

Comparative Performance of Nanofiltration and Forward Osmosis Membranes in a Lab-Scale Forward Osmosis Membrane Bioreactor

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Abstract

Nanofiltration (NF) and commercial HTI Forward Osmosis (FO) membranes were tested in a live membrane bioreactor (MBR) for performance comparison. Inorganic draws (NaCl, Na₃PO₄), surfactants (TEAB, SDS), and polyelectrolytes (PDAC, PGBE) were all tested as draw solutes; water flux, reverse solute transport (RST), toxicity and viscosity were observed and compared for each. Synthetic municipal wastewater was selected as a feed and *Bacillus subtilis* species was inoculated in the solution and grown overnight for development of a monoculture bioreactor. Deionized (DI) water was also used as a feed for control. The results indicate that the NF membrane shows good promise in the FOMBR process when used with high molecular weight draw solutions. In comparison to the FO membrane, it shows a significantly higher water flux with only a slightly higher RST. The NF membrane is recommended for further investigation in the FOMBR, provided fouling control is in place. Although the observed reverse solute transport values were not toxic to the bacteria under observation, long-term accumulation of draw solute in the bioreactor of an FOMBR wastewater treatment plant is an issue which requires further investigation.

Key words: FOMBR, waste water recycle, draw solution, water flux, toxicity, viscosity.

1 Introduction

Forward osmosis (FO) is the transport of water across a selectively permeable membrane from a solution of higher water chemical potential, having low osmotic pressure, to a solution of lower water chemical potential, having higher osmotic pressure. It results in concentration of the feed stream (FS) and dilution of the draw stream (DS) (Achilli et al., 2009). The FO process is considered by many to show lower fouling potential when compared to conventional, pressure driven membrane filtration processes, such as nanofiltration (NF) and reverse osmosis (RO) (Lutchmiah et al., 2014; Zhao et al., 2012), although a consensus on this point has yet to be reached. Extensive research has been carried out in the field of FO in recent years while its application to wastewater treatment still remains in its infancy (Lutchmiah et al., 2014).

Selection of an FO membrane with a suitable configuration is important for its application. Commercial FO membranes are asymmetric in nature, comprising of a highly porous support layer (SL) and a selective active layer (AL) (Alsvik & Hagg, 2013). Currently, the most widely used commercial FO membrane is a flat sheet FO membrane made up of cellulose triacetate (CTA) coated on a polyester mesh and sourced from Hydration Technology Innovations (HTI). Since the forward osmosis system relies on the chemical potential difference to drive water molecules across the membrane, and therefore does not require a hydraulic pressure gradient, membrane strength is not as important an issue as it is for RO, NF and ultrafiltration (UF). Therefore, work on the development of single layer FO membranes without a separate SL has been ongoing (Gai & Zhang, 2015).

In an FO membrane bioreactor (MBR), a semipermeable membrane is placed in an activated sludge bioreactor that is continuously aerated to supply oxygen for the microbial growth. An osmotic pressure difference results in the permeation of water from the feed solution in the reactor tank to the draw solution. The diluted draw is then regenerated separately, using processes such as membrane distillation and RO (Achilli et al., 2009).

Both submerged and external configuration membranes can be set in place for the FO-MBR. The process offers several advantages when compared to other membrane technologies for waste water treatment, such as much higher solute rejection (by using an RO-type membrane versus a microporous membrane) at a lower applied hydraulic pressure, more reversible fouling as compared to pressure-driven systems, and less frequent backwashing required (Khan et al, 2016). These factors all reduce energy consumption. It is also possible to perform osmotic backwashing in AL-FS mode, in which clean water flows osmotically from the support side of the membrane to the active side, thereby reversing the direction of flow through the FO membrane and potentially removing foulants on the active layer surface.

One major technical limitation of the FO-MBR is the salinity build-up occurring in the submerged OMBR tank; this is due to retention behind the membrane of salts from the wastewater feed, as well as reverse solute transport from the draw solution. This build-up affects the biodegradation efficiency, due to the finite salinity tolerance of the organisms present in the reactor tank. Optimising draw solutions, the careful selection of membranes, and operation at lower sludge retention times are all recommended to improve the performance of the FO-MBR (Wang et al., 2016). Although a continuous removal of sludge can reduce the salinity build-up in the feed, extended and independent operation of the FO-MBR can still face operational issues including fouling, power cost, and so on (Blandin et al, 2018).

A number of studies showing the removal efficiency of FO-MBRs are presented in Table 1, while operational data on FOMBRs is given in more detail in Table 2. It can be observed from Table 1 that greater removal efficiencies are achieved with FO-MBRs than with MBRs.

Table 1: A Summary of the Removal Efficiencies of FO-MBRs for Organic Compounds, Nitrogen and Phosphorus. (Wang et al., 2016).

Type	Wastewater	Removal efficiency					References
		TOC	COD	NH ₄ ⁺ -N	TN	TP	
Submerged FOMBR	Synthetic sewage	>90%	–	–	–	–	Wang et al., 2014
Submerged FOMBR	Synthetic sewage	99.8%	–	97.7%	–	–	Achilli et al., 2009
Submerged AnFOMBR*	Synthetic sewage	–	96.7%	–	–	100%	Chen et al., 2014
Submerged AnFOMBR	Synthetic sewage	–	95%	–	–	100%	Gu et al., 2015
Submerged FOMBR	Synthetic sewage	98%	–	80–90%	–	>99%	Qiu & Ting., 2014
Submerged FOMBR	Synthetic sewage	>99%	–	–	–	–	Lay et al., 2011
Submerged FOMBR	Synthetic sewage	98%	–	98%	–	–	Qiu & Ting, 2013
Submerged MFFO-MBR**	Synthetic sewage	>99%	–	>98%	–	–	Wang et al., 2014
Submerged FOMBR	Real sewage	–	>96%	–	>82%	>99%	Holloway et al., 2014
MBR	High strength landfill leachate	-	70%	96%	95%	-	El-Fadel & Hashisho, 2014

* Anaerobic FO-MBR, ** Hybrid Microfiltration FO-MBR

Table 2: Summary of Operational Data for Forward Osmosis Membrane Bioreactors (FO-MBRs) in the Literature (Wang et al., 2016).

Configuration	Membrane	Producer	Type	Orientation	Draw solution	Temperature (°C)	Sludge Concentration (g/L)	SRT (d)	Operating time	Stable salinity	Initial flux (LMH)	Steady flux (LMH)	References
Submerged	CTA-FO	HTI	FS	AL-FS	1 M NaCl	25±0.5	1.02±0.10	10	32 d	50 mS/cm	7.36	2.45	Wang et al., 2014
Submerged	CTA-FO	HTI	FS	AL-FS	1 M NaCl	25±0.5	1.06±0.12	15	39 d	65 mS/cm	8.62	1.82	
Submerged	TFC-FO	Made in NTU	HF