Vibration-assisted forward osmosis process for mitigation of concentration polarization in submerged hollow fiber membrane system

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**VIBRATION-ASSISTED FORWARD OSMOSIS
PROCESS FOR MITIGATION OF CONCENTRATION
POLARIZATION IN SUBMERGED HOLLOW FIBER
MEMBRANE SYSTEM**

LOW KAY SIANG

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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MEMBRANE SYSTEM**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirements for the degree of
Master of Engineering

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Authorship Attribution Statement

Chapter 3 of this thesis has been submitted to Journal of Membrane Science as:

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Corresponding author: Professor Rong Wang

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The contributions of the co-authors are as follows:

- Dr. Wang Yi-Ning offered guidance in the modelling of the FO process, vetted and edited the manuscript drafts and contributed ideas for design of the experiments.
- Mr. Daniel Ng fabricated the membranes for the study and contributed suggestion for improvement of experimental design and the manuscript.
- Dr. Goh Kunli and Dr. Li Ye contributed suggestion for improvement in the preparation of the manuscript.
- Professor Wang Rong provided the general direction of the study, vetted and edited the manuscript drafts.
- I performed all the laboratory work and collected experimental data at Singapore Membrane Technology Center (SMTTC), designed the membrane module and the experimental set-up.

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Abstract

Vibration-assisted forward osmosis process for mitigation of concentration polarization in submerged hollow fiber membrane system

Concentration polarization results in significant reduction in the difference in osmotic pressure between the draw solution and the feed solution in forward osmosis (FO) and is regarded as a major challenge in the FO process. Hence, mitigating concentration polarization is essential for increasing the efficiency of the FO process. In the current study, vibration of hollow fiber (HF) membranes was systematically studied as a method for the mitigation of concentration polarization in submerged FO process. A membrane module consisting of polyether sulfone (PES) HF membranes with inner selective layer was designed and fabricated. Using a water flux model that takes into account the internal concentration polarization (ICP) and external concentration polarization (ECP) on both the lumen and shell sides of the HF membranes, the vibrating frequency and amplitude were evaluated with regards to the change of mass transfer coefficient. Results showed that when low vibration frequency and amplitude of (3 Hz and 1.2 cm) were applied, the mass transfer coefficient increases from 0.7×10^{-5} m/s (at no vibration) to 1.8×10^{-5} m/s, which approaches the optimal value as determined from the FO modelling results. The effects of the vibration of membranes were then evaluated in the active layer facing feed solution (AL-FS) and active layer facing draw solution (AL-DS) orientations. Results showed that in the AL-FS orientation, vibration could enhance mass transfer coefficient significantly at low water flux. However, in the AL-DS orientation, the enhancement of mass transfer coefficient was minimal at low water flux level due to minimal concentrative ECP present. Interestingly, there was significant improvement of mass transfer coefficient at high DS concentration/high water flux level attributed to the significant concentration polarization under high water flux condition. In addition, the vibration-assisted FO process was carried out using polyelectrolyte poly (sodium-4-styrenesulfonate) (PSS) as a draw solute. The change of draw solute to PSS has limited effects on the vibration, as the low diffusion coefficient and high viscosity of PSS offsets the benefits of vibration of membranes. In summary, this study demonstrated a facile method for mitigating concentration polarization in submerged FO process, whereby vibration of HF membranes at low frequency and amplitude could enhance FO water flux by improving hydrodynamic mixing and induce boundary layer disturbances at the shell side of submerged HF membranes. The method could possibly be adopted for improving FO efficiency in submerged osmotic processes.

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LIST OF SYMBOLS

A	Water permeability coefficient
B	Solute permeability coefficient within membrane
C_f	Salt concentration in the feed
C_p	Salt concentration in the permeate
ΔC	Concentration gradient across the active layer of the membrane
D_D	Solute diffusion coefficient in the bulk draw solution
D	Solute diffusion coefficient
D_m	Solute diffusion coefficient in the membrane support layer
d_h	Hydraulic diameter
J_s	Reverse solute flux
J_v	FO water flux
k_f	Mass transport coefficient adjacent to membrane surface at feed solution
k_m	Mass transport coefficient in the porous support layer
k_d	Mass transfer coefficient of adjacent to membrane surface at draw solution
K	Solute resistivity
L	Length of channel
l	thickness of support layer
R	Sodium chloride rejection
Re	Reynolds number
S	Membrane structural parameter
Sc	Schmidt number
Sh	Sherwood number
ΔP	Applied hydraulic pressure difference

Greek

$\Delta\pi$	Difference in osmotic pressure across membrane
π_{draw}	Osmotic pressure of draw solution
π_{feed}	Osmotic pressure of feed solution
$\pi_{D,b}$	Bulk osmotic pressure of the draw solution
$\pi_{F,b}$	Bulk osmotic pressure of the feed solution
$\pi_{D,i}$	Osmotic pressure of draw solution at the surface of porous support
$\pi_{F,i}$	Osmotic pressure of feed solution at the surface of porous support
$\pi_{D,m}$	Osmotic pressure of draw solution at interface of selective layer
$\pi_{F,m}$	Osmotic pressure of feed solution at interface of selective layer
δ_D	Thickness of boundary layer at the draw solution side
δ_F	Thickness of boundary layer at the feed solution side
τ	Tortosity of the support layer
ε	Porosity of the support layer

CHAPTER 1

INTRODUCTION

In the last decade, forward osmosis (FO) has attracted much attention from the scientific community as a sustainable and versatile technology for water purification and addressing the issue of global water scarcity. Currently, the most widely used technology for desalination is reverse osmosis (RO), a process that requires external hydraulic pressure and is regarded as both energy and cost-intensive (Cath, Childress et al. 2006).

Forward osmosis is an osmotically driven such that spontaneous water permeation occurs across a semipermeable membrane. Unlike reverse osmosis, application of high pressure is not required. The driving force behind the FO process is based on the difference between the bulk osmotic pressure of the draw solution, $\pi_{D,b}$ and the bulk osmotic pressure of feed solution, $\pi_{F,b}$ (Cath, Childress et al. 2006). This osmotic pressure difference triggers a spontaneous flow of water molecules from the feed solution to the draw solution of higher osmotic pressure, thereby, achieving separation of water molecules from its solute in the feed solution. The FO process does not require external pressure or heating (Elimelech and Phillip 2011). Due to its relatively low consumption of energy (Kravath and Davis 1975, McCutcheon, McGinnis et al. 2005, McCutcheon, McGinnis et al. 2006), the FO process has been reported in various applications such as the desalination of sea water and wastewater treatment plants. Recently, an emerging technology, known as osmotic membrane bioreactor (OMBR) which integrates the forward osmosis process and membrane bioreactor (MBR) have been reported for use in various applications (Cornelissen, Harmsen et al. 2008, Achilli, Cath et al. 2009, Lay, Zhang et al. 2011). The advantages of OMBR are relatively high water flux, high efficiency for removal of contaminants as well as lower fouling propensity. In addition, it is potentially less energy consuming, at the same time, higher quality of water is obtained (Cornelissen, Harmsen et al. 2008, Achilli, Cath et al. 2009, Lay, Zhang et al. 2011).

Concentration polarization (CP) is a major challenge in the FO process. There are two types of concentration polarization, namely internal concentration polarization (ICP) and external concentration polarization (ECP). Both ICP and ECP may be dilutive or concentrative. The undesirable effects of CP is that it leads to reduction in the difference in osmotic pressure between draw and feed solution, which is the main driving force behind the FO process. This results in a significant reduction of the FO water flux (Cath, Childress et al. 2006, Johnson,

Suwaileh et al. 2018). The severity of ICP is usually reflected by the structural parameter, S value, of the membrane. A higher S value indicates more severe ICP. There have been numerous studies reported on minimising the structural parameter of the membrane. These studies include fabrication of substrate layer via co-casting method (Liu and Ng 2014, Xiao, Nghiem et al. 2015) and electrospinning (Song, Liu et al. 2011, Bui and McCutcheon 2013). Nanoparticles have also been successfully incorporated into the substrate layer, with the aim of increasing the hydrophilicity of substrate layer, thereby reducing S value of the membrane (Ma, Wei et al. 2013, Liu and Ng 2015, Park, Phuntsho et al. 2015). Recently, the use of ultrasound has been reported to be effective in mitigating ICP effects in the FO process (Heikkinen, Kyllönen et al. 2017, Choi, Hwang et al. 2018). In addition, reverse solute diffusion (RSD) is also another challenge in the FO process and in which draw solutes from the draw solution is transported across the FO membrane and permeates into the feed solution. RSD increase the severity of ICP in the FO mode and results in lower osmotic pressure difference (Phillip, Yong et al. 2010, Suh and Lee 2013).

Many research groups have attempted to improve the performance of the FO process and much of these research studies were focused on improving the FO membrane structures (Tiraferri, Yip et al. 2011, Qiu, Setiawan et al. 2012, Tiraferri, Kang et al. 2012, Fang, Liu et al. 2015) as well as novel draw solutes (Cai, Shen et al. 2013, Stone, Rae et al. 2013, Stone, Wilson et al. 2013, Cai, Wang et al. 2015). There are very few published works that addresses the mitigation of ECP for the improvement of the performance of the FO process. The effect of ECP is certainly non-negligible, especially for membranes that exhibit high water flux and can lead to significant reduction in water flux (McCutcheon and Elimelech 2006, Gruber, Johnson et al. 2011). To date, there are very few reports of effective mitigation of ECP in the FO process. These studies mainly focuses on improving the hydrodynamics conditions such as increasing cross-flow velocity, inducing vortices and using suitable feed spacers (Zhang, Cheng et al. 2014, Abid, Johnson et al. 2017).

Several authors have reported the use of Vibratory Shear Enhanced Process (VSEP) for reduction of fouling in reverse osmosis and nano-filtration (NF) systems (Akoum, Jaffrin et al. 2004, Petala and Zouboulis 2006, Shi and Benjamin 2008, Zouboulis and Petala 2008). In these studies, shear stress was generated on the membrane surface when the membranes are vibrate. Thereafter, various modules such as rotating disks, vibrating flat sheet membranes as well as vibrating hollow fibres based on VSEP have been developed (Bouzerar, Ding et al. 2000, Akoum, Jaffrin et al. 2002, Low, Juan et al. 2005). Applications of VSEP as an anti-fouling

strategy have been reported in various fields such as treatment of dairy process waters (Frappart, Akoum et al. 2006), concentration of milk proteins (Akoum, Jaffrin et al. 2005) as well as removal of natural organic matter (Petala and Zouboulis 2006, Shi and Benjamin 2008).

Application of shear stress as a strategy to induce boundary layer disturbance for mitigating concentration polarization effects and controlling fouling have been reported for reverse osmosis membranes (Zamani, Chew et al. 2015, Zsirai, Qiblawey et al. 2016). However, to date, there have been no reports that utilises vibration of membranes to induce shear stress on the membrane surface in submerged FO hollow fiber membranes for the mitigation of concentration polarization. Therefore, the effect of vibration of membranes as a means to induce boundary layer disturbance for the mitigation of ECP in the FO process will be investigated in the current study.

1.1 Objectives

The current study aims to investigate the effects of vibration of hollow fiber membrane in submerged FO process. The specific objectives are to:

- develop a systematic approach to study the effect of vibrating frequency and amplitude on the vibration-assisted FO process.
- evaluate the effects of vibration under different FO conditions such as (1) membrane orientations, (2) different draw solution concentrations and (3) type of draw solutes.
- analyse the mass transfer coefficient under the different FO conditions.

