Synthesis Fumaric Acid Solution as Feed Solution

The purpose of this experiment was to investigate the efficiency of the CTA flat sheet membrane in seizing fumaric acid and permeates water. The samples were taken from the Feed Solution and the Draw Solution tanks at the beginning of the experiment and after 32 hours and were analysed by HPLC to measure the amount of fumaric acid in both tanks.

Figure 4.15 illustrates the initial and the final fumaric acid concentration in both the Feed Solution and the Draw Solution tanks. The initial fumaric acid concentration was 5 g/L and 0 g/L in the Feed Solution tank and the Draw Solution tank, respectively. After 32 hours of the experiment, the final concentration of fumaric acid in the Feed Solution tank decreased to 2.783

g/L meanwhile fumaric acid was found in the Draw Solution tank at 1.822 g/L. In other words, the concentration of fumaric acid increased inside the Draw Solution tank from 0 g/L to 1.822 g/L, which means that both water and fumaric acid passed through CTA flat sheet membrane to the Draw Solution tank. That means, the CTA membrane did not reject fumaric acid and allowed it to cross easily to the Draw Solution tank. Taking in considerations that the main function of the membrane is to trap fumaric acid and allow only the water molecules, the membrane failed due to its chemical incompatibility with fumaric acid. The incompatibility is attributed to the reaction between the surface of the CTA membrane and fumaric acid molecules which hydrolysed and deformed the membrane.

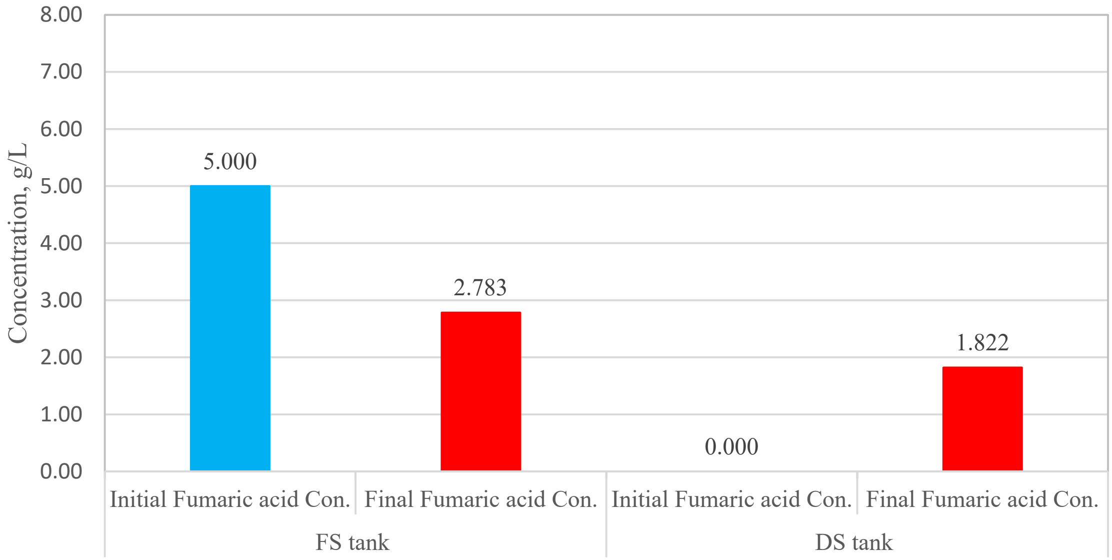


Figure 4.15: Changing of fumaric acid concentration in both the Feed Solution and the Draw Solution tanks using CTA flat sheet membrane

For the previous reason, the incompatible CTA membrane was replaced by the TFC aquaporin protein membrane and the experiment under the same conditions was repeated. That was intended to study the efficiency of TFC aquaporin protein membrane in seizing fumaric acid and permeates water.

The concentration of fumaric acid in both the Feed Solution and the Draw Solution tanks were determined by same procedures via HPLC analysis. The results were plotted in Figure 4.16.

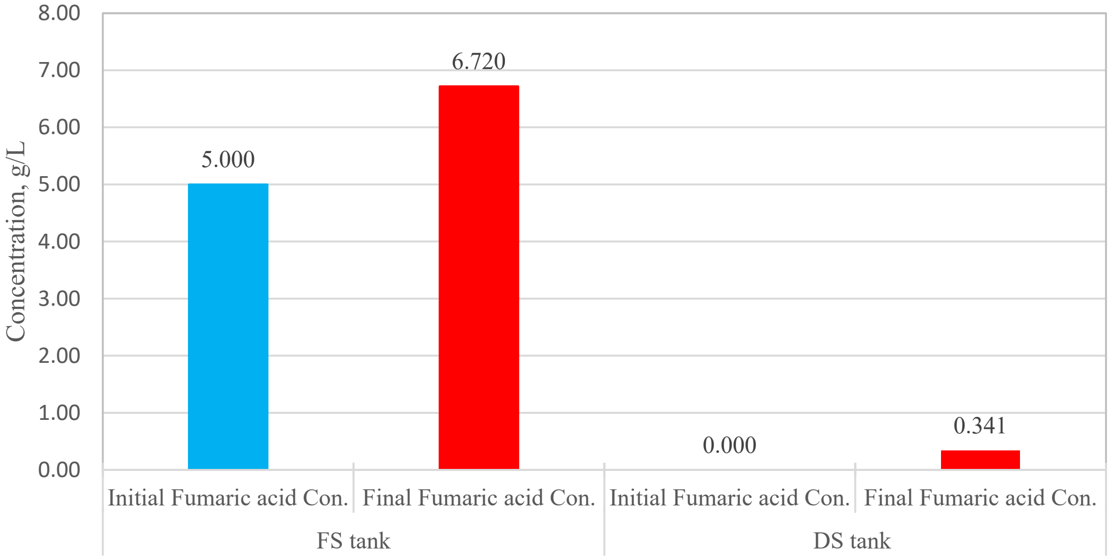


Figure 4.16: Changing of fumaric acid concentration in both the Feed Solution and the Draw Solution tanks using TFC aquaporin protein flat sheet membrane

Figure 4.16 demonstrates that when the TFC aquaporin protein membrane was used, fumaric acid in the Feed Solution concentrated by 34.40% after 32 hours. Fumaric acid concentration increased from 5 g/L as an initial concentration to 6.72 g/L as a final concentration. Also it was observed at the end of the experiment that fumaric acid with 0.341 g/L of was found in the Draw Solution tank which is much smaller amount compared to the one when the CTA membrane was used. Thus, the required function of the TFC aquaporin protein membrane to seize fumaric acid and pass only the water molecule was found. At this point, the previous results show that the TFC aquaporin protein membrane was compatible in concentrating synthesis fumaric acid solution, while the CTA membrane was incompatible.

4.3.2 Findings and Discussions of Using Fumaric Acid Produced by Fermentation Process as Feed Solution

The concentration of fumaric acid produced by industrial fermentation process was investigated as another application by FO. The TFC aquaporin protein membrane was used instead of the CTA membrane to avoid the hydrolysis problem. The HPLC results demonstrated the existence of several components including fumaric acid, glucose, succinic acid, lactic acid, acetic acid, ethanol, etc., see the appendix. However, the highest concentrations among these components were due to fumaric acid and glucose. Figures 4.17 and 4.18, therefore; were plotted only using the data of fumaric acid and glucose.

The effluence of the temperature on the concentration of fumaric acid efficiency was investigated. Two experiments were taken place in two labs with different temperature. The first temperature was 17 °C while the second temperature was 32 °C. Figure 4.17 shows the changing of fumaric acid and glucose concentrations in both the Feed Solution and the Draw Solution tanks at 32 °C. The reduction of water content of the fumaric acid solution made it to concentrate by 26.00% after 32 hours. The concentration raised from 6.020 g/L as an initial concentration to 7.584g/L as a final concentration. Similarly, the concentration of glucose in the Feed Solution tank increased by 29.45%. Inconsiderable amounts of both fumaric acid and glucose were crossed the TFC aquaporin protein membrane into the Draw Solution tank as observed in the figure.