1.2 Thesis Outline

This thesis comprises of 4 chapters, which are outlined as follow:

Chapter 1: Introduction

Background of FO process and objectives of the current study are provided.

Chapter 2: Literature review and theory

The theory and basic principles of the FO process will be explained.

FO membranes and their modules are reviewed. Applications of submerged FO processes such as osmotic membrane bioreactor will be discussed.

The thesis will not review all draw solutes used in FO but rather focus on draw solutions that have been evaluated for use in submerged FO processes.

In addition, concentration polarization and various strategies for mitigation of ICP and ECP are reviewed in this chapter. Lastly, the use vibration in various submerged membrane systems are also presented in this chapter.

Chapter 3: Understanding transverse vibration on HF membranes in submerged FO processes.

In this chapter, the methods and experiments of the vibration-assisted FO process are presented. The effects of the vibration under different FO conditions are evaluated and mass transfer coefficient under these operating conditions is analysed. Key findings are presented.

Chapter 4: Recommendations for future work are presented in this chapter.

CHAPTER 2

LITERATURE REVIEW AND THEORY

In this chapter, the theory and basic principles of the FO process are explained. Thereafter, specific topics in FO such as the different types of FO membranes and modules will be discussed. Submerged FO applications such as osmotic membrane bioreactor as well as draw solutions will be reviewed.

Concentration polarization, which is regarded as a key limitation to the performance of the FO process will be explained. At the same time, the various strategies employed for the mitigation of concentration polarization will be reviewed. Lastly, the use of vibration in various submerged membrane systems is reviewed.

2.1. Principles of forward osmosis

The water flux for forward osmosis (FO), pressure retarded osmosis (PRO) and reverse osmosis (RO) can be described by the equation:

$$J_v = A(\Delta\pi - \Delta P) \quad (2.1)$$

where J_v is the water flux, A is the water permeability constant of the membrane, $\Delta\pi$ is the difference in osmotic pressure across membrane and ΔP is the applied hydraulic pressure difference.

Figure 2.1. Schematic of solvent flow in FO, PRO and RO processes.

As illustrated in Fig. 2.1, the driving force behind the FO process is the difference in osmotic pressure across membrane, water diffuses to the draw solution. Applied hydraulic pressure, ΔP is zero. PRO is considered as an intermediate between FO and RO, water diffuses to the draw solution under positive pressure ($\Delta\pi > \Delta P$). In the case of RO, water diffuses to the feed solution under applied hydraulic pressure ($\Delta\pi < \Delta P$). In the FO process, no pressure is applied ($\Delta P = 0$), hence, spontaneous water permeation through the asymmetric membrane is solely due to the difference in the osmotic pressures between the draw and feed solutions as described in Eq. (2.2)

$$J_v = A(\pi_{D,b} - \pi_{F,b}) \quad (2.2)$$

where $\pi_{D,b}$ is the bulk osmotic pressure of the draw solution and $\pi_{F,b}$ is the bulk osmotic pressure of the feed solution.

A plot of water flux as a function applied pressure is illustrated in Fig. 2.2.

Figure 2.2. Water Flux as a function of applied hydraulic pressure, adapted from (Cath, Childress et al. 2006)

2.2. FO membranes

The desirable qualities of an ideal FO membrane are high water flux, high salt rejection and at the same time, exhibit low concentration polarization, low fouling propensity and good mechanical strength. The earliest reported FO membranes was that of Loeb research work (Mehta and Loeb 1978, Loeb, Titelman et al. 1997), which was based on conventional RO membranes which have thick support structures. Experimental results show that these membranes suffer from severe ICP due to their inherent thick support structures.

2.2.1. Cellulose-based FO membranes

In the 1990s, Hydration Technology Inc., (HTI) fabricated a FO membrane, of which, cellulose triacetate (CTA) material was used as the support structure. The thickness of the membrane was about 50 μm . The HTI FO membrane exhibited superior performance as ICP effects were largely reduced as compared to conventional RO membranes which have thick support layer. Since the membrane was available commercially, many research groups have utilised the HTI membrane for FO desalination (Cath, Gormly et al. 2005, Gray, McCutcheon et al. 2006, McCutcheon, McGinnis et al. 2006). Cellulose acetate (CA) has also been studied by various groups as the porous support for FO membranes as it is more hydrophilic than CTA due to more hydroxyl groups. This suggests that water permeability of membrane could be improved and ICP effects could be further reduced (Sairam, Sereewatthanawut et al. 2011). Although CA FO membranes exhibited higher water permeability than CTA membranes, it has relatively lower rejection compared to CTA membranes. Hence, a blend of CTA and CA have been reported for a compromise between water permeability and selectivity of the FO membrane (Nguyen, Yun et al. 2013). The advantages of cellulose-based membranes are that they are very hydrophilic, have low fouling propensity and low cost of production. However, a drawback is their narrow pH working ranges which severely limits their applications in the industries (Chen, Wang et al. 2015). A summary of the performance of cellulose-based membranes is given in Table 2.1.

Table 2.1
Summary of Cellulose-based FO membranes

Summary of Cellulose-based FO membranes							
Membrane	A	B	FO performance		DS	FS	Ref
	(LMH/bar)	(LMH)	(AL-FS)				
			J_v (LMH)	J_s (gMH)			
HTI CA FO membrane	1.13	0.46	10	6	1.0 M NaCl	DI	(Gray, McCutcheon et al. 2006)
CTA flat sheet	-	-	9.0	6.2	2.0 M NaCl	DI	(Ong and Chung 2012)
CA flat sheet	0.17	0.07	10.3	0.8	2.0 M MgCl ₂	DI	(Zhang, Wang et al. 2010)
CA flat sheet	0.51	0.4	12	5.1	2.0 M NaCl	DI	(Ong and Chung 2012)
CA-hollow fibre	0.76	0.38	17.1	2.5	2.0 M MgCl ₂	DI	(Su, Chung et al. 2012)
CA propionate hollow fiber	0.80	0.22	8.0	1.3	2.0 M NaCl	DI	(Su, Ong et al. 2013)

2.2.2. Thin-film composite membranes

Thin-film Composite (TFC) membranes have been fabricated for RO applications by Cadotte (Cadotte, King et al. 1981) in the 1980s and have been used for RO and nanofiltration (NF) applications by various research groups (Petersen 1993, Ghosh, Jeong et al. 2008). In recent years, TFC membranes have been widely used for FO desalination and is fabricated via phase inversion (for the porous support) followed by interfacial polymerization of the selective polyamide layer (Wei, Qiu et al. 2011). Both flat sheet (Yip, Tiraferri et al. 2010, Bui, Lind et al. 2011, Widjojo, Chung et al. 2011, Yu, Seo et al. 2011, Tiraferri, Kang et al. 2012) as well as hollow fiber (Chou, Shi et al. 2010, Wang, Shi et al. 2010) configurations have been fabricated for FO desalination. The general scheme of interfacial polymerization of TFC FO membrane is depicted in Fig. 2.3.

Figure 2.3. Interfacial polymerization using TMC and MPD. Trimesoyl chloride (TMC) and m-phenylenediamine (MPD) in aqueous solution are the two main reagents used to form the active later at the surface of the microporous support (Wei, Qiu et al. 2011). The substrate is first soaked in MPD solution, after which TMC in n-hexane solution was poured over the substrate soaked in MPD and allowed to react to form the selective polyamide layer.

Yip et al. pioneered the work the on TFC flat sheet membrane using polysulfone (PSf) for the substrate (Yip, Tiraferri et al. 2010). Thereafter, many groups fabricated the TFC FO membranes using different polymeric materials such as polyethersulfone (PES), sulphonated polyethersulfone (SPES), polyacrylonitrile (PAN) and polyetherimide (PEI). Meanwhile, Wang et al. pioneered the research work for the TFC FO membrane in the hollow fiber configuration using PEI as substrate (Wang, Shi et al. 2010). The performance of these FO membranes are summarized in Table 2.2.

Table 2.2
Summary of TFC FO membrane with various phase inversion substrates.

Summary of TFC FO membrane with various phase inversion substrates.								
Membrane	<i>S</i> (μm)	A	B	FO performance		DS	FS	Ref
/substrate		(LMH/bar)	(LMH)	(AL-FS)				
				<i>J_v</i> (LMH)	<i>J_s</i> / <i>J_v</i> (g/L)			
Flat-sheet PSf	492	1.16	0.47	18.16	-	1.5 M	DI	(Yip, Tiraferri et al. 2010)
Flat-sheet PSf	312	1.90	0.33	25.0	-	1.0 M	DI	(Tiraferri, Yip et al. 2011)
Flat-sheet PAN	389	0.91	0.57	9.25	0.11	0.5 M	DI	(Klaysom, Hermans et al. 2013)
Flat-sheet SPES	245	2.9	0.18	17	0.38	0.5 M	DI	(Sahebi, Phuntsho et al. 2016)
HF-PES	595	2.22	0.2	14	0.13	0.5 M	DI	(Wang, Shi et al. 2010)
HF-PES	219	1.18	0.135	34.5	0.29	2.0 M	DI	(Sukitpaneenit and Chung 2012)

2.3. FO membrane modules

Plate-and-frame configuration

The plate-and-frame module can be used for packing the flat sheet FO membranes. The plate-and-frame module can be produced in various sizes such as a lab scale device holding a single membrane or full-scale systems holding more than 1000 membranes. The two main drawbacks using the above configuration are firstly the absence of suitable membrane support and secondly low packing density of FO membranes results in higher operating costs. Other limitations include problems such as internal and external sealing, membrane integrity, and a small operational window (Cath, Childress et al. 2006). In a recent study using plate and frame FO module, the point of osmotic equilibrium in the FO module channel was studied as a function of crossflow direction (Attarde, Jain et al. 2015). It was demonstrated that counter flow offers advantage of gradual decrease in water flux with higher feed water recovery and dilution factor of DS. The advantages of plate- and-frame FO module are that they are suited for the treatment of wastewater, better backwashing leading to lower fouling propensity and also higher cross-flow velocities can be attained in this configuration.

Tubular configuration

The tubular module for FO membranes can be in the form of tubes or hollow fibers (Chou, Shi et al. 2010, Wang, Shi et al. 2010, Li, Chou et al. 2015). There are several advantages associated with the use of tubular membranes for FO applications. Firstly, it can support high hydraulic pressure as they are self-supported. Secondly, it allows for high packing density of the FO membranes. Thirdly, there is free movement of fluids on the shell and lumen side of the hollow fiber membranes, which is appropriate fluid flow patterns rendering it suitable for FO applications. Moreover, since thick porous support layer is not necessary in the case of tubular FO membranes, this implies that ICP is inherently reduced, resulting in enhanced FO water flux. The limitations are that there might be limited mixing of fluids at the membrane surface and it may be prone to ECP as the boundary film may thicken if the HF FO module is placed in a tank of stagnant fluid.

Spiral-wound configuration

As the commercial spiral-wound membrane module for RO is operated with only the feed stream under direct control, it cannot be adapted for FO applications. Metha developed a

spiral wound module that is suitable both for FO and PRO applications, whereby the flow pattern of the draw solution and feed solution is depicted in the Fig. 2.4 (Mehta 1982). The advantages of this configuration are that it allows for high packing density of the FO membranes and ease of cleaning of foulants. The drawback is that there is limited pressure in the membrane envelop.

Figure 2.4. Spiral-wound module for FO membranes. Adapted from (Mehta 1982).

2.4. FO applications

In the last decade, FO has been widely studied for various applications such as wastewater reclamation (Wang, Chang et al. 2016), seawater desalination (Valladares Linares, Li et al. 2014), food processing (Petrotos, Quantick et al. 1998), osmotic pumps for drug delivery (Herrlich, Spieth et al. 2012) as well as osmotic power generation (Aaberg 2003). Most of these applications adopt the cross flow configuration. In the following section, FO applications utilizing the submerged osmotic processes, namely wastewater reclamation and food processing will be reviewed.

2.4.1. Submerged FO processes

Most of research efforts in FO are mainly centered on cross-flow configurations whereby feed and draw solution are circulated through a module where filtration occurs. Recently, submerged FO applications are gaining attention for bioreactors such as osmotic membrane bioreactor (Holloway, Achilli et al. 2015). In the OMBR, FO membranes are utilised for the dewatering of activated sludge into a concentrated draw solution. The FO membranes used in OMBR has the distinct advantages of high rejection and low fouling propensity compared to the MF and UF membranes used in the conventional MBRs.

Osmotic membrane bioreactor (OMBR) has been widely used for wastewater treatment (Cornelissen, Harmsen et al. 2008, Coday, Xu et al. 2014, Valladares Linares, Li et al. 2014). Cornelissen et al. (Cornelissen, Harmsen et al. 2008) investigated the effects of membrane fouling and draw solute leakage in a lab-scale OMBR using activated sludge solution and found that fouling and draw solution leakage were negligible throughout the FO process. However, the performance of the OMBR was limited by ICP. Achilli et al. investigated the use of OMBR-RO hybrid process to produce potable water (Achilli, Cath et al. 2009). It was found that high FO water flux and low reverse solute flux could be achieved by the OMBR. Ansari et al. summarized the use of FO module in three types of set-up for OMBR, namely (1) the aerobic OMBR, (2) anaerobic OMBR and (3) pre-concentration by FO module before anaerobic treatment as depicted in Fig. 2.5 (Ansari, Hai et al. 2017).

Figure 2.5. Schematic of aerobic FOMBR, anaerobic FOMBR and pre-concentration before anaerobic treatment, adapted from (Ansari, Hai et al. 2017).

Furthermore, Luo et al. compared the performance of OMBR-RO to conventional MBR-RO system in advanced wastewater treatment and found that fouling was significantly reduced in the OMBR-RO system as the FO membrane prevented foulants from permeating into the draw solution, resulting in mitigation of fouling in downstream RO (Luo, Phan et al. 2017). In contrast, there was severe fouling in the RO membrane in the MBR-RO system. A schematic of OMBR coupled to RO system is depicted in the following Fig. 2.6.

Figure 2.6. Schematic of OMBR coupled to RO system, adapted from (Holloway, Achilli et al. 2015).

The FO process is also commonly used in the food processing industry. Many studies have been done on using FO membrane in the food processing industries, particularly in the concentration of citrus juices (Berk 2016), tomato juices (Petrotos, Quantick et al. 1998, Petrotos, Quantick et al. 1999), xylose (Kim, Choi et al. 2018), sucrose (Garcia-Castello, McCutcheon et al. 2009) and whey (Wang, Wang et al. 2017).

In summary, use of FO consumes less energy than thermal or pressure driven membrane processes mainly because high temperatures and high pressures are not required. Most of these tests are done in the cross flow configuration. One limitation of using the cross flow configuration is that at high concentration, flow through the module may be limited due to high viscosity. In contrast, submerged FO operation may have the advantage of achieving higher concentration of juices since there is no need pump the fluid through the modules.

It is expected that ECP will significantly limit the performance of the submerged FO system since FO membranes are immersed in a tank of stagnant fluid. Therefore, it is the objective of the current study to investigate the effects of vibration of FO membranes as a method to mitigate the undesirable effects of ECP. The findings of the current study may be suitable for improving the efficiency of submerged FO processes.

2.5. Draw solutes

Draw solutes play a critical role in the performance of the FO process. In this section, emphasis is placed on review of draw solutes that have been used in submerged FO process. There are several criteria for choosing a draw solute for submerged FO applications such as OMBR, namely, they should be able to generate a high water flux, exhibit low reverse solute flux (RSF) as well as non-toxic to microorganisms (Achilli, Cath et al. 2010). A low RSF is important for OMBR so that the salt will not accumulate in the activated sludge, causing a decrease in the water flux.

Inorganic salts are widely used in FO and OMBR applications. Inorganic salts with divalent ions such as MgCl_2 exhibits lower RSF as well as lower induced water flux (at the same osmotic pressure) than salts with monovalent ions such as NaCl . This is due to the lower diffusion coefficient of the divalent ions, which in turn exacerbated the detrimental effects of ICP (Hancock and Cath 2009, Achilli, Cath et al. 2010).

Specific RSF (SRSF) which is the ratio of RSF to water flux is also used as an indicator for selection of draw solute for OMBR. A low SRSF value is desired. The potassium salts KCl , KBr as well as NH_4HCO_3 exhibited the highest SRSF, indicating that they are not suitable as draw agents for OMBR (Achilli, Cath et al. 2010). On the other hand, sulfate salts such as MgSO_4 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ exhibited the lowest SRSF. However, a drawback is that sulfate salts may result in scaling of the FO membranes. Holloway and co-workers investigated the effect of mixed salt draw solutions using MgCl_2 as additive to majority NaCl . Results show that there is reduced RSF while water flux was not affected. This strategy taps on the advantages of low RSF of MgCl_2 as well as the high flux induced by NaCl (Holloway, Maltos et al. 2015).

Bowden et al. investigated the effects of using organic ionic salts as draw solutes in OMBR and found that they were suitable as they exhibited significantly lower SRSF compared to their inorganic counterparts (Bowden, Achilli et al. 2012). However, effects of ICP with the use of these organic salts were not evaluated. The low diffusion coefficient of the organic anions may have exacerbated the effects of ICP. A comparison of these draw solutes are presented in Table 2.3.

Table 2.3
Comparison of water flux, RSF, SRSF for inorganic draw solute and organic ionic salts in OMBR.

Draw solute	Conc. of DS (M)	J_v (L m ⁻² h ⁻¹)	RSF (g m ⁻² h ⁻¹)	SRSF (g L ⁻¹)	Ref.
NaCl	1.19	14.5	11	0.75	(Achilli, Cath et al. 2009)
Sodium formate	1.02	11.7	7.6	0.65	(Bowden, Achilli et al. 2012)
Sodium acetate	1.69	10.4	3.5	0.34	(Bowden, Achilli et al. 2012)
Sodium propionate	1.06	10.7	2.3	0.21	(Bowden, Achilli et al. 2012)
Magnesium acetate	1.85	8.9	1.1	0.12	(Bowden, Achilli et al. 2012)

Polyelectrolytes such as polyacrylic acid sodium salts (PAA-Na) (Ge, Su et al. 2012) and poly (sodium 4-styrenesulfonate) (PSS) have also been investigated as draw solutes for the FO process (Tian, Hu et al. 2015). Compared to conventional NaCl draw solute, polyelectrolytes exhibit lower RSF into the feed solution due to their bigger size and molecular weight. A drawback of using these polyelectrolyte is that they have higher viscosity and lower diffusion coefficient and therefore leads to more severe concentration polarization. To date, polyelectrolytes have yet to be investigated in submerged FO applications such as OMBR.

Micellar solutions were investigated as draw solution in the FO process using both flat-sheet and hollow fiber membranes (Gadelha, Nawaz et al. 2014). Results showed that above critical micellar concentration (CMC), the micellar draw solute exhibited more stable water flux as well as significantly lower RSF as compared to using brine. Interestingly, the study also demonstrated that ECP effect on flat sheet FO membrane was mitigated for surfactant with osmotic pressure above the CMC. Micellar solution was further investigated as draw solution in OMBR, achieving significantly low reverse solute transport (Nawaz, Parveen et al. 2016).

To date, there are limited studies focusing on the use of novel draw solutes in submerged FO processes. Furthermore, there are no systematic studies done to compare the CP effects of different types of draw solutes in the FO process. However, it is known that viscosity and diffusivity of draw solutes is related to CP. Hence, optimizing molecular structure and

molecular weight of draw solutes may be a viable way to mitigate CP in the FO process. For instance, fully dissociated organic ionic draw solutes with expanded structures could be used to investigate their effects on CP and RSF in submerged FO processes.

2.6. Concentration polarization

Two types of concentration polarization can take place in the FO process, namely internal concentration polarization (ICP) and external concentration polarization (ECP). They may be dilutive or concentrative (Cath, Childress et al. 2006). Both ICP and ECP leads to a decrease in effective osmotic pressure and poses a serious limitation to the performance of FO membranes (Ng, Tang et al. 2006, Tan and Ng 2013). In particular, McCutcheon and Elimelech modelled ECP based on the boundary film theory (McCutcheon and Elimelech 2007).

2.6.1 External concentration polarization

Concentrative ECP occurs on the feed side where solvent permeates through the asymmetric FO membrane. This results in an increase in concentration of the solute as the solutes are retained by the membrane. The concentrative ECP modulus is defined as:

$$\frac{\pi_{F,m}}{\pi_{F,b}} = \exp\left(\frac{J_v}{k}\right) \quad (2.3)$$

where J_v is the experimental water flux, $\pi_{F,m}$ is the osmotic pressure of the feed solution at the membrane surface and $\pi_{F,b}$ is the osmotic pressure of the bulk feed solution and k is the mass transfer coefficient.

Dilutive ECP occurs when convective flow of fluid displaces the draw solute from the membrane surface on the permeate side. The draw solution is diluted by the permeate entering the draw side and this leads to dilutive ECP. A modulus for dilutive ECP can be defined as:

$$\frac{\pi_{D,m}}{\pi_{D,b}} = \exp\left(-\frac{J_v}{k}\right) \quad (2.4)$$

where J_v is the experimental water flux, $\pi_{D,m}$ is the osmotic pressure of the draw solution at the membrane surface and $\pi_{D,b}$ is the osmotic pressure of draw solution at the bulk and k is the mass transfer coefficient.

2.6.2. Internal concentration polarization

Concentrative ICP occurs in the AL-DS orientation when the concentration of the salt increases in the porous support of the FO membrane. This occurs when the salt present in the feed solution is transported into the porous support via convective water flow, thereafter entrapped in the support layer as it is unable to penetrate the selective layer from the porous support. As a result, there is a reduction of osmotic pressure difference. The solute resistivity, K , would be an indication of the severity of ICP as it measures the ease of which a solute is transported across the porous support.

$$K = \frac{t\tau}{D\epsilon} \quad (2.5)$$

where t , τ , ϵ are the thickness, tortuosity and porosity of the support layer and D is the diffusion coefficient.

According to McCutcheon and Elimelech (McCutcheon and Elimelech 2006), the concentrative ICP modulus is defined as:

$$\frac{\pi_{F,i}}{\pi_{F,b}} = \exp(J_v K) \quad (2.6)$$

where $\pi_{F,i}$ is the osmotic pressure of the feed at the surface of the porous support and $\pi_{F,b}$ is the bulk feed osmotic pressure. The positive exponent implies a concentrative effect.

In the AL-FS orientation, dilutive ICP occurs since the concentration of the draw solution is reduced within the porous support layer by the permeate water through the selective polyamide layer. According to McCutcheon and Elimelech (McCutcheon and Elimelech 2006), the dilutive ICP modulus is given as:

$$\frac{\pi_{D,i}}{\pi_{D,b}} = \exp(-J_v K) \quad (2.7)$$

where $\pi_{D,i}$ is the osmotic pressure of the draw at the surface of the porous support and $\pi_{D,b}$ is the bulk draw osmotic pressure. The negative exponent indicates dilutive effect.