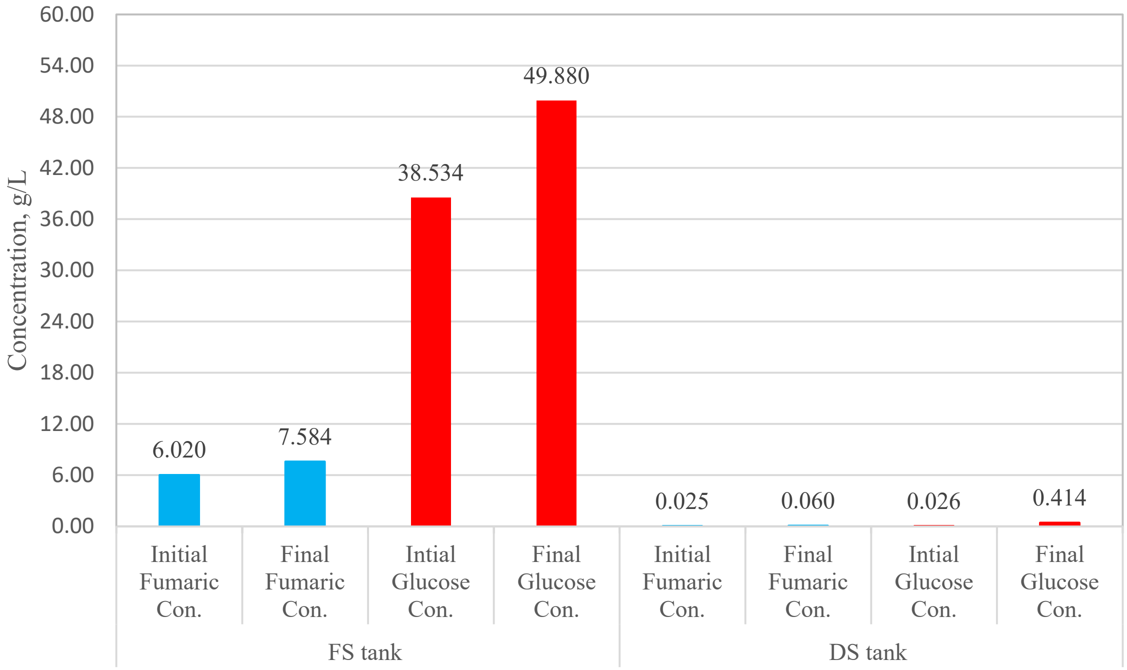


Figure 4.17: Changing of fumaric acid and glucose concentrations in both Feed Solution and Draw Solution tanks at 32 °C using TFC aquaporin protein flat sheet membrane

Figure 4.18 demonstrates the changing of fumaric acid and glucose concentrations in both the Feed Solution and the Draw Solution tanks at 17 °C . The results demonstrated that at the end of the experiment fumaric acid and glucose in the Feed Solution tank concentrated by 19.80% and 19.90%, respectively. As a result, it was observed that by increasing the lab temperature from 17°C to 32°C, the final concentrations of fumaric acid and glucose grew by 31.26% and 47.99%, respectively. This observation indicated a positive effect of increasing the temperature in FO process. By increasing the temperature, better water recovery was obtained and consequently more concentration percentage of fumaric acid was achieved.

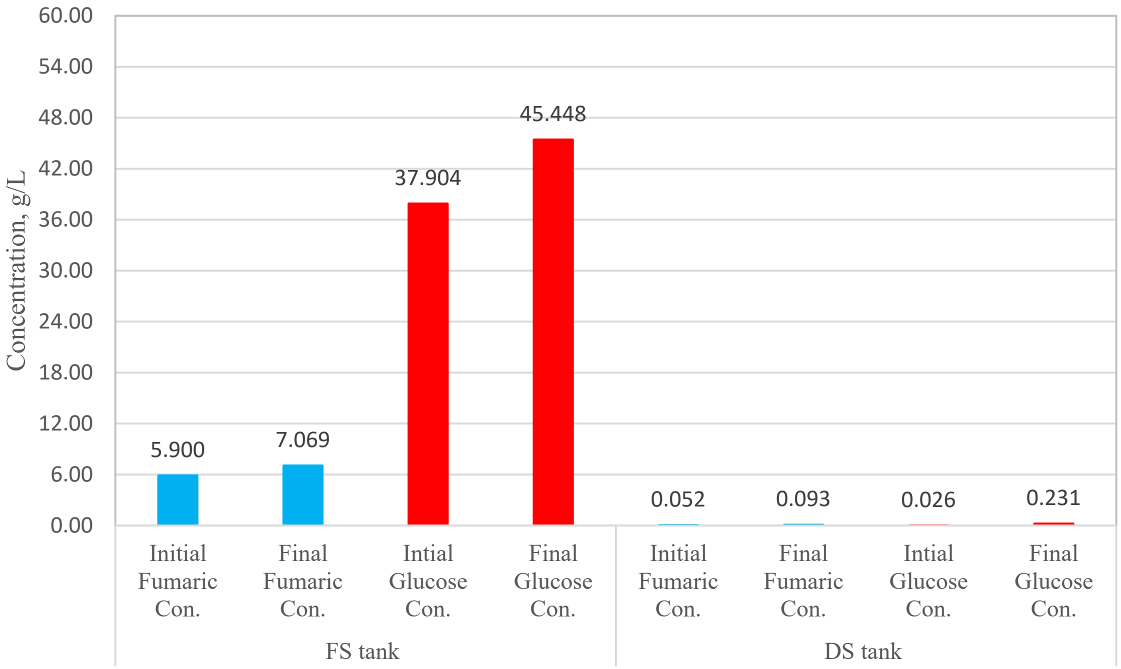


Figure 4.18: Changing of fumaric acid and glucose concentrations in both Feed Solution and Draw Solution tanks at 17 °C using TFC aquaporin protein flat sheet membrane

This study also demonstrated that the positive effect of temperature was observed on the water flux. As it shown in Figure 4.19 the water flux obtained at 32℃ was higher than the one obtained at 17℃. Water flux of 8.50 LMH and reverse solute diffusion of 0.01 GMH can be achieved at 32℃ with 0.085 g/mL L-Alanine as a Draw Solution (26 atm), which is superior to other reported Draw Solutions in water recovery application from fermentation downstream via FO. Kalafatakis et al. (2016) reported that crude glycerol Draw Solution with osmotic pressure of 462.37 atm, which is approximately 17-fold than that of 0.085 g/mL L-Alanine solution, achieved water flux up to 8.39 LMH at 37 ℃ while fermentation downstream with osmotic pressure of 13 atm was used as a Feed Solution. In the same study, pre-treated wheat straw hydrolysate (with osmotic pressure of 42 atm) was also investigated as a Draw Solution and achieved water fluxes ranging from 1.33 LMH to 5.37 MLH (Kalafatakis et al. 2016).

Figure 4.19 also manifested that water flux produced by L-Alanine when distilled water was used as a Feed Solution was higher than the water flux when fumaric acid was used as a Feed Solution. The low water flux can be attributed to two possible reasons including fouling effect and decrease the osmotic pressure gradient between the Feed Solution and the Draw Solution with time.

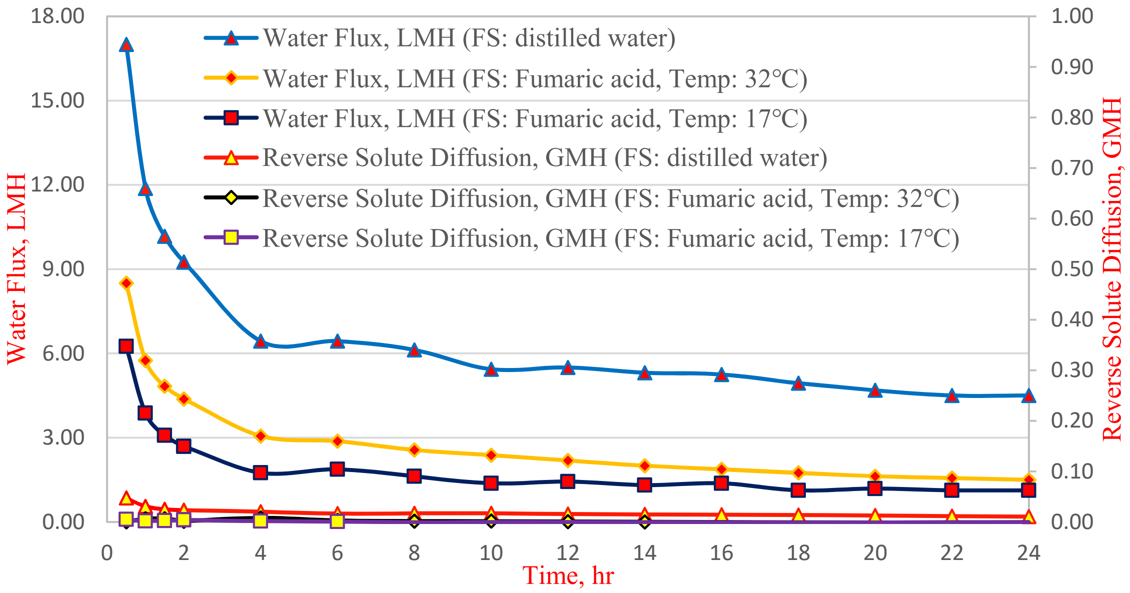
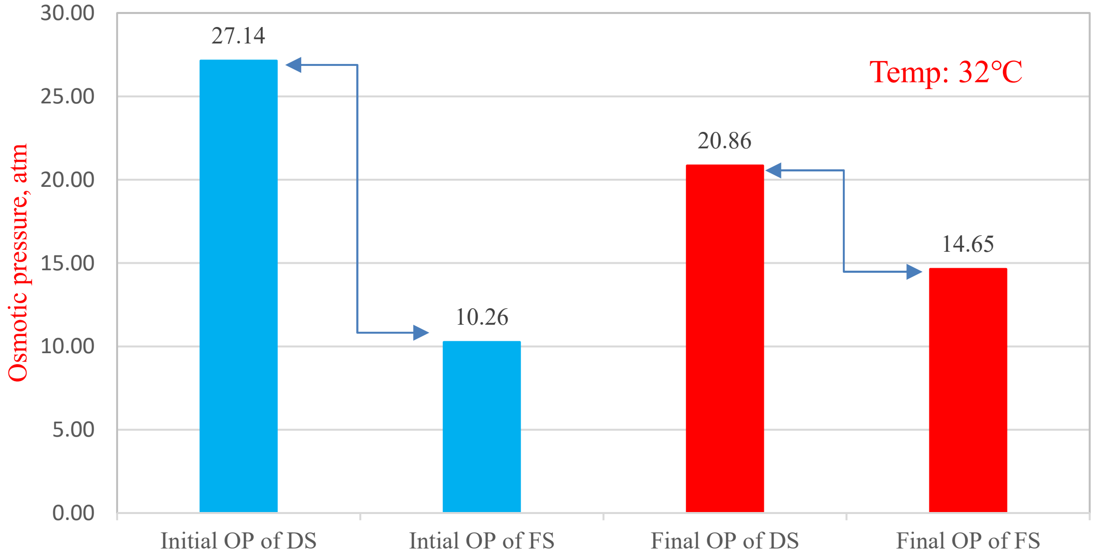


Figure 4.19: Comparison between the water flux and the reverse solute diffusion of L-Alanine at 0.085 g/mL using TFC aquaporin protein flat sheet membrane and two types of Feed Solution with different temperatures

In regards to the first cause which is the fouling, increasing the temperature to 32°C enhanced the growth of Rhizopus oryzae microorganism and with time the microorganisms flocculated and produced considerable foulants. It was observed that the colour of fumaric acid became less clear with time as a result of the microorganism growing. The foulants depressed on the surface of TFC aquaporin protein membrane therefore forming a fouling layer. As a result, the hydraulic resistance of the membrane increased and water flux decreased. The water flux achieved at 32°C decreased sharply than at 17°C.

The second cause of decreasing the water flux rate sharply was the decrease in osmotic pressure gradient between the Feed Solution and the Draw Solution with time. Reducing the gap between osmotic pressure of the Draw Solution and the Feed Solution happened as a result of transmission the water molecules from the Feed Solution side to the Draw Solution side. Osmotic pressure of the Draw Solution decreased gradually with time due to its dilution meanwhile osmotic pressure of the Feed Solution increased gradually due to its concentration. Consequently, the effective driven force through the membrane was decreased by the gradual reduction of osmotic pressure gradient which led to drop in the water flux. Figure 4.20 illustrates that the osmotic pressure gradient decreased at 32°C more than at 17°C. Both experiments conducted in two separate labs. The first experiment was under 32°C, where the gap of the osmotic pressure reduced from 16.88 atm to 6.21 atm after 32 hours. However, under 17°C, the gab reduced from 16.48 atm to 9.47 atm. Furthermore, the high residual concentration of glucose in the Feed Solution limited the high concentration of the fumaric acid process. The limitations are due to the reduction of the osmotic pressure (OP) gradient through the membrane.

(a)



(b)

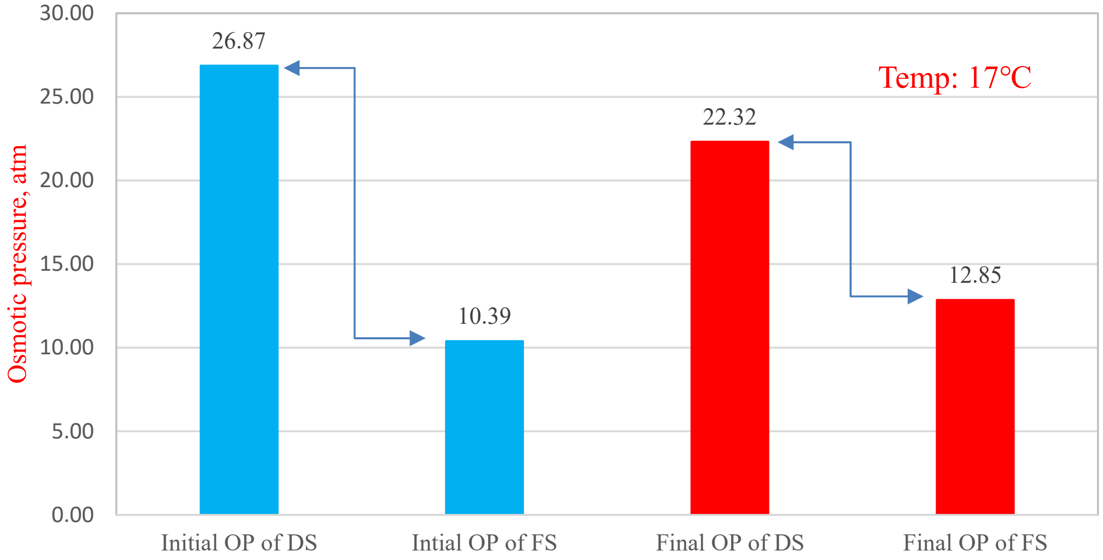


Figure 4.20: Osmotic pressure gradient between the Draw Solution and the Feed Solution during FO process at different temperatures a) 32°C, b) 17°C

CHAPTER 5

Conclusions and Recommendations

5.1 The FO System

High growth of osmotic pressure and low viscosity were observed by increasing the concentration of L-Alanine and DADMAC Draw Solutions. In contrast, a progressive increase of osmotic pressure and high increase of viscosity was observed by increasing the concentration of PolyDADMAC. Water flux and reverse solute diffusion were affected by various conditions such as; the characteristics of the Draw Solution, osmotic pressure gradient, membrane orientation, and change in the pumping pattern of the solutions inside the FO membrane cell. The majority of water flux trends decreased dramatically during the first four hours, then the decrease became progressively slow with time.

Both CTA and TFC aquaporin protein flat sheet membranes were operated under FO and PRO modes. In FO mode, water flux through the CTA flat sheet membrane was higher than the one through the TFC aquaporin protein flat sheet membrane. This observation is attributed to the low thickness, loose fibre support layer and hydrophilic nature of the CTA membrane.

The highest two initial water flux through the CTA flat sheet membrane were achieved by L-Alanine at 0.085 g/mL and DADMAC at 0.155 g/mL were used as a Draw Solution with 22 LMH and 20 LMH, respectively. These concentrations of L-Alanine and DADMAC also produced the highest initial water flux through the TFC aquaporin protein flat sheet with 17 LMH and 11.50 LMH, respectively. In contrast, PolyDADMAC at 0.035 g/mL produced the lowest initial water flux through both CTA and TFC Aquaporin protein flat sheet membranes with 4 LMH and 2.75 LMH, respectively. Low osmotic pressure and relatively high viscosity played intrinsic role of that behaviour.

The TFC aquaporin protein flat sheet membrane provided better results of reverse solute diffusion than the CTA flat sheet membrane. The three Draw Solutions had low and nearly constant reverse diffusion across the TFC aquaporin protein flat sheet membrane. However, reverse solutes diffusion across the CTA flat sheet membrane was high and decreasing gradually with time. L-Alanine at 0.085 g/mL achieved the lowest reverse solute diffusion across both TFC aquaporin protein and CTA membranes. The initial value of the reverse solute of L-Alanine was 0.05 GMH and reached to 0.01 GMH at the end of the experiment. Nevertheless, DADMAC at 0.155 g/mL had the highest reverse solute diffusion across the CTA flat sheet membrane with initial value 16.77 GMH.

The variation of the osmotic pressure values of the Draw Solutions affected the water flux. Water flux achieved by the Draw Solutions with osmotic pressure less than 15 atm dropped dramatically within 2 hrs after commencing the experiments while the osmotic pressure decreased faintly. However, the water flux declined slightly after the first 2 hrs while the decrease of osmotic pressure was more apparent. Similar behaviour of the water flux drop was observed when the TFC aquaporin protein membrane was operated under FO mode. It was also observed that when L-Alanine, DADMAC, and PolyDADMAC with various concentrations were used as Draw Solutions, the water flux across the CTA membrane reached approximately the same level at the end of experiments irrespective of the initial values of the water flux. For example, the water flux produced by L-Alanine and DADMAC were much closer to 4 LMH at the end of the experiments. The same was observed when the TFC aquaporin protein membranes were used.

The effect of viscosity appeared when PolyDADMAC was used. The high viscosity of PolyDADMAC contributed the declination of water flux. For example, water flux obtained by PolyDADMAC at 0.155 g/mL was lower than the one at 0.120 g/mL concentration.

The effect of changing the membranes' orientation on water flux and reverse solute diffusion were observed. The Solutions of L-Alanine and DADMAC at 0.120 g/mL concentration were used as Draw Solutions, meanwhile distilled water was used as a Feed Solution. It was observed that the initial water flux through both CTA and TFC aquaporin protein membranes under PRO mode was higher than water flux under FO mode. However in PRO mode, water flux through the CTA flat sheet membrane dropped sharper than that of the TFC aquaporin protein flat sheet membrane. This high declination in water flux is attributed to increasing the ICP inside the CTA flat sheet membrane with time more than the ICP inside the TFC aquaporin protein flat sheet membrane. The results demonstrated that the reverse solute diffusion across both CTA and TFC aquaporin protein flat sheet membranes in PRO mode was higher than the one in FO mode.

Moreover, it was observed that the water flux and the reverse solute diffusion were also affected by the pattern of pumping the solutions inside the FO membrane cell. Pumping the Draw Solution first and thereafter pumping the Feed Solution affected the efficiency of membrane.