(a) AL-FS orientation

(b) AL-DS orientation

Figure 2.7. Schematic of ECP and ICP in the (a) AL-FS orientation and (b) AL-DS orientation. where $\pi_{D,b}$ is the bulk draw osmotic pressure, $\pi_{D,m}$ is the osmotic pressure at the membrane surface on the draw side, $\pi_{F,b}$ is the bulk feed osmotic pressure, $\pi_{F,m}$ is the osmotic pressure at the membrane surface on the feed side, $\pi_{F,i}$ is the osmotic pressure of the feed at the surface of the porous support and $\pi_{D,i}$ is the osmotic pressure of the draw at the surface of the porous support. δ_D is the thickness of boundary at the draw solution side and δ_F is the thickness of boundary at the feed solution side.

All of the ECP and ICP moduli lead to a reduction of osmotic driving force. An increase in bulk osmotic driving pressure will only result in diminishing increase in FO water flux. A schematic of the boundary layer and osmotic driving profiles in AL-FS and AL-DS orientations is depicted in Fig. 2.7.

Many research groups have attempted to model the FO water flux, taking into account ICP and ECP. Tiraferri et al. (Tiraferri, Yip et al. 2013) reported flux model based on the film theory, taking into account dilutive ICP and concentrative ECP on the feed side of the FO membrane for the FO mode, defined as:

$$J_v = A \left(\frac{\pi_D \exp\left[-J_v \left(\frac{S}{D}\right)\right] - \pi_F \exp\left(\frac{J_v}{k}\right)}{1 + \frac{B}{J_v} \left\{ \exp\left(\frac{J_v}{k}\right) - \exp\left(-J_v \left(\frac{S}{D}\right)\right) \right\}} \right) \quad (2.8)$$

The above equation only takes into account mass transfer coefficient on the feed side of the FO membrane, the mass transfer coefficient on the draw side is not accounted for. In order to improve the accuracy of the flux model, Bui et al. (Bui, Arena et al. 2015) proposed that the water flux for a flat-sheet FO membrane, taking into account ICP and ECP on both the feed and draw sides is given as:

$$J_v = A \left(\frac{\pi_{D,b} \exp\left[-J_v \left(\frac{1}{k_d} + \frac{S}{D_D}\right)\right] - \pi_{F,b} \exp\left(\frac{J_v}{k_f}\right)}{1 + \frac{B}{J_v} \left\{ \exp\left(\frac{J_v}{k_f}\right) - \exp\left(-J_v \left(\frac{1}{k_d} + \frac{S}{D_D}\right)\right) \right\}} \right) \quad (2.9)$$

where k_d and k_f are the mass transfer coefficients of the draw and feed respectively, D_D and D_F are the solute diffusion coefficients in the bulk draw and feed solution respectively.

For the purpose of the current study, cross-flow of fluid is applied only to the lumen side of the HF membranes for both AL-FS and AL-DS configurations. Hence, ECP on the lumen side is assumed to be dependent on cross-flow velocity and assumed to be constant in this context. Conversely, ECP on the shell side of the HF membranes will be significant as the HF membranes are submerged in a tank of stagnant fluid and it shall be the interest of this study. A flux model for hollow fiber membranes will be discussed in chapter three.

2.7. Different methods of mitigating CP in FO process

In this section, the different strategies of mitigation ICP and ECP are reviewed. These strategies include (1) research efforts aimed at improving the structures of FO membrane itself as well as using (2) external methods to enhance hydrodynamic conditions aimed at reducing the boundary layer.

2.7.1. Mitigating ICP by reducing membrane structural parameter

The membrane structural parameter, S , is a critical property of FO membrane and it defined in the following equation:

$$S = \frac{l \times \tau}{\varepsilon} \quad (2.10)$$

where l is the thickness of support layer, τ is the tortosity and ε is the porosity.

A large S value is not desired as it implies severe ICP. Many authors have explored various strategies to fabricate substrates of lower membrane structural parameter so as to minimize the effects of ICP in the FO process. From literature, when concentration of polymer of substrate layer is reduced, S value decreased. For instance, Tiraferri et al. (Tiraferri, Yip et al. 2011) reduced the concentration of PSf from 18% to 9% and S value decreased from 2000 μm to 389 μm while FO water flux increased from 7.5 LMH to 21 LMH. In another study, Hajighahremanzadeh et al. decreased concentration of PAN from 16% to 7%, S value decreased from 228 μm to 84 μm . These studies demonstrated that decreasing polymer concentration in substrate is an effective method for mitigating ICP (Hajighahremanzadeh, Abbaszadeh et al. 2016). Further, it is reported that the blending of hydrophilic sulphonated poly(ether ketone) (SPEK) into PSf substrate has also led to low S value of 107 μm , reducing ICP effects significantly (Han, Chung et al. 2012).

Furthermore, substrates fabricated via the electrospinning technique could result in nanofibers that have high porosity, leading to reduction in tortuosity (Song, Liu et al. 2011). There were many attempts to fabricate substrates using different polymeric materials with relatively low S values, as presented in Table 2.4. Substrates fabricated via electrospinning method generally have lower structural parameter value due to their nanofiber structures and therefore it is an effective way for mitigating the effects of ICP.

Table 2.4

TFC membranes with nanofiber substrates.

TFC/ nanofiber substrate	S (μm)	A (LMH/bar)	B (LMH)	FO performance (AL-FS)		DS [NaCl]	FS	Ref
				J_v (LMH)	J_s/J_v (g/L)			
PES	80	1.7	1.1	37.8	-	0.5 M	DI	(Song, Liu et al. 2011)
PAN/CA	311	1.8	0.58	27.6	0.14	1.5 M	DI	(Bui and McCutcheon 2013)
Nylon 6,6	190	1.66	0.54	21	0.24	1.0 M	DI	(Huang and McCutcheon 2014)
PVA	66	1.69	0.24	27.2	-	0.5 M	DI	(Puguan, Kim et al. 2014)
PVDF	193	1.28	0.25	15	0.15	0.5 M	DI	(Huang, Arena et al. 2016)
PAN	168	1.47	0.28	17.5	0.23	0.5 M	DI	(Pan, Dong et al. 2017)

In addition, several authors have reported the use of co-casting technique to fabricate thinner and more permeable substrate. These substrates have reduced structural parameter value as compared to the pristine substrate. As such, this is also another effective way of mitigating the effects of ICP, as illustrated in Table 2.5. For instance, Liu et al. demonstrated that the double-blade casting technique is effective in fabricating substrates with superior structural features (Liu and Ng 2014). In a separate study, the double-blade co-casting technique was adapted for a silica-PSf TFC membrane (Liu and Ng 2015). The resultant TFC membranes have layered configuration with reduced structural parameter. The top layer of the substrate was free of silica and was suitable for the interfacial polymerization of the selective polyamide layer.

PEI was used as the sacrificial layer for co-casting beneath a PSf layer. Structural parameter was reduced from 241 μm to 167 μm and FO water flux also improved (Xiao, Nghiem et al. 2015). In addition, it was demonstrated the co-casting technique on a SPEEK blended PSf (SPSF) substrate and the structural parameter reduced from 361 μm to 191 μm (Chen, Liu et al. 2017). The above studies showed that co-casting technique is effective in the reducing membrane structural parameters, which in turn, mitigate ICP, leading to enhanced FO water flux.

Table 2.5
Performance of TFC membranes using the co-casting technique.

Substrate	S (μm)	A (LMH/bar)	B (LMH)	FO performance				Ref
				(AL-FS)		DS [NaCl]	FS	
				J_v (LMH)	J_s/J_v (g/L)			
PSf	195	1.82	0.28	31.1	0.27	1.0 M	DI	(Liu and Ng 2014)
Silica-PSf	167	1.65	0.12	20.1	-	0.5 M	DI	(Xiao, Nghiem et al. 2015)
PEI co-casted beneath PSf	169	1.64	0.29	31.0	0.24	1.0 M	DI	(Liu and Ng 2015)
SPSF	191	2.16	0.16	22.4	-	1.0 M	DI	(Chen, Liu et al. 2017)

PEI: polyetherimide

SPSF: SPEEK blended PSf

As summarized in Table 2.6, many authors have also reported that addition of nanoparticles in the substrate layer that have resulted in lower S value, reduced ICP and increase in water flux. Hydrophilicity of the substrate is increased with the addition of the nanoparticles. The increase in hydrophilicity and hence, wettability of substrate resulted in the

increase of mass transfer area. For instance, it was reported that acid functionalized CNT incorporated into PEI substrate of TFC FO membrane enhanced porosity by 18% and led to improved FO water flux of 33.0 LMH in the AL-FS orientation using 1M NaCl draw solution (Tian, Wang et al. 2015). In another study, addition of reduced graphene oxide (rGO) modified graphitic carbon nitride, CN/rGO into PES substrate was reported (Wang, Ou et al. 2015). The TFC membrane with modified PES substrate exhibited a 20% increase in FO water flux compared to the control.

Table 2.6
Nanoparticles in substrates for improving structural parameter value

TFC membrane with nanoparticles in substrate	Substrate	S (μm)	FO performance		DS [NaCl]	FS	Ref.
			(AL-FS)				
			J_v (LMH)	J_s/J_v (g/L)			
GO	PSf	191	20	0.15	0.5 M	DI	(Park, Phuntsho et al. 2015)
Zeolite	PSf	340	21	0.52	0.5 M	DI	(Ma, Wei et al. 2013)
CNT	PEI	310	26	0.11	0.5 M	DI	(Tian, Wang et al. 2015)
CN/rGO	PES	163	41.1	0.23	2.0 M	DI	(Wang, Ou et al. 2015)
SiO ₂ /MWCNTs nano-rod	PVDF	240	22.1	0.19	1.0 M	DI	(Lee, Goh et al. 2019)
GO	PSf	130	33.8	0.20	1.0 M	DI	(Lim, Park et al. 2017)
SiO ₂	PAN	65	56.2	0.15	1.0 M	DI	(Bui and McCutcheon 2016)
SiO ₂	PEI	174	42.0	0.12	1.0 M	DI	(Tian, Wang et al. 2017)
MOF: UIO-66	PSf	351	24.5	0.18	1.0 M	DI	(Ma, Han et al. 2017)

There were many attempts to incorporate GO in the substrate layer for the mitigation of ICP. As GO is incorporated in the substrate layer of the TFC membrane, the lateral layered arrangements of the 2D nanomaterial increases, forming interconnected nanochannels. The non-oxidised hydrophobic surface of GO enabled the water molecules to permeate through at extremely fast speeds (Mi 2014). Furthermore, Gai et al. conducted molecular simulation dynamic studies using functionalized single-layer GO as a FO membrane. Results showed that

ICP was zero and FO water flux was 1.7×10^3 times that of CTA FO membranes. Indeed, graphene-based FO membrane may have great potential going forward (Gai and Gong 2014).

2.7.2. Other methods of mitigating ICP in the FO process

Various research groups have reported different strategies to increase the hydrophilicity of the substrate. Han et al. fabricated a TFC FO membrane using hydrophilic poly(etherketone) (SPEK) (Han, Chung et al. 2012). The addition of SPEK increased the hydrophilicity of substrate and led to reduced ICP effects.

Liang et al. used the bidirectional freezing process to fabricate FO membrane in which there are vertical pores within the substrate, achieving high water flux of 93.6 LMH using 2M NaCl as draw solution, DI as feed in the AL-FS configuration (Liang, Hung et al. 2017). Low structural parameter of $\sim 100 \mu\text{m}$ was reported, effectively mitigating ICP. Han et al. reported the fabrication of TFC-HF membrane with double polyamide selective layer which effectively block out salts and foulants, exhibiting excellent salt rejection properties. In the study, there was effective mitigation of both ICP and fouling of FO membranes (Han, Cheng et al. 2017).