Low water flux and high amount of reverse solute diffusion though the CTA membrane was observed as a result of the severe ICP inside the support layer of membrane. The CTA flat sheet membrane was affected badly more than the TFC aquaporin protein flat sheet membrane in the case of pumping the Draw Solution first. For instance, when DADMAC at 0.085 g/mL was used as a Draw Solution, it was observed a dramatic collapse of water flux through the CTA flat sheet membrane from 15.75 LMH to 0.25 LMH after 10 hours of the experiment. A massive of reverse diffusion of DADMAC was discovered in the Feed Solution tank. In contrast, the results for the TFC aquaporin protein flat sheet membrane illustrated more stability and low effect of pumping the Draw Solution before the Feed Solution.

5.2 The Reconcentration System

Diluted Draw Solutions of L-Alanine, DADMAC, and PolyDADMAC were effectively reconcentrated by NF system. Reconcentration system of NF90 Nanofiltration membrane with dead end stirred cell was used.

The average ion rejection of L-Alanine, DADMAC, and PolyDADMAC by NF90 membrane were 96.00%, 96.00%, and 85.00%, respectively. Poor rejection of PolyDADMAC ions is imputed to high density of cationic charge of PolyDADMAC solution which affected badly the negative charged surface of NF90 membrane. Pores size of negative charged membrane was deformed due to exposing to high amount of positive charges of PolyDADMAC solution. Thus, the percentage of ions rejection would be reduced and high water flux would be found. Decreasing the ions rejection percentage was directly proportional to increasing the concentration of cumulative concentrate inside the dead end stirred cell with time.

Initial water fluxes in reconcentration experiments were measured after 2 hrs from the start time. Initial water fluxes were 4.79, 6.76, and 9.93 LMH for L-Alanine, DADMAC, and PolyDADMAC, respectively. Moreover, the concentration of L-Alanine, DADMAC, and PolyDADMAC rose from 0.035 g/mL to 0.085 g/mL after 19, 15, and 9 hours, respectively. Therefore, higher water flux was achieved, quicker reconcentration was obtained.

The external applied pressure was adjusted every two hours to keep the difference between the external applied pressure and the internal osmotic pressure of the diluted solution. However, declination of water flux with time was observed. Three parameters contribute the decreasing of the water flux with time including concentration polarization, membrane compaction, and scale formation. The stirred cell membrane was used to minimize the effect of concentration polarization which happens due to increase the concentration of dissolved or colloidal solute molecules close or atop of the membrane surface. The limited solubility of L-Alanine increases the opportunity of scale formation on atop of the membrane surface. Therefore, lowering of water flux in case of reconcentration L-Alanine was observed comparing with DADMAC and PolyDADMAC.

5.3 The potential Application

Both CTA and TFC aquaporin protein flat sheet membranes were tested in FO set up for water recovery from a synthesis fumaric acid. Then only the TFC aquaporin protein flat sheet was chosen and utilised in water recovery from fumaric acid solution produced by a fermentation process.

The CTA membrane was chemically incompatible with fumaric acid. The membrane was hydrolysed and fumaric acid molecules were passing through the membrane layers free from the Feed Solution side to the Draw Solution side. To overcome the hydrolysis phenomenon, the CTA membrane was replaced by the TFC aquaporin protein membrane in the reconcentration experiments. The TFC aquaporin protein membrane showed positive results in terms of preventing the fumaric acid molecules to pass through. Synthesis fumaric acid solution was reconcentrated by 34.40% after 32 hours via the TFC aquaporin protein membrane.

Due to the compatibility of the TFC aquaporin protein membrane with fumaric acid, it was employed in water recovery from fumaric acid solution produced by a fermentation process experiments. Two experiments were run separately under two different degree; 32℃ and 17℃ to investigate the influence of temperature on the reconcentration. HPLC samples analysis of fumaric acid solution produced by a fermentation process showed that the dominant components were fumaric acid and glucose. The concentrations of fumaric acid and glucose approximately 6 g/L and 38 g/L, respectively. Besides that, small amounts of other organic acids such as succinic, lactic, and acetic acids and ethanol were also measured.

The reduction of water content of the fumaric acid solution due to the FO process made it to concentrate by 26.00% and 19.80% at 32°C and 17°C, respectively. Likewise, glucose in the Feed Solution tank also concentrated by 29.45% and 19.90% at 32℃ and 17°C, respecetivly. Therefore, it was observed that increasing the temperature has positive impact on increasing the water recovery and thus the concentration of fumaric acid in FO process.

Water flux through the TFC aquaporin protein membrane dropped with time from 8.5 LMH to 1.5 LMH in 32°C. It also dropped from 6.25 LMH to 1.13 LMH in 17℃. Concentration polarization, decreased the osmotic pressure gradient between the Feed Solution and the Draw Solutions with time, and fouling formation were the main factors to cause the declination of water flux rate in hot laboratory than in cold one. Lab with temperature 32°C was suitable to grow Rhizopus oryzae microorganism which flocculated and started to form fouling on the membrane surface.

Achieving high percentage of water recovery from fumaric acid solution has been limited due to the high initial concentration of glucose in the Feed Solution. With the time the glucose also concentrated and created high osmotic pressure. It reduced the effective net driving force through the membrane results in low water flux and limited concentration of fumaric acid.

5.4 Recommendations

Choosing a suitable Draw Solution for FO process is still one of the most debatable and effective keys of improvement the FO technology performance. Accelerated studies have been conducted for that purpose. Thus, wide range of materials have been proposed as novel Draw Solutions to generate a considerably high osmotic driving force. However, other intrinsic characters besides the osmotic pressure of the Draw Solution should be taken into account to investigate the mass transport through the membrane. The interaction between the Draw Solution and the charged surface of membranes affects the mass transport. Therefore,

- Further effort should be devoted to investigate this interaction based on the characteristics of both Draw Solutions and membranes surface.

Besides that, many studies had investigated the use of FO technology in wastewater, desalination, and other common applications and how much it holds great promise. However,

- Further studies should be done to explore the efficacy of utilisation FO technology in other promising applications such as downstream bioprocessing of organic acids (fumaric acid, succinic acid, malic acid, etc). These organic acids should have more attention to utilise a proper process like FO process for its concentration and extraction.

This study demonstrates that the existence of glucose component with high concentration limited the water recovery from fumaric acid by FO process. Glucose component with high concentration can generate high osmotic pressure and then reduce the net driving osmotic force through the membrane. Therefore,

- Proper solutions should be given first to minimize glucose concentration in the fermentation downstream and in the same time to maintain the fumaric acid without consuming.

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Appendix

HPLC analysis results of Draw Solution sample after 24hr
Feed Solution: Synthesis Fumaric acid solution with initial concentration 5 g/L
Membrane: CTA flat sheet under FO mode. **Temperature:** 22℃±1℃

```
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Acq. Instrument : HPLC                            Location : Vial 52
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                                                Inj Volume : 5.000 µl
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Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
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                  in gradual increments to 0.6 ml/min
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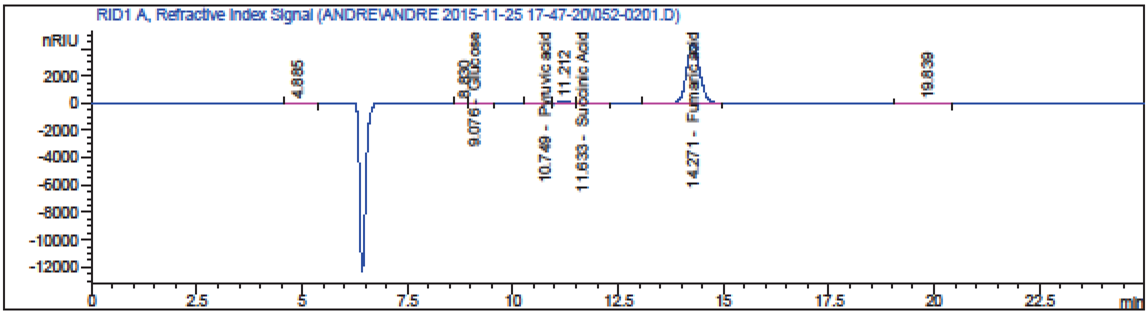

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Dilution:                     :       2.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area    Amount    Grp   Name
 [min]          [nRIU*s]               [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.294          -          -          -          Citric Acid
  8.550          -          -          -          Oxaloacetic Acid
  9.076 VB     749.72406 1.08530e-5 1.62735e-2    Glucose
  9.722          -          -          -          Malic acid
 10.749 BV     662.83698 1.68185e-5 2.22958e-2    Pyruvic acid
 11.633 VB     835.75226 1.56350e-5 2.61340e-2    Succinic Acid
 12.808          -          -          -          Lactic acid
 13.502          -          -          -          Glycerol
 14.271 BB    9.44712e4  1.47281e-5    2.78276    Fumaric acid
 15.157          -          -          -          Acetic Acid
 22.278          -          -          -          Ethanol

Totals :                               2.84746


2 Warnings or Errors :
```

HPLC analysis results of Feed Solution sample after 24hr

Feed Solution: Synthesis Fumaric acid solution with initial concentration 5 g/L

Membrane: CTA flat sheet under FO mode. **Temperature**: 22℃±1℃

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Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
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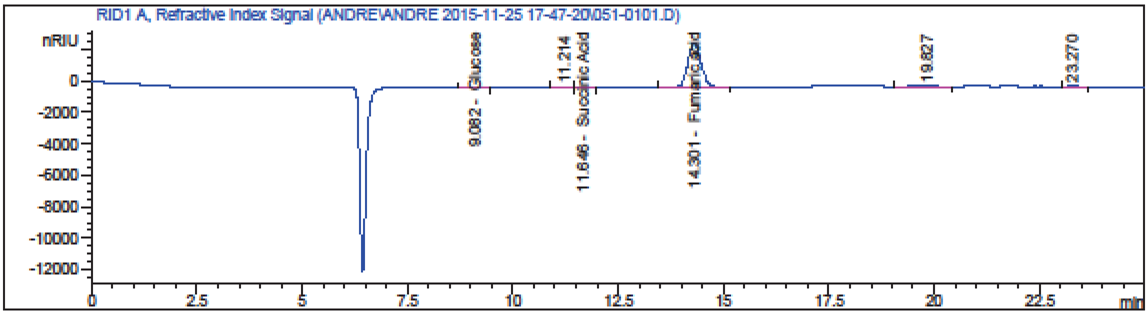

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Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.294           -          -          -         Citric Acid
  8.550           -          -          -         Oxaloacetic Acid
  9.082 BB     1252.30603 1.15961e-5 2.90438e-2   Glucose
  9.722           -          -          -         Malic acid
 10.875           -          -          -         Pyruvic acid
 11.646 VB      406.49866 1.47312e-5 1.19764e-2   Succinic Acid
 12.808           -          -          -         Lactic acid
 13.502           -          -          -         Glycerol
 14.301 BB     6.07418e4  1.50012e-5    1.82240   Fumaric acid
 15.157           -          -          -         Acetic Acid
 22.278           -          -          -         Ethanol

Totals :                                1.86342


2 Warnings or Errors :
```

HPLC analysis results of Draw Solution sample after 24hr

Feed Solution: Synthesis Fumaric acid solution with initial concentration 5 g/L

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature:** 22℃±1℃

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Last changed    : 10/6/2015 12:18 by Michael
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
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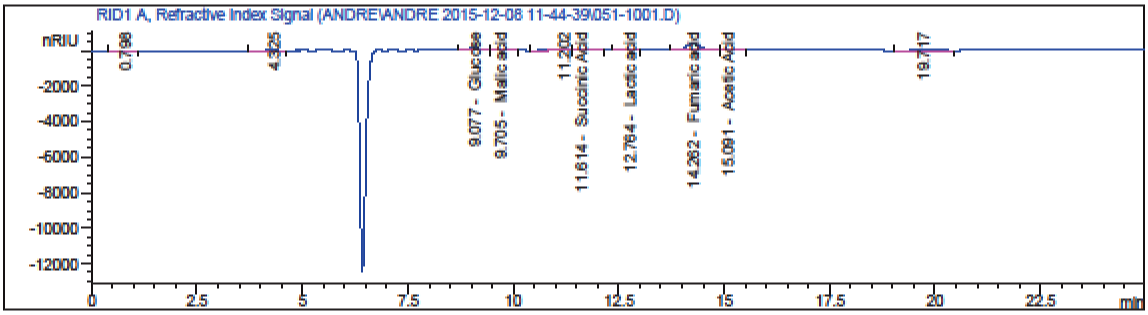

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                      External Standard Report
======================================================================

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Multiplier:                  :      1.0000
Dilution:                    :      2.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]               [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.294             -          -          -         Citric Acid
  8.550             -          -          -         Oxaloacetic Acid
  9.077 BV     2741.38110 1.21983e-5 6.68803e-2     Glucose
  9.705 VB     1120.78418 3.43524e-5 7.70032e-2     Malic acid
 10.875             -          -          -         Pyruvic acid
 11.614 VB     1628.38086 1.60516e-5 5.22763e-2     Succinic Acid
 12.764 BB      198.31519 4.80190e-5 1.90458e-2     Lactic acid
 13.502             -          -          -         Glycerol
 14.262 BV     8705.77637 1.95734e-5 3.40804e-1     Fumaric acid
 15.091 VB      394.60803 4.41191e-5 3.48195e-2     Acetic Acid
 22.278             -          -          -         Ethanol

Totals :                             5.90829e-1


2 Warnings or Errors :
```
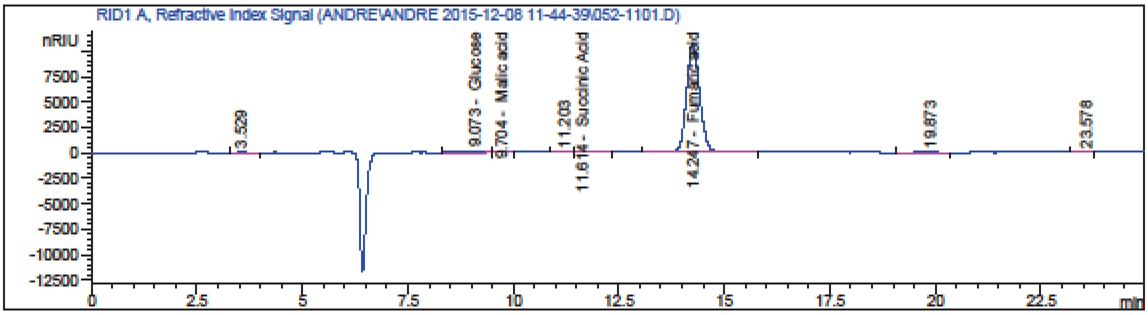

HPLC analysis results of Feed Solution sample after 24hrs
Feed Solution: Synthesis Fumaric acid solution with initial concentration 5 g/L
Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature:** 22℃±1℃

```
=====================================================================
Acq. Operator   : Michael                         Seq. Line :  11
Acq. Instrument : HPLC                             Location : Vial 52
Injection Date  : 12/8/2015 16:18                       Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\ANDRE\ANDRE 2015-12-08 11-44-39\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



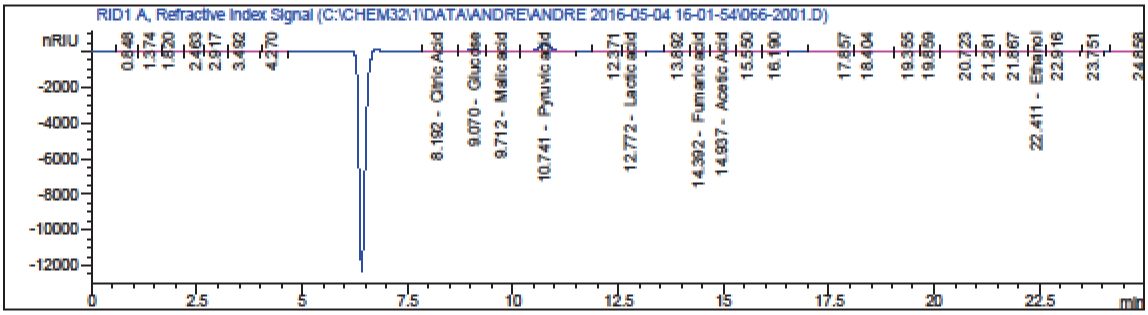
```
=====================================================================
                     External Standard Report
=====================================================================

Sorted By              :      Signal
Calib. Data Modified   :      10/6/2015 12:17
Multiplier:                   :       1.0000
Dilution:                     :       2.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]         [nRIU*s]                  [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.294          -           -          -         Citric Acid
  8.550          -           -          -         Oxaloacetic Acid
  9.073 BV    1928.07153 1.19847e-5 4.62146e-2    Glucose
  9.704 VB     586.06818 5.07268e-5 5.94587e-2    Malic acid
 10.875          -           -          -         Pyruvic acid
 11.614 VB    1119.08972 1.58517e-5 3.54790e-2    Succinic Acid
 12.808          -           -          -         Lactic acid
 13.502          -           -          -         Glycerol
 14.247 BB    2.32753e5  1.44359e-5    6.71999    Fumaric acid
 15.157          -           -          -         Acetic Acid
 22.278          -           -          -         Ethanol

Totals :                               6.86114


2 Warnings or Errors :
```

HPLC analysis results of Draw Solution sample at time zero

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. Temperature: 17℃ & 32 ℃

```
=======================================================================
Acq. Operator   : Michael                          Seq. Line :  20
Acq. Instrument : HPLC                              Location : Vial 66
Injection Date  : 5/5/2016 00:21                         Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\ANDRE\ANDRE 2016-05-04 16-01-54\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