You et al. developed a thin film inorganic (TFI) FO membrane consisting of microporous silica xerogels immobilized onto a stainless steel mesh substrate. The structural parameter value of the reported TFI membrane was $38 \mu\text{m}$, implying extremely low ICP. The advantages of the TFI membrane are robust mechanical strength and high chemical resistance (You, Tang et al. 2013).

In addition to research efforts targeted at lowering the structural parameter value of the substrate layer of the TFC membrane and the optimization of the selective polyamide layer, there are other ways to minimize CP in the FO process. The use of ultrasound has been reported to be effective in mitigating the effects of ICP. Heikkinen et al. investigated the use ultrasound in the FO process and achieved 75% increase in FO water flux, mitigating ICP (Heikkinen, Kyllönen et al. 2017). Similarly, Choi et al. demonstrated that the use of ultrasound can effectively reduce ICP in the FO process by enhancing the diffusion rate of the draw solution (Choi, Hwang et al. 2018). In addition, it was demonstrated ultrasound was effective in partially mitigating ECP and dilutive ICP in the FO concentration of fruit juices (Chanukya and Rastogi 2017). However, the limitations of using ultrasound is that firstly, FO membrane may be damaged by high frequency and secondly, it results in an increase in reverse solute flux which is undesirable for the FO process.

2.7.3. Methods of mitigating ECP in the FO process

To date, there are very few published reports that focus on mitigating ECP in the FO process. These studies mainly focus on improving the hydrodynamics conditions such as increasing cross-flow velocity, inducing vortex and using suitable feed spacers (Zhang, Cheng et al. 2014, Abid, Johnson et al. 2017) with the aim of inducing turbulence and enhancing mixing which will lead to levelling of the difference in concentration between the bulk and adjacent solution to the membrane surface. This results in the thinning of the boundary layers, therefore mitigating ECP.

Li et al. investigated the use of hair spacers in the FO process and found that it led to enhanced mixing within the concentration boundary layer (Li, Chen et al. 2016). This enhanced the mass transfer coefficient and resulted in improvement in membrane efficiency. However, these methods may not be suitable in the case of submerged FO system as cross-flow is hardly utilised. Blandin et al. investigated the effects of stirring and air scouring as strategies for mitigating ECP in submerged FO reactor and found that stirred reactor showed 30% increase in water flux vs. the unstirred tank (Blandin, Rodriguez-Roda et al. 2018). However, stirring is an energy-intensive method and might not be suitable for submerged FO process, hence the authors also investigated air scouring as an alternative and found it to be effective in mitigating ECP, resulting in an improvement in water flux.

Furthermore, it was reported that vibration of a CTA flat-sheet FO membrane was more effective than magnetic stirring in mitigating dilutive ECP in the AL-DS configuration (Yuan and Zhang 2013). However, a high vibrating frequency of 40 to 250 Hz was used in the study and this may result in relative high energy consumption. In a separate study, the use of corrugated wall channel module (CWCM) for the mitigation of ECP in a CTA flat-sheet FO membrane was demonstrated (Zhang, Shen et al. 2018). Results show that the CWCM could induce vortices and improve the hydrodynamics in the module. According to the authors, ECP and membrane fouling were reduced, resulting in an increase in water flux. To date, very few studies have addressed the problem of ECP in the FO process as ICP has always been regarded as the more significant factor in limiting the FO water flux. In addition, research on mitigation of ECP has been restricted only to flat-sheet membranes and none were reported for hollow fiber FO membranes.

It is expected that vibration of HF membranes would improve hydrodynamic conditions and turbulence, generating vortices and higher shear rates near the surface of membranes. This

would reduce the boundary layer, thus effectively mitigating concentration polarization in the FO process.

Hence, the objective of the current study is to investigate the effect of vibration of membranes as a direct and facile method for mitigating ECP in submerged FO hollow fiber membranes. In the submerged FO process, cross-flow mode is not utilised and mixing of the feed solution is not optimised. As such, ECP would be a significant factor for limiting the performance of submerged FO process (Blandin, Rodriguez-Roda et al. 2018).

2.8. Use of vibration in various submerged membrane systems

The use of vibration has been reported in many membrane processes. Armando and co-workers were among the pioneers to introduce the vibratory shear enhancement process (VSEP) commercially for flat sheet membranes (Armando, Culkin et al. 1992). Thereafter, VSEP has been widely used in as an anti-fouling strategy in RO and NF systems (Akoum, Jaffrin et al. 2004, Petala and Zouboulis 2006, Shi and Benjamin 2008, Zouboulis and Petala 2008). In these studies, shear stress were generated near the surface of membrane and was proven to be effective as anti-fouling strategy.

The concept of vibration of membranes was also utilised for submerged HF membranes mainly as an anti-fouling strategy (Genkin, Waite et al. 2006, Altaee, Al-Rawajfeh et al. 2009, Li, Law et al. 2014). One distinct advantage is that relative low vibration frequencies were used in these HF systems as compared to the VSEP system and this translates to lower energy consumption. In a study by Genkin et al., it was found that combined axial and transverse vibration of submerged HF membranes resulted in five-fold increase in critical flux at low frequency of 1.7 Hz (Genkin, Waite et al. 2006). Altaee and co-workers demonstrated a critical flux increase of $15 \text{ L m}^{-2} \text{ h}^{-1}$ to $56 \text{ L m}^{-2} \text{ h}^{-1}$ in a study where submerged HF membranes were vibrated at 8.35 Hz in a microfiltration process (Altaee, Al-Rawajfeh et al. 2009). In a study on filtration of yeast suspension, 325% improvement in critical flux was achieved at maximum degree of vibration of hollow fiber membranes (Beier, Guerra et al. 2006).

Li and Law et al. carried out a systematic study to compare the effects of transverse vs. longitudinal vibration on membrane fouling control in submerged HF system and found that transverse vibration was more effective than longitudinal vibration (Li, Law et al. 2014). Transverse periodic movement of the HF membranes resulted in separating boundary layers and stream of secondary flow pattern. Vortices are generated and it further increase the shear rate near the surface of the HF membranes. It was also demonstrated that application of low frequency transverse vibration was an effective anti-fouling strategy in submerged HF membranes (Kola, Ye et al. 2012). Transverse vibration of HF membranes was also utilised as a fouling mitigation strategy in anaerobic membrane bioreactor (Kola, Ye et al. 2014). In addition, it was demonstrated that transverse vibration was an effective strategy for fouling control in submerged membrane bioreactor (Li, Law et al. 2014, Li, Law et al. 2016). Transverse vibration of HF membranes was adopted throughout the FO experiments in the current study in view of its superiority over longitudinal vibration.

Air bubbling system is widely adopted method for mitigating fouling in MBRs (Cui, Chang et al. 2003). However, it has several limitations such as generating relatively weak shear forces on the surface of membranes; implying that only moderate flux can be used. Furthermore, it is difficult to obtain even distribution of bubbling in the MBR, implying that there may be dead zones (Cui, Chang et al. 2003). In another study, axial vibration of membrane (AVM) system and submerged aeration membranes (SAM) systems were investigated to compare the performance of filtration and control of fouling. It was found that AVM system was a more effective fouling control strategy and yielded better filtration performance (Zhao, Chu et al. 2016).

To date, there are very few studies that investigated the effect of vibration of membranes for the mitigation of CP. In one study, it was demonstrated that vibration of flat-sheet CTA FO membrane resulted in more significant water flux enhancement as compared to the using magnetic stirring. The study was carried out in the AL-DS orientation (Yuan and Zhang 2013). In two other studies, the effects of vibration of flat-sheet membranes on rejection of contaminants in the FO process were investigated (Nezami and Khanjani 2017, Nezami and Khanjani 2017).

Currently, there are no reported studies on the effect of vibration of HF membranes for mitigating concentration polarization in the submerged FO process. In consideration of the effectiveness of vibration in submerged systems as fouling mitigation strategy as well as its advantages over the air bubbling system, it is hypothesized that vibration in HF submerged system will also effectively mitigate the effects of CP in the FO process. Specifically, transverse vibration of HF membranes would improve hydrodynamic conditions, generating vortices and higher shear rates near the surface of membranes. This could reduce the boundary layer, thus effectively mitigate CP in the FO process.

CHAPTER 3

UNDERSTANDING THE EFFECT OF TRANSVERSE VIBRATION ON HF MEMBRANES FOR SUBMERGED FO PROCESSES

3.1 Introduction

Forward osmosis (FO) is an osmotically driven process that utilises the difference in osmotic pressure as a driving force to trigger spontaneous water permeation across a semi-permeable membrane (Cath, Childress et al. 2006). This process boasts several advantages, including low/no hydraulic pressure requirement and low temperature operation, in comparison with conventional pressure driven membrane processes and thermal processes (Cath, Childress et al. 2006, Chung, Luo et al. 2015). As such, the potential application of FO lies in the concentration of waste streams or valuable products (Ling and Chung 2011, Nguyen, Chen et al. 2013, Ge and Chung 2015, Ng, Wu et al. 2019), the utilization of FO-based hybrid processes for low-energy production of fresh water (Bamaga, Yokochi et al. 2011, Blandin, Verliefde et al. 2015, Wang, Goh et al. 2017), and addressing the problem of high salinity feed water (McGinnis, Hancock et al. 2013, Shaffer, Werber et al. 2015, Liden, Carlton et al. 2019, McCutcheon 2019).

One of the biggest challenges of FO is that the osmotic driving force is often significantly diminished due to the presence of concentration polarization, which includes internal concentration polarization (ICP) and external concentration polarization (ECP). The ICP is closely related to the membrane structure. Hence, the fabrication of FO membrane with a small structural parameter (i.e., thin, porous, less tortuous (connected pores) and hydrophilic substrate) is one of the most effective ways to reduce ICP (Gray, McCutcheon et al. 2006, McCutcheon and Elimelech 2006). Other methods such as the utilization of ultrasound (Heikkinen, Kyllönen et al. 2017) were also demonstrated to be effective in reducing ICP. Compared with ICP, it is relatively simpler to mitigate ECP during the operation of osmotically driven membrane processes. Several strategies have been demonstrated, such as increasing the crossflow velocity of the feed/draw streams as they flow in a direction parallel to the membrane surface (Wang, Wang et al. 2017) and adopting a spacer to improve hydrodynamic mixing near the surface of flat-sheet membranes (Li, Chen et al. 2016). Nevertheless, such strategies are not feasible for submerged FO systems where the use of cross-flow is sparse and the hollow fiber membrane configuration is more dominantly used in the membrane bioreactor (MBR)

systems (Zhang, Loong et al. 2012, Gu, Wang et al. 2013, Blandin, Rodriguez-Roda et al. 2018). A prior study on the effect of air scouring and feed tank recirculation on submerged osmotic processes (Blandin, Rodriguez-Roda et al. 2018) had demonstrated the effectiveness of air scouring in reducing ECP (Blandin, Rodriguez-Roda et al. 2018). Biogas scouring is also reportedly used to reduce fouling in submerged anaerobic osmotic membrane bioreactor (Chen, Gu et al. 2014, Gu, Chen et al. 2015). However, there are limitations associated with the bubbling system such as weak shear forces on membrane surface and uneven bubbling in the MBR (Cui, Chang et al. 2003). Thus, the mitigation of ECP remains a challenge for submerged hollow fiber FO processes. Apart from gas scouring (Achilli, Cath et al. 2009, Chen, Gu et al. 2014, Gu, Chen et al. 2015, Blandin, Rodriguez-Roda et al. 2018), vibrating submerged membranes is also effective in creating turbulence on the membrane surfaces. It had been used as a membrane fouling mitigation strategy in membrane bioreactors (Kola, Ye et al. 2014, Li, Law et al. 2014, Li, Law et al. 2016). Moreover, since prior study (Li, Law et al. 2014) demonstrated that transverse vibration is more effective than longitudinal vibration for fouling control in submerged HF system, it is hypothesized that a similar vibration approach would be effective for the mitigation of ECP in the submerged FO process.