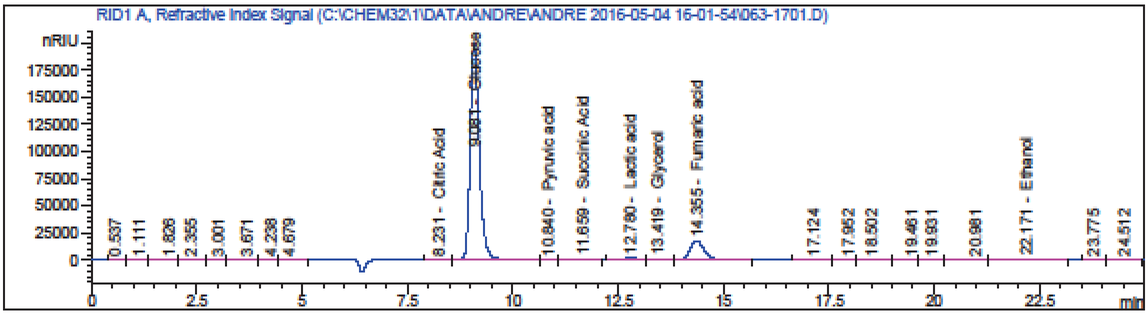
```
=======================================================================
                       External Standard Report
=======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :        1.0000
Dilution:                    :        1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type      Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                 [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.192 BV     1481.24951 8.67821e-6 1.28546e-2    Citric Acid
  8.550            -          -          -         Oxaloacetic Acid
  9.070 VV     2155.96802 1.20608e-5 2.60026e-2    Glucose
  9.712 VB      954.52533 3.74784e-5 3.57741e-2    Malic acid
 10.741 BV     8682.75195 1.68666e-5 1.46448e-1    Pyruvic acid
 11.681            -          -          -         Succinic Acid
 12.772 VB      423.43372 3.44408e-5 1.45834e-2    Lactic acid
 13.502            -          -          -         Glycerol
 14.392 VB      379.62543 1.36631e-4 5.18686e-2    Fumaric acid
 14.937 BV      322.33261 4.75702e-5 1.53334e-2    Acetic Acid
 22.411 VV      607.57526 1.47809e-5 8.98051e-3    Ethanol

Totals :                             3.11846e-1


 2 Warnings or Errors :
```

HPLC analysis results of Feed Solution sample at time zero

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature:** 17 ℃

```
=====================================================================
Acq. Operator   : Michael                           Seq. Line :  17
Acq. Instrument : HPLC                               Location : Vial 63
Injection Date  : 5/4/2016 23:04                          Inj :   1
                                                   Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\ANDRE\ANDRE 2016-05-04 16-01-54\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



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=====================================================================
                      External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.231 BB     3153.41064 9.17871e-6 2.89442e-2    Citric Acid
  8.550             -          -          -         Oxaloacetic Acid
  9.081 BV     2.98360e6  1.27042e-5   37.90432    Glucose
  9.722             -          -          -         Malic acid
 10.840 VB      813.33295 1.68281e-5 1.36869e-2    Pyruvic acid
 11.659 BB     1.54922e4  1.64448e-5 2.54765e-1    Succinic Acid
 12.780 BV     4.06594e4  2.26039e-5 9.19060e-1    Lactic acid
 13.419 VB     2.33179e4  1.10235e-5 2.57044e-1    Glycerol
 14.355 BB     4.11199e5  1.43493e-5    5.90040    Fumaric acid
 15.157             -          -          -         Acetic Acid
 22.171 BV     2.73681e4  3.11098e-5 8.51416e-1    Ethanol

Totals :                               46.12963

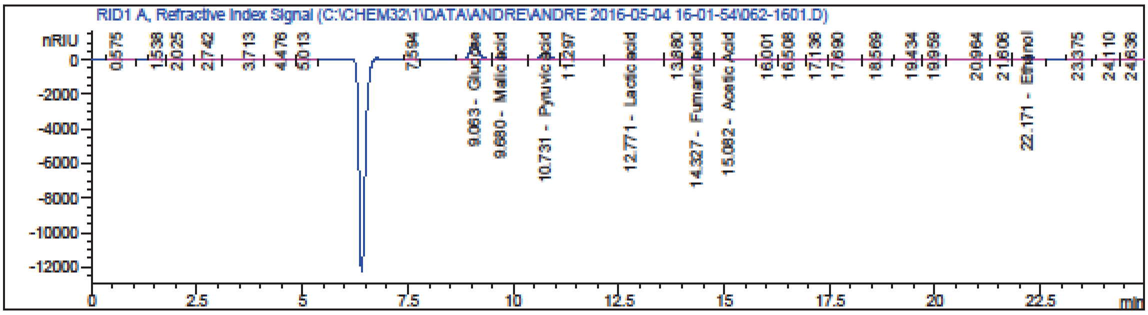

2 Warnings or Errors :
```

HPLC analysis results of Draw Solution sample at 24 hrs

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature:** 17 ℃

```
=====================================================================
Acq. Operator   : Michael                         Seq. Line :  16
Acq. Instrument : HPLC                             Location : Vial 62
Injection Date  : 5/4/2016 22:38                        Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\ANDRE\ANDRE 2016-05-04 16-01-54\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



```
=====================================================================
                     External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

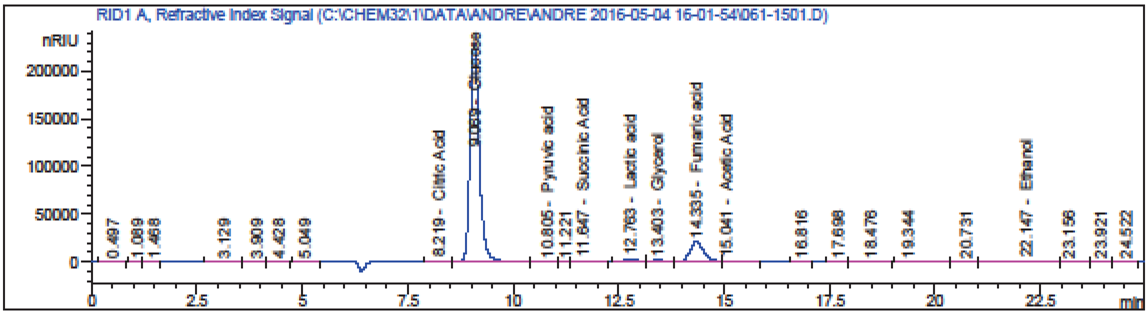
Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.294            -          -          -        Citric Acid
  8.550            -          -          -        Oxaloacetic Acid
  9.063 VV    1.45177e4  1.26091e-5 1.83055e-1    Glucose
  9.680 VB    2554.74072 2.42789e-5 6.20263e-2    Malic acid
 10.731 BV    6161.65869 1.68649e-5 1.03916e-1    Pyruvic acid
 11.681            -          -          -        Succinic Acid
 12.771 BB    1631.75610 2.55833e-5 4.17456e-2    Lactic acid
 13.502            -          -          -        Glycerol
 14.327 VB    1434.62305 4.66240e-5 6.68878e-2    Fumaric acid
 15.082 BV     971.61365 3.49787e-5 3.39858e-2    Acetic Acid
 22.171 VB    1639.49133 2.52919e-5 4.14658e-2    Ethanol

Totals :                            5.33082e-1


2 Warnings or Errors :
```

```
 HPLC analysis results of Feed Solution sample at 24 hrs
 Feed Solution: Fumaric acid produced by fermentation process.
 Membrane: TFC aquaporin protein flat sheet under FO mode. Temperature: 17 ℃
=====================================================================
Acq. Operator   : Michael                          Seq. Line :  15
Acq. Instrument : HPLC                              Location : Vial 61
Injection Date  : 5/4/2016 22:12                         Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\ANDRE\ANDRE 2016-05-04 16-01-54\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



```
=====================================================================
                      External Standard Report
=====================================================================

Sorted By                :      Signal
Calib. Data Modified     :      10/6/2015 12:17
Multiplier:                     :       1.0000
Dilution:                       :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area     Amt/Area    Amount    Grp   Name
 [min]          [nRIU*s]              [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.219 BB     3430.24463 9.21449e-6 3.16080e-2    Citric Acid
  8.550             -          -          -        Oxaloacetic Acid
  9.069 BV     3.43192e6  1.27043e-5   43.60013    Glucose
  9.722             -          -          -        Malic acid
 10.805 VV     3321.28516 1.68602e-5 5.59974e-2    Pyruvic acid
 11.647 VB     1.81389e4  1.64515e-5 2.98411e-1    Succinic Acid
 12.763 BV     4.89787e4  2.25827e-5    1.10607    Lactic acid
 13.403 VB     2.73619e4  1.13347e-5 3.10138e-1    Glycerol
 14.335 BV     4.69132e5  1.43353e-5    6.72514    Fumaric acid
 15.041 VB     7950.42139 2.94917e-5 2.34471e-1    Acetic Acid
 22.147 VV     3.02177e4  3.11448e-5 9.41123e-1    Ethanol

Totals :                              53.30309

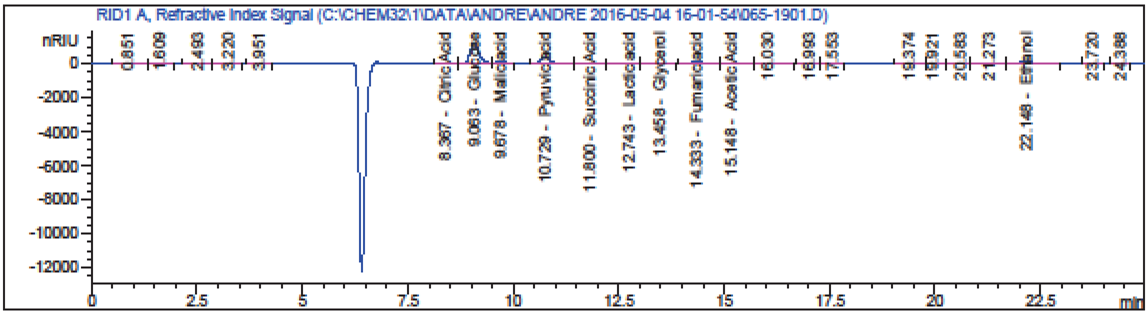

2 Warnings or Errors :
```

HPLC analysis results of Draw Solution sample at 32 hrs

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature:** 17 ℃

```
=====================================================================
Acq. Operator   : Michael                          Seq. Line :  19
Acq. Instrument : HPLC                              Location : Vial 65
Injection Date  : 5/4/2016 23:55                         Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\ANDRE\ANDRE 2016-05-04 16-01-54\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



```
=====================================================================
                     External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area     Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]               [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.367 BB      549.31439 7.07690e-6 3.88744e-3     Citric Acid
  8.550             -          -          -         Oxaloacetic Acid
  9.063 BV     1.82954e4  1.26288e-5 2.31049e-1     Glucose
  9.678 VB     2289.41016 2.51914e-5 5.76734e-2     Malic acid
 10.729 BB     6946.06689 1.68656e-5 1.17149e-1     Pyruvic acid
 11.800 BB      345.15683 1.44184e-5 4.97661e-3     Succinic Acid
 12.743 BB      735.76959 2.93631e-5 2.16045e-2     Lactic acid
 13.458 BB      910.43286    0.00000    0.00000     Glycerol
 14.333 BV     3280.76099 2.83989e-5 9.31699e-2     Fumaric acid
 15.148 VB      892.03918 3.55364e-5 3.16998e-2     Acetic Acid
 22.148 VB     3996.65186 2.89419e-5 1.15671e-1     Ethanol

Totals :                             6.76881e-1

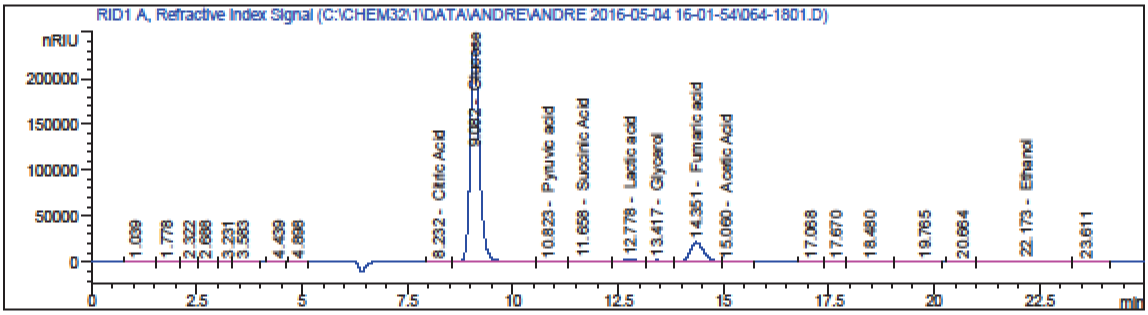

3 Warnings or Errors :
```

HPLC analysis results of Feed Solution sample at 32 hrs

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature**: 17 ℃

```
=======================================================================
Acq. Operator   : Michael                           Seq. Line :  18
Acq. Instrument : HPLC                               Location : Vial 64
Injection Date  : 5/4/2016 23:30                          Inj :   1
                                                   Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\ANDRE\ANDRE 2016-05-04 16-01-54\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



```
=======================================================================
                       External Standard Report
=======================================================================

Sorted By              :      Signal
Calib. Data Modified   :      10/6/2015 12:17
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area     Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]               [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.232 BB     4123.90820 9.28305e-6 3.82824e-2    Citric Acid
  8.550             -          -          -        Oxaloacetic Acid
  9.082 BV     3.57733e6  1.27043e-5   45.44754    Glucose
  9.722             -          -          -        Malic acid
 10.823 VB     3336.21802 1.68602e-5 5.62493e-2    Pyruvic acid
 11.658 BB     1.79908e4  1.64512e-5 2.95969e-1    Succinic Acid
 12.778 BV     5.20096e4  2.25767e-5    1.17420    Lactic acid
 13.417 VB     2.89683e4  1.14342e-5 3.31228e-1    Glycerol
 14.351 BV     4.93268e5  1.43305e-5    7.06875    Fumaric acid
 15.060 VB     8834.59375 2.94152e-5 2.59872e-1    Acetic Acid
 22.173 VV     3.38985e4  3.11812e-5    1.05700    Ethanol

Totals :                             55.72909

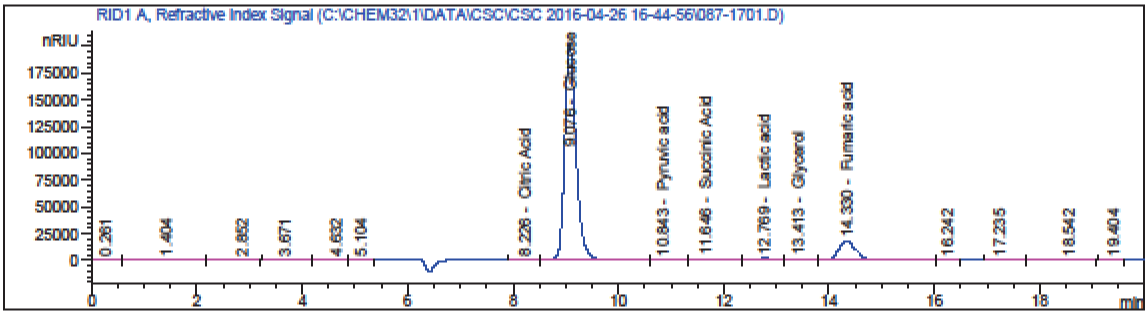

2 Warnings or Errors :
```

HPLC analysis results of Feed Solution sample at time zero

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature**: 32 ℃

```
========================================================================
Acq. Operator   : Michael                        Seq. Line :  17
Acq. Instrument : HPLC                            Location : Vial 87
Injection Date  : 4/26/2016 22:18                      Inj :   1
                                                Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\CSC\CSC 2016-04-26 16-44-56\F_0727_A.M
Last changed    : 8/20/2015 17:30 by Charles
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



```
========================================================================
                       External Standard Report
========================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                 [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.226 BB     2968.51123 9.15109e-6 2.71651e-2    Citric Acid
  8.550            -          -          -         Oxaloacetic Acid
  9.076 BV     3.03313e6  1.27042e-5   38.53356    Glucose
  9.722            -          -          -         Malic acid
 10.843 VV     2513.75146 1.68568e-5 4.23739e-2    Pyruvic acid
 11.646 VB     1.51877e4  1.64438e-5 2.49744e-1    Succinic Acid
 12.769 BV     3.58124e4  2.26207e-5 8.10102e-1    Lactic acid
 13.413 VV     2.50915e4  1.11723e-5 2.80329e-1    Glycerol
 14.330 VB     4.19566e5  1.43470e-5    6.01952    Fumaric acid
 15.157            -          -          -         Acetic Acid
 22.278            -          -          -         Ethanol

Totals :                               45.96279

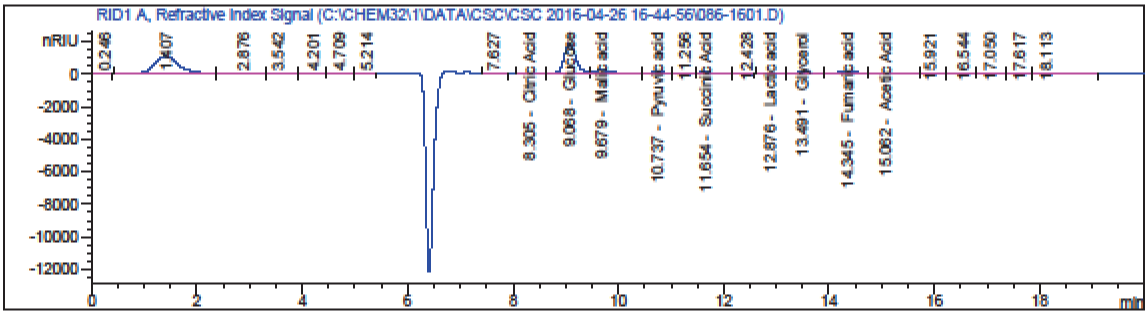

2 Warnings or Errors :
```

HPLC analysis results of Draw Solution sample at 24 hrs

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature**: 32 ℃