At present, there are only a few studies that investigate the effect of membrane vibration on FO performance and these studies only utilized flat-sheet membranes (Yuan and Zhang 2013, Nezami and Khanjani 2017, Nezami and Khanjani 2017). Moreover, these are only preliminary studies with no fundamental understanding on how vibration parameters such as amplitude and frequency can affect the change in mass transfer coefficients. Also, the scope of study has yet to expand to include factors such as membrane orientation and different draw solutes, which are of research interest in the FO process.

Hence, to close the research gap, the current study aims to elucidate the effect of vibration on hollow fiber membrane performance in a submerged FO process. Specifically, the effect of vibrating frequency and amplitude, as well as the effect of vibration at different FO conditions such as membrane orientations (AL-FS and AL-DS), different draw solution concentration and the type of draw solutes are studied. In addition, the mass transfer coefficients under different conditions are analysed. Overall, this work demonstrates clearly that transverse vibration on hollow fiber membranes is an effective alternative strategy for reducing the ECP effect in submerged FO processes.

3.2 Materials and methods

3.2.1 Chemicals and materials

Polyethersulfone (PES, GafoneTM 3000P, Solvay, Belgium), N-methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck Chemicals, Singapore), polyethylene glycol 200 (PEG, CAS#25322-68-3, Merck Chemicals, Singapore) and glycerol (85%, Merck Chemicals, Singapore) were used for the fabrication of the hollow fiber (HF) substrates for thin film composite (TFC) FO membrane. 1,3,5-benzenetricarbonyl trichloride (TMC, CAS#4422-95-1, Sigma-Aldrich, USA), m-phenylenediamine (MPD, CAS#108-45-2, Sigma-Aldrich, Singapore), and cyclohexane (CAS#110-82-7, Merck Chemicals, Singapore) were used to form the selective layer of the TFC membrane. Ultrapure water obtained from a Milli-Q system (Millipore, USA) was used to prepare all water solutions. Poly (sodium-4-styrenesulfonate) (PSS, Mw = 70,000, Sigma-Aldrich) was used to prepare a 25 wt.% PSS draw solution for several FO runs. All chemicals were of analytical grade with purity over 99% and were used as received.

3.2.2 Membrane modules preparation

The substrates used in the current study were PES hollow fiber membranes. The inner and outer diameters of the membrane substrate are 900 μm and 1185 μm and the thickness is $\sim 142 \mu\text{m}$ (Ng, Chen et al. 2019). The porosity of the membrane is $\sim 77\%$ measured using gravity method (Ng, Chen et al. 2019). The substrates were fabricated by a non-solvent induced phase separation process. Briefly, polymer dopes were prepared by dissolving a certain amount of PES and PEG in NMP to give a homogenous solution by constant stirring at 60 $^{\circ}\text{C}$. The resultant polymer dopes were then degassed overnight in a vacuum desiccator and extruded through a stainless-steel spinneret via a dry jet-wet spinning technique to afford the hollow fiber membranes. The fibers were then immersed in tap water for three days to complete the solvent leaching process. The fabrication conditions for the PES substrates are provided in Table A1 (Appendix A). More details on the fabrication procedures can be found in our previous publications (Setiawan, Wang et al. 2011, Chou, Wang et al. 2013).

The fabricated hollow fiber membranes were immersed in a 50 wt% glycerol solution overnight and then air-dried for one day prior to the use as substrates for the preparation of TFC membranes. Five pieces of PES hollow fibers (23 cm in length, 900 μm in diameter with a total effective surface area of 32.5 cm^2) were potted into one module by using epoxy resin (Araldite rapid 5 minutes, Huntsman). The TFC membranes were prepared via an interfacial polymerization technique, which involved the pumping of a MPD solution (in water), followed by a TMC solution (in cyclohexane) through the lumen of the hollow fibers at controlled flow rates. A polyamide selective layer was then formed on the lumen surface of the hollow fiber membranes. The detailed procedures were described elsewhere (Wang, Shi et al. 2010). The prepared TFC membrane modules were stored in ultrapure water for one day prior to use. The FO hollow fiber membrane module is depicted in Appendix B.

3.2.3 FO experiments

A schematic of the FO setup used in this study is shown in Fig. 3.1. Different from a conventional crossflow FO setup, the membrane module with an active membrane area of 32.5 cm^2 was connected to a vibrating motor and submerged in a tank (45 cm $\times$ 9 cm $\times$ 16 cm) filled with 3 L of solution. Transverse vibration, with moving direction perpendicular to the length of the hollow fibers, was adopted throughout all experiments. The vibrating frequency and amplitude were varied from 0 to 3 Hz and 0 to 1.2 cm, respectively. Another stream of solution was pumped using a peristaltic pump (Masterflex, USA) from another tank rest on a digital balance (Mettler Toledo, Switzerland). It flowed through the lumen of the fibers (active layer side) and was re-circulated back to the tank at a cross-flow rate of ~ 40 cm/s (High cross-flow velocity was chosen to minimize ECP at the lumen side). The weight change of this tank reflects the membrane water flux. The reverse solute flux was calculated based on the conductivity measurements of feed solution. All experiments were performed at a temperature of $23 \pm 1^\circ\text{C}$. NaCl draw solution was used to conduct most of the experiments, and the PSS was adopted as draw solute when the effect of different draw solutes was studied.

Figure 3.1. A schematic of the FO setup with submerged hollow fiber membrane module connected to a vibrating motor.

3.2.4 Membrane characterization and flux modelling

The presence of ECP and ICP adjacent and within a FO membrane gives rise to concentration profiles that can be described in Fig. 3.2. In the current submerged FO system, the use of cross-flow on the lumen side (adjacent to the rejection layer) diminished the ECP effect as a result of high shear stress (i.e., enhanced mass transfer coefficient) at the membrane surface of the lumen side. In contrast, ECP at the shell side (support layer surface) is much more severe when no vibration is applied. A thicker boundary layer could be developed at the support layer surface as a result of the significantly lower mass transfer coefficient, regardless of AL-DS or AL-FS orientation. Hence, it is expected that transverse vibration could help reduce the thickness of this boundary layer.

AL-FS

AL-DS

(b)

Figure 3.2. Schematic illustrations of concentration profiles across a FO membrane cross-section: (a) dilutive ECP occurs at the shell side in AL-FS orientation; and (b) concentrative ECP occurs at the shell side in AL-DS orientation. In this study, high cross-flow velocity is applied at the membrane active layer surface (lumen) only. The highlighted boundary layer is the subject of this study with the objective of increasing the mass transfer coefficient (or decrease the thickness of this boundary layer) via transverse vibration of the FO hollow fiber membrane. C_f : concentration in bulk feed solution, C_d : concentration in bulk draw solution, C_{al} : concentration adjacent to membrane active layer, C_i : concentration at the interface of active layer and support layer, C_{sl} : concentration at support layer.

A water flux model for the FO hollow fiber membranes, taking into account the ICP in the membrane support layer and the ECP on both sides of the membrane, was developed for both AL-FS (FO mode) and AL-DS (PRO mode) orientations (Xiao, Li et al. 2012) and presented in Eq. (3.1) and (3.2) respectively:

AL-FS (FO mode):

$$J_v = \left(\frac{1}{k_f} + \frac{1}{k_m} + \frac{1}{k_d} \right)^{-1} \cdot \ln \frac{A\pi_{D,b} + B}{A\pi_{F,b} + B + J_v \exp\left(-\frac{J_v}{k_f}\right)} \quad (3.1)$$

AL-DS (PRO mode):

$$J_v = \left(\frac{1}{k_f} + \frac{1}{k_m} + \frac{1}{k_d} \right)^{-1} \cdot \ln \frac{A\pi_{D,b} + B - J_v \exp\left(\frac{J_v}{k_d}\right)}{A\pi_{F,b} + B} \quad (3.2)$$

where J_v is the FO water flux, A is the water permeability, B is salt permeability, k_f , k_m and k_d are the mass transport coefficients adjacent to the membrane surface at the feed solution side, in the porous support layer and adjacent to the membrane surface at the draw solution side, respectively, $\pi_{D,b}$ is the osmotic pressure of the bulk draw solution and $\pi_{F,b}$ is the osmotic pressure of the bulk feed solution.

The water permeability A and solute permeability B were evaluated in a RO testing mode. In the current study, the two parameters were measured at a pressure of 2 bar with ultrapure water and 500 mg/L NaCl solution as feed, respectively. A value was determined by dividing the water flux, J_v , by the transmembrane pressure, ΔP (Eq. 3.3):

$$A = \frac{J_v}{\Delta P} \quad (3.3)$$

NaCl rejection, R , was determined based on conductivity measurements of the feed and permeate solutions (Eq. 3.4). The conductivity is a linear function of the salt concentrations at a low salinity range.

$$R = 1 - \frac{C_p}{C_f} \times 100\% \quad (3.4)$$

where C_f is the salt concentration in the feed and C_p is the salt concentration in the permeate.

The salt permeability, B , was calculated according to Eq. (3.5):

$$B = \left(\frac{1}{R} - 1\right) \cdot J_v \quad (3.5)$$

The mass transfer coefficient at lumen side, k_{lumen} (i.e., k_f in the AL-FS or k_d in the AL-DS) was calculated as follows (Eqs. 3.6 – 3.10) (Wang, Li et al. 2017):

$$\text{Reynolds number: } Re = \rho u d_h / \eta \quad (3.6)$$

$$\text{Sherwood number: } Sh = k d_h / D \quad (3.7)$$

$$\text{Schmidt number: } Sc = \nu / D \quad (3.8)$$

$$\text{Characteristic linear dimension: } d_h = \frac{4 \times \text{volume of flow channel}}{2 \times \text{wetted surface}} \quad (3.9)$$

$$Sh = 1.62 \left(Re Sc \frac{d_h}{L} \right)^{\frac{1}{3}} \quad (3.10)$$

where ρ is the density of the fluid, u is the velocity of the fluid, η is the dynamic viscosity of the fluid, ν is the kinetic viscosity of the fluid, D is the diffusion coefficient, and L is the length of membrane fiber that water can permeate through.

k_m is correlated with the membrane structural parameter (S) using the following Eq. (3.11):

$$k_m = \frac{D_m}{S} \quad (3.11)$$

where D_m is the diffusion coefficient in the membrane support layer. The S value of the membrane could be determined from the FO experiments with crossflows at both shell and lumen sides (Appendix C).

In the submerged system, the mass transfer coefficient at shell side, k_{shell} (i.e., k_d in the AL-FS or k_f in the AL-DS) was determined using Eqs. 3.1–3.2 after other parameters were obtained and substituted into the equations.

3.3. Results and discussion

3.3.1 Characteristics of the FO membrane

The intrinsic properties of the FO hollow fiber membrane are summarized in Table 3.1. The water permeability (A) and NaCl permeability (B) of the membrane are ~ 4.0 L/m²h/bar and ~ 0.2 L/m²h, respectively, resulting in a low B/A value of 5 kPa. As such, we expect a low reverse solute flux in the FO process with the use of this membrane ($J_s/J_v = B/A(\beta R_g T)$ (Tang, She et al. 2010)). The S value was calculated to be about 290 ± 56 μm by averaging from both orientations (Appendix C), which is in good agreement with porous substrate with interconnected pores (note that the membrane has a thickness of 142 μm and porosity of 77% (Ng, Chen et al. 2019)). This low S value implies a relatively less ICP effect during the FO process.

Table 3.1. Intrinsic properties of the FO hollow fiber membrane^a.

Water permeability, A (L/m ² h/bar) ^b	NaCl rejection, R (%) ^c	NaCl permeability, B (L/m ² h) ^c	B/A (kPa)	Structural parameter, S (μm) ^d
4.00 ± 0.33	96.7%	0.217 ± 0.045	5.4	290 ± 56

Notes:

^a Experimental errors are reported as a standard deviation of 3 independent measurements.

^b Evaluated in the RO testing mode over an applied pressure of 2 bar with DI as feed water.

^c Evaluated in the RO testing mode at 2 bar with 500 ppm NaCl as feed.

^d The structural parameter was calculated using Eq. (3.1-3.2). It is the average result considering both AL-FS and AL-DS orientations (Appendix C).

3.3.2 Modelling of mass transfer coefficient at the shell side on the FO water flux

By using Eq. 3.1–3.2, a relationship can be established between FO water flux and k_{shell} (mass transfer coefficient at the shell side) at different NaCl draw solution (DS) concentrations in both AL-FS and AL-DS orientations. NaCl solutions of concentration 0.2–1.5 M were used as DS, while ultrapure water was used as FS. Other assumptions were made in our calculations: (1) the FO membrane has constant intrinsic properties of $A = 4 \text{ L/m}^2\text{h/bar}$, $B = 0.19 \text{ L/m}^2\text{h}$, and $S = 290 \text{ }\mu\text{m}$, and (2) k_m and k_{lumen} are constant (crossflow velocity of $\sim 40 \text{ cm/s}$ at the lumen side) when the k_{shell} is increased. The effect of increasing k_{shell} on the FO water flux is presented in Fig. 3.3. It can be seen that the water flux is increased when k_{shell} increases from $0.5 \times 10^{-5} \text{ m/s}$ to $3.5 \times 10^{-5} \text{ m/s}$ in both the AL-FS (Fig. 3.3a) and AL-DS (Fig. 3.3b) orientations. In both orientations, increasing k_{shell} leads to a greater increase in water flux at higher DS concentrations (i.e., higher water flux level), which could be explained by a more severe ECP at a higher water flux, hence, the increased mass transfer coefficient leads to a greater decrease in ECP.

In the AL-FS orientation (Fig. 3.3a), the rate of flux increase with k_{shell} is greater at a relatively low mass transfer coefficient range. For example, at the condition of 1.5 M NaCl DS, increasing k_{shell} from 0.5×10^{-5} to $1.0 \times 10^{-5} \text{ m/s}$ results in a flux increase from $23.6 \text{ L/m}^2\text{h}$ to $29.2 \text{ L/m}^2\text{h}$, but the change of k_{shell} from 3.0×10^{-5} to $3.5 \times 10^{-5} \text{ m/s}$ only gives rise to a $0.6 \text{ L/m}^2\text{h}$ flux increment (i.e., from $35.2 \text{ L/m}^2\text{h}$ to $35.8 \text{ L/m}^2\text{h}$). The rate of flux increase (dJ_v/dk_{shell}) can also be clearly observed in Fig. 3.3c. The highest rate corresponds to the lowest k_{shell} , and it decreases drastically with increasing k_{shell} .

The same trend can be also observed for the AL-DS orientation (Fig. 3.3b-c); and it is obvious that the increased rate at the low k_{shell} range is much larger in the AL-DS orientation as compared with that in the AL-FS orientation for DS concentration greater than 0.2 M. At the condition of 1.5 M DS in the AL-DS orientation, the flux increase is about $9.5 \text{ L/m}^2\text{h}$ when the k_{shell} is increased from 0.5×10^{-5} to $0.75 \times 10^{-5} \text{ m/s}$. Interestingly, such a great enhancement can be achieved even when the water flux is already very high at $\sim 60 \text{ L/m}^2\text{h}$, indicating that increasing mass transfer coefficient is an effective strategy to address conditions where ECP is severe. As the rate of flux increase quickly diminishes with the increasing k_{shell} , further increasing the k_{shell} beyond a certain range (e.g., $> 2.0 \times 10^{-5} \text{ m/s}$) does not contribute much to the flux enhancement.

Figure 3.3. Estimated FO water flux in the AL-FS (a) and AL-DS (b) orientations by varying the mass transfer coefficient at the shell side of the membrane; and (c) flux increase rate (dJ_v/dk_{shell}) increase in J_v per step increase in k_{shell} . NaCl solutions of concentration 0.2–1.5 M were used as draw solutions. Ultrapure water was used as the feed solution. Membrane intrinsic properties are $A = 4$ L/m²h/bar, $B = 0.19$ L/m²h, and $S = 290$ μ m. The mass transfer coefficient (k_{lumen}) at the lumen side is 2.69×10^{-5} m/s. Both k_{lumen} and k_m are assumed constant when the mass transfer coefficient at shell side (k_{shell}) is increased.

It is worth noting that the flux increment as a result of increased k_{shell} is minimal at 0.2 M NaCl DS in the AL-DS orientation, although the water flux (25.3 L/m²h) is more than doubled of that in the AL-FS orientation at $k_{shell} = 0.5 \times 10^{-5}$ m/s. The greatest flux increment is merely 0.7 L/m²h when k_{shell} is increased from 0.5×10^{-5} to 0.75×10^{-5} m/s (Fig. 3.3c). The flux is increased to only 26.7 L/m²h (~5% overall increment) even if the k_{shell} is increased to 2.0×10^{-5} m/s. It is probably due to the less severe concentrative ECP in the AL-DS orientation, as compared with the dilutive ECP at the membrane shell side in the AL-FS. Similar

explanation has been reported for ICP where the dilutive ICP in the AL-FS orientation is more severe than the concentrative ICP in the AL-DS, leading to a much lower water flux in the AL-FS orientation (Gray, McCutcheon et al. 2006, Tang, She et al. 2010, Wang, Wicaksana et al. 2010). In this case, the FS is ultrapure water and the reversed salt flux is minimal (as shown by the small B/A), resulting in a negligible concentrative ECP effect in the AL-DS configuration at a relatively low water flux. In contrast, the dilutive ECP effect still plays a role in spite of the relatively low DS concentration in the AL-FS orientation. Hence, increasing k_{shell} to 2.0×10^{-5} m/s helps increase water flux from 11.1 to 14.3 L/m²h, corresponding to a significant 28.8% increment.

3.3.3 Effect of vibrating frequency and amplitude

With an understanding of the optimal mass transfer coefficient required to maximize ECP reduction, the effects of varying vibrating amplitude and frequency on FO performance are evaluated and shown in Fig. 3.4 and Fig. 3.5, respectively. The FO membrane was oriented in the AL-FS configuration and the shell side was facing the 1 M NaCl DS, so that the vibration would mainly have an effect on reducing the dilutive ECP. In Fig. 3.4a, it is observed that increasing amplitude (from 0 to 1.2 cm with 0.4 cm as one step increase) while maintaining a constant frequency at 3 Hz could lead to an increase in water flux. The most significant flux increase (from 25.6 L/m²h to 28.2 L/m²h) occurs when the amplitude is increased from 0 cm (no vibration) to 0.4 cm. Further increase in the amplitude helps to increase the flux but at a much slower rate (i.e., ~ 1 L/m²h increment per step increase in amplitude). Interestingly, the corresponding mass transfer coefficient at shell side, k_{shell} increased at a greater rate than that of water flux, and the rate of increase did not decrease too much with the increasing amplitude (Fig. 3.4b). The mass transfer coefficient was 0.9 , 1.3 , 1.5 , and 1.9×10^{-5} m/s at vibrating amplitude of 0, 0.4, 0.8 and 1.2 cm, respectively. It is noteworthy to mention here that the mass transfer coefficient obtained at the highest vibrating amplitude is close to the optimized mass transfer coefficient of 2.0×10^{-5} m/s, as exemplified by the modelling in Section 3.3.2. Increasing vibrating amplitude has obvious effect in increasing k_{shell} . The k_{shell} of $\sim 1.9 \times 10^{-5}$ m/s at the highest amplitude corresponds to an effect that can be brought by a ~ 12 cm/s crossflow velocity at the lumen side for this hollow fibre membrane. Since it was already shown in

previous calculations that water flux increase is negligible beyond k_{shell} of 2×10^{-5} m/s (Fig. 3.3a), the current intensity of vibration is effective enough for mitigating ECP and further increase in amplitude is unnecessary.

Figure 3.4. Effect of vibration amplitude on the FO performance (a) and mass transfer coefficient at the shell side of the membrane (b) in the AL-FS orientation at frequency of 3 Hz. The draw solution concentration used was 1.0 M.

(a)

(b)

Figure 3.5. Effect of vibration frequency on the FO performance (a) and mass transfer coefficient at the shell side of the membrane (b) in the AL-FS orientation at amplitude of 1.2 cm. The draw solution concentration used was 1.0 M.

Next, the effect of vibrating frequency was studied by varying it from 0 to 3 Hz, while keeping the amplitude at 1.2 cm. As shown in Fig. 3.5, an increased frequency results in a higher water flux. Initially, the water flux was 25.6 L/m²h without vibration. By applying a relatively low vibrating frequency of 1 Hz, the water flux increased to 28.9 L/m²h, corresponding to a 13% flux increase, and a 65% increase in mass transfer coefficient. Further increase in frequency can continue to bring about a ~15% increase in k_{shell} per Hz increment, but not much improvement in water flux is obtainable. This observation is similar to the effect of increasing vibrating amplitude where the initial increase in the frequency/amplitude (i.e., from no vibration to the lowest intensity of vibration) results in the greatest enhancement in mass transfer coefficient and water flux; and a further increase in frequency/amplitude could still result in a small degree of increase in k_{shell} , but an insignificant improvement for the water flux. This observation is consistent with the modelling of water flux- k_{shell} relationship as shown in Fig. 3.3.

Besides the performance of water flux, the reverse solute flux (RSF, J_s) is also an important parameter for the FO process. A low RSF is desirable as there is less necessity to replenish the draw solute and lower impact on the quality of the concentrated feed. It is noticed that the specific solute flux J_s/J_v was almost constant (~0.14 g/L in Fig. 4-5) under all testing conditions, ranging from 0 to 1.2 cm vibrating amplitude and 0 to 3 Hz frequency, indicating that the integrity of membrane was well-maintained during the vibration processes. The J_s/J_v value is ideally constant because both J_v and J_s are related to the concentration gradient across the membrane, and increasing the mass transfer coefficient or reducing boundary layer increases both J_v and J_s simultaneously.

3.3.4 Effects of vibration for different orientations and DS concentrations

To understand the vibration effect on FO water flux performance in different membrane orientations (AL-DS and AL-FS) and at different DS concentrations (0.5 M ~ 1.5 M NaCl), a vibrating amplitude of 1.2 cm and a frequency of 3 Hz were adopted for all the conditions. The water flux performance under the conditions of no vibration and with vibration is shown in Fig. 3.6. In AL-FS orientation (Fig. 3.6a), 0.5 M, 1.0 M and 1.5 M NaCl DS generated FO water fluxes of 17.7, 25.6 and 28.7 L/m²h at the condition of no vibration; the corresponding fluxes were increased to 21.8, 30.4 and 34.4 L/m²h when transverse vibration was applied to the membrane module. The flux improvement was similar (i.e., 21% ± 2%) for the three DS concentrations evaluated. In contrast, in the AL-DS orientation, the flux increment as a result of vibration increases significantly with increasing DS concentration. Much higher water fluxes of 42.8, 54.8, 61.5 L/m²h were achieved even if no vibration was applied, mainly due to the absence of dilutive ICP in this orientation. When vibration was administered, the flux was increased by 4.7 L/m²h (corresponding to 11% improvement) at 0.5 M NaCl DS while that was increased by 14.9 L/m²h (corresponding to a 24% improvement) at 1.5 M NaCl DS. In fact, regardless of membrane orientation and DS concentration, the mass transfer coefficient k_{shell} (k_d in the AL-FS or k_f in the AL-DS) was determined to be $0.7 \times 10^{-5} \pm 0.1 \times 10^{-5}$ m/s at no vibration and $1.8 \times 10^{-5} \pm 0.2 \times 10^{-5}$ m/s with the vibration (see Fig. 3.6c), implying that the mass transfer coefficient is mainly governed by the hydrodynamic conditions that are closely related to the vibration intensity in our case (other factors such as fluid viscosity is almost constant under these testing conditions).

Although similar increase in k_{shell} was achieved at the same vibration intensity for different membrane orientations and DS concentrations, the extent of water flux increase was different for these conditions, which is affected by the significance of ECP. The remarkable flux enhancement in the AL-DS orientation at a relatively higher DS concentration was attributed to the reduction in the more severe concentrative ECP as a result of the enhanced k_{shell} driven by the transverse vibration at the shell side. Besides the severe ECP arising from high water flux, dilutive ECP in the AL-FS orientation was also mitigated from the enhanced k_{shell} , where more than 20% water flux increase could be achieved regardless of DS concentration/ water flux level. In contrast, the flux improvement at low DS concentration in the AL-DS was minimal, due to the absence of severe ECP under this condition. The results

suggest that a reasonably high mass transfer coefficient is essential for reducing severe ECP (e.g., the dilutive ECP as well as the ECP arising from the elevated water flux), and the current transverse vibration intensity could achieve such a purpose.

Fig. 3.6. Effect of vibration on FO water flux in the AL-FS (a) and AL-DS (b) orientation using 0.5–1.5 M NaCl draw solutions; and water flux (with and without vibration) as a function of k_{shell} (c). k_{shell} was calculated using Eqs 3.1-3.2. The vibration frequency and amplitude used were 3 Hz and 1.2 cm, respectively.

3.3.5 Effects of vibration for different draw solutes

To understand the vibration effect for different draw solutes, apart from NaCl, PSS with molecular weight of 70,000 Da was chosen to make a draw solution comprising 25 wt.% PSS. This DS had an osmotic pressure of ~ 25 bar (Qi, Li et al. 2015), which is equivalent to that of a ~ 0.5 M NaCl solution. The same vibration frequency of 3 Hz and amplitude of 1.2 cm were applied for this DS. As shown in Fig. 3.7, the FO water flux at no vibration was 12.5 and 25.0 L/m²h in the AL-FS and AL-DS orientation, respectively. These fluxes were much lower than that obtained using 0.5 M NaCl DS (Fig. 3.6), due to the severe concentration polarization (including both ICP and ECP) resulted from the low mass transfer coefficients (lower diffusivity and the higher viscosity of the PSS solution).

The increased water flux due to the use of vibration is 2.2 L/m²h and 2.6 L/m²h in the AL-FS and AL-DS, respectively, corresponding to a 17% and 11% increase (Fig. 3.7). Although the water flux increase in absolute value are not attractive for the FO process, the percentage of increase are in the same range as that achieved by NaCl DS. Again, at this low water flux, it is observed that the flux increment (%) is less in AL-DS than in AL-FS. Therefore, the PSS DS does not gain more benefits from the vibration than NaCl DS, although more severe ECP is present for the case of PSS DS. While vibration could bring about better hydrodynamic conditions, similar to the effect of increasing cross-flow velocity, the relatively low diffusivity and high viscosity (Qi, Li et al. 2016) which are inherent properties of the PSS solution could not be altered by the improved hydrodynamic conditions, thus there was no significant improvement in water flux as compared to using NaCl DS.

Figure 3.7. Effect of vibration on FO water flux using 25 wt.% PSS solution as draw solution. The vibration frequency and amplitude used were 3 Hz and 1.2 cm, respectively.

3.4. Conclusions

This study demonstrates that transverse vibration on submerged hollow fiber membranes could help improve FO water flux through mitigating the ECP at the shell side of hollow fiber membrane. Increasing the vibrating frequency and amplitude could increase the vibration intensity. The highest intensity achieved at 3 Hz and 1.2 cm in this study could result in an increase in mass transfer coefficient from $\sim 0.7 \times 10^{-5}$ m/s to $\sim 1.8 \times 10^{-5}$ m/s, approaching the optimized mass transfer coefficient. Specific reverse solute flux was maintained at ~ 0.14 g/L throughout the vibration experiments, suggesting that integrity of membrane was preserved during the vibration.

The trends observed from the experimental results are consistent with the modelling of water fluxes. The effect of vibration/enhancing mass transfer coefficient was more significant when the existing ECP was severe, such as in the AL-FS orientation where dilutive ECP is present and in the condition of high water flux (especially in the AL-DS orientation at high DS concentration). Although severe concentration polarization resulted from the low diffusivity and high viscosity of PSS draw solutes, additional benefits could not be derived from vibration or improved hydrodynamic mixing. Herein, a facile method for mitigation of ECP in submerged FO process is demonstrated.

CHAPTER 4

RECOMMENDATIONS FOR FUTURE WORK

Since the current study demonstrated that vibration system can indeed enhance the hydrodynamic conditions near the membrane surface, leading to enhanced mass transport coefficient and water flux, the following recommendations are made for future research:

- Investigate the effects of the vibration system to various submerged osmotic applications such as osmotic membrane bioreactor to determine whether FO efficiency can be improved.
- Since prior studies demonstrated that there was improved anti-fouling effects from vibration of membranes in RO systems, a study can be done to investigate the anti-fouling effects due to the vibration of HF membranes in submerged FO processes. Effects of both transverse and longitudinal vibrations on fouling control could be studied.
- Future studies could compare energy/savings of the current strategy to other existing strategies of mitigating ECP in submerged osmotic processes such as cross-flow system or bubbling system.
- The vibration-assisted FO process could be performed with other types of draw solutions such as organic ionic salts, hydrogels and nanoparticles to investigate the effectiveness of the vibration system when other types draw solutes are used.
- Since results show that the most significant dJ_v/dk_{shell} is achieved for AL-DS orientation at high water flux level, further studies can be done to investigate whether the vibration system can improve the performance of PRO processes.
- In the current study, relatively low vibrational frequency and amplitude were employed. Future studies could be done to investigate the effect of the vibration on the integrity and durability of the HF membranes compared to FO processes with no vibration applied. The scope of study could aim to investigate how the integrity of membrane is affected under different vibrational conditions (frequency and amplitude).

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Appendices

Appendix A

Fabrication conditions for PES HF substrates

The fabrication conditions of PES HF substrate are listed in Table A1. The inner and outer diameters of the membrane substrate are 900 μm and 1185 μm and the thickness is $\sim 142 \mu\text{m}$ (Ng, Chen et al. 2019). The porosity of the membrane is $\sim 77\%$ measured using gravity method (Ng, Chen et al. 2019).

Table A1. Fabrication conditions for PES hollow fiber substrate.

Fabrication conditions	
Bore fluid composition	ultrapure water
Flow rate (mL/min)	10
Dope composition (wt%)	PES/NMP/PEG (20/40/40%)
Dope flow rate (mL/min)	6.7
Take up speed (m/s)	0.27
Air gap (cm)	5
Room temperature ($^{\circ}\text{C}$)	23 ± 1
Coagulation bath composition	Tap water
Coagulation bath temperature ($^{\circ}\text{C}$)	22 ± 1
Relative humidity (%)	75

Appendix B

Membrane module design

As illustrated in Fig. B1, the FO hollow fiber membrane module consisted of five pieces of PES-HF membranes in a parallel arrangement. The fibers are of 23 cm in length, 900 μm in diameter, and have a total effective surface area of 32.5 cm^2 . The hollow fiber membranes were held in place by epoxy resin (Araldite rapid 5 minutes, Huntsman) at both ends. The module also consisted of acrylic plates support held together by screws at both ends. The module was submerged transversely into a rectangular tank. There was no housing for the module in the current study so that the hollow fiber membranes can experience maximum shear force in the draw/feed solution upon vibration. In this way, the effects of vibration on mitigation of ECP (at membrane shell side) can be studied.

Fig. B1. Photo of hollow fibre FO membrane module used for vibration study.

Appendix C

Membrane structural parameter (*S* value) determination

0.5 M NaCl draw solution and ultrapure water were used as feed solutions. Crossflow velocity at shell and lumen side was 0.23 cm/s and 0.8 cm/s, respectively. Water flux obtained was ~50.4 LMH in the AL-DS orientation, and 20.3 ± 1.8 LMH in the AL-FS orientation. The *A* value of the membrane is 3.9 ± 0.3 LMH/bar and the *B* value was 0.19 ± 0.02 LMH. By using Eqs. 3.1–3.2, the *S* value was calculated as ~330 μm and ~250 μm in the AL-DS and AL-FS, respectively. The average *S* value was, thus, about 290 μm .

Appendix D

Effect of increasing k_{shell} at similar water flux level in different orientations

A comparison of estimated FO water flux with increasing k_{shell} in AL-FS and AL-DS orientations is shown in Fig. D. At $k_{shell} = 0.5 \times 10^{-5}$ m/s, similar water flux is obtained at 0.2 M NaCl DS in AL-DS and at 1.5 M NaCl DS in AL-FS orientation. It is clear that increasing k_{shell} leads to more significant flux increase in the AL-FS orientation, which can be explained by the decrease of the more severe dilutive ECP in the AL-FS orientation. In addition, even if the water flux at 0.5 M in AL-DS is higher than that at 3.0 M in AL-FS orientation, the latter still gains more flux increase from the increased k_{shell} . Hence, increasing k_{shell} would be more beneficial to the AL-FS orientation than AL-DS orientation at similar water flux level.

Fig. D. Effect of increasing mass transfer coefficient k_{shell} on FO water flux in AL-FS and AL-DS orientations. The comparison of the two orientations is made on the similar water flux level.

Appendix E

Calculation of water flux and reverse solute flux

Water flux, J_v , was calculated by weight change of the feed solution:

$$J_v = \frac{\Delta V_{feed}}{A_m \times \Delta t} = \frac{\Delta m_{feed} / \rho_{feed}}{A_m \times \Delta t}$$

where ΔV_{feed} is the change of volume of feed solution, Δm_{feed} is the change in weight of feed solution, ρ_{feed} is the density of feed solution, Δt is the time interval and A_m is the surface area of membrane.

Reverse solute flux, J_s , was calculated based on conductivity measurement:

$$J_s = \frac{V_t \times c_t - V_0 \times c_0}{A_m \times \Delta t}$$

where V_0 and V_t are the initial and final volumes of the feed solution, c_0 and c_t are the initial and final salt concentration of the salt solution, calculated based on conductivity measurements.