```
=====================================================================
Acq. Operator   : Michael                          Seq. Line :  16
Acq. Instrument : HPLC                              Location : Vial 86
Injection Date  : 4/26/2016 21:58                        Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\CSC\CSC 2016-04-26 16-44-56\F_0727_A.M
Last changed    : 8/20/2015 17:30 by Charles
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



```
=====================================================================
                      External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                 [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.305 BB      306.98764 5.06782e-6 1.55576e-3    Citric Acid
  8.550             -          -          -        Oxaloacetic Acid
  9.068 BV     2.71767e4  1.26536e-5 3.43884e-1    Glucose
  9.679 VB     3784.48486 2.17205e-5 8.22008e-2    Malic acid
 10.737 BB     1048.25269 1.68376e-5 1.76501e-2    Pyruvic acid
 11.654 VB     1028.93884 1.57957e-5 1.62528e-2    Succinic Acid
 12.876 VB      543.00232 3.18069e-5 1.72712e-2    Lactic acid
 13.491 BV     1088.24097    0.00000    0.00000    Glycerol
 14.345 VV     2180.52026 3.55450e-5 7.75066e-2    Fumaric acid
 15.062 VV     1387.27368 3.31058e-5 4.59268e-2    Acetic Acid
 22.278             -          -          -        Ethanol

Totals :                             6.02248e-1

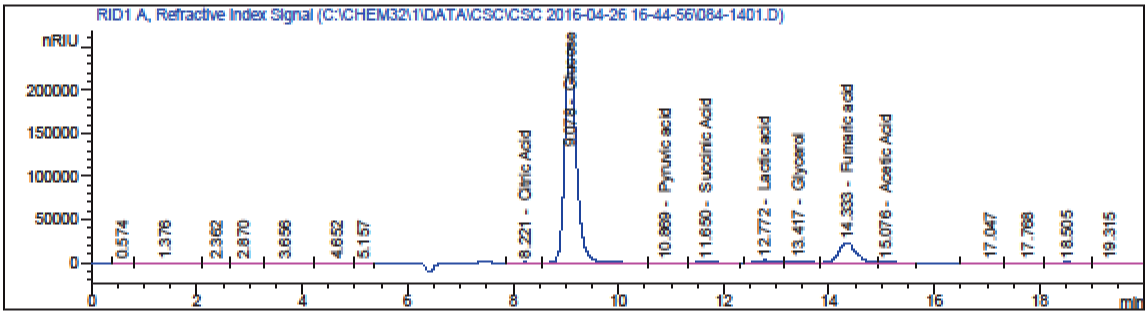

 3 Warnings or Errors :
```

HPLC analysis results of Feed Solution sample at 24 hrs

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature:** 32 ℃

```
=====================================================================
Acq. Operator   : Michael                         Seq. Line :  14
Acq. Instrument : HPLC                             Location : Vial 84
Injection Date  : 4/26/2016 21:16                       Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\CSC\CSC 2016-04-26 16-44-56\F_0727_A.M
Last changed    : 8/20/2015 17:30 by Charles
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



```
=====================================================================
                      External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                 [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.221 BB     4610.41357 9.31882e-6 4.29636e-2    Citric Acid
  8.550             -          -          -        Oxaloacetic Acid
  9.078 BV     3.80994e6  1.27043e-5   48.40278    Glucose
  9.722             -          -          -        Malic acid
 10.869 VB     3852.18896 1.68616e-5 6.49540e-2    Pyruvic acid
 11.650 BB     2.10367e4  1.64569e-5 3.46200e-1    Succinic Acid
 12.772 BV     4.58069e4  2.25899e-5    1.03477    Lactic acid
 13.417 VB     2.92700e4  1.14516e-5 3.35189e-1    Glycerol
 14.333 BV     5.09785e5  1.43274e-5    7.30389    Fumaric acid
 15.076 VB     1.15203e4  2.92550e-5 3.37026e-1    Acetic Acid
 22.278             -          -          -        Ethanol

Totals :                               57.86777


2 Warnings or Errors :

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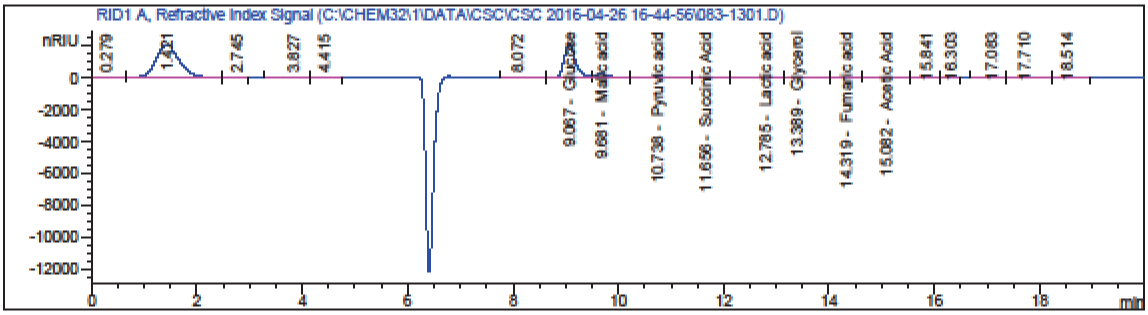
```

HPLC analysis results of Draw Solution sample at 32 hrs
Feed Solution: Fumaric acid produced by fermentation process.
Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature:** 32 ℃

```
=====================================================================
Acq. Operator   : Michael                          Seq. Line :  13
Acq. Instrument : HPLC                              Location : Vial 83
Injection Date  : 4/26/2016 20:55                        Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\CSC\CSC 2016-04-26 16-44-56\F_0727_A.M
Last changed    : 8/20/2015 17:30 by Charles
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



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=====================================================================
                     External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                 [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.294          -           -           -          Citric Acid
  8.550          -           -           -          Oxaloacetic Acid
  9.067 VV     3.26908e4  1.26622e-5 4.13939e-1     Glucose
  9.681 VB    4089.81763 2.13237e-5 8.72099e-2     Malic acid
 10.738 BV    2404.58105 1.68562e-5 4.05321e-2     Pyruvic acid
 11.656 VB     643.24170 1.53788e-5 9.89231e-3     Succinic Acid
 12.785 BV     750.99701 2.92235e-5 2.19468e-2     Lactic acid
 13.389 VB    1040.91174    0.00000    0.00000     Glycerol
 14.319 BV     929.53210 6.42229e-5 5.96972e-2     Fumaric acid
 15.082 VV    1512.69775 3.27428e-5 4.95299e-2     Acetic Acid
 22.278          -           -           -          Ethanol

Totals :                              6.82747e-1


3 Warnings or Errors :
```
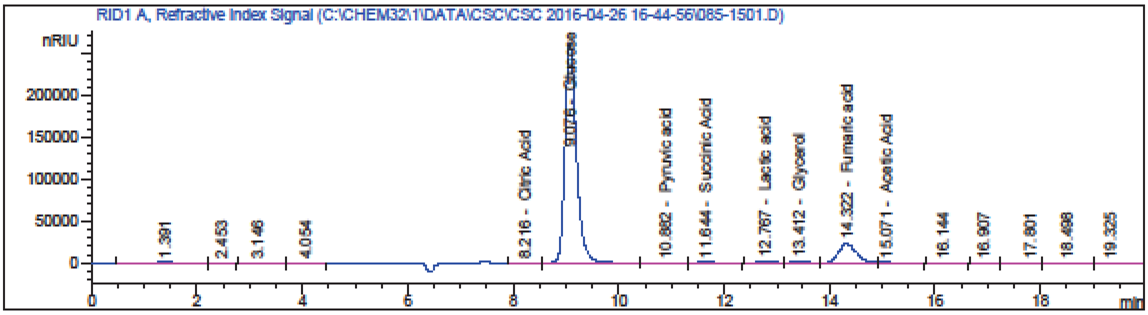

HPLC analysis results of Feed Solution sample at 32 hrs

Feed Solution: Fumaric acid produced by fermentation process.

Membrane: TFC aquaporin protein flat sheet under FO mode. **Temperature:** 32 ℃

```
=====================================================================
Acq. Operator   : Michael                          Seq. Line :  15
Acq. Instrument : HPLC                              Location : Vial 85
Injection Date  : 4/26/2016 21:37                        Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\CSC\CSC 2016-04-26 16-44-56\F_0727_A.M
Last changed    : 8/20/2015 17:30 by Charles
Analysis Method : C:\CHEM32\1\METHODS\F_0731_A.M
Last changed    : 10/6/2015 12:18 by Michael
Method Info     : For analysis of Succinic-, Lactic acid in glucose at 60°C.
                  Always start flow rate at 0.2ml/min, switch T to 60C and increase flow rate
                  in gradual increments to 0.6 ml/min
```



```
=====================================================================
                      External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10/6/2015 12:17
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [nRIU*s]                 [mg/ml]
-------|------|----------|----------|----------|--|------------------
  8.216 BV     5033.86719 9.34433e-6 4.70381e-2    Citric Acid
  8.550             -          -          -        Oxaloacetic Acid
  9.076 VV     3.92625e6  1.27043e-5   49.88042    Glucose
  9.722             -          -          -        Malic acid
 10.882 VB     7799.03320 1.68661e-5 1.31539e-1    Pyruvic acid
 11.644 BB     2.44289e4  1.64616e-5 4.02140e-1    Succinic Acid
 12.767 BV     4.73118e4  2.25863e-5    1.06860    Lactic acid
 13.412 VB     3.29698e4  1.16399e-5 3.83764e-1    Glycerol
 14.322 BV     5.29459e5  1.43240e-5    7.58397    Fumaric acid
 15.071 VB     1.52863e4  2.91251e-5 4.45215e-1    Acetic Acid
 22.278             -          -          -        Ethanol

Totals :                                59.94268


2 Warnings or Errors :

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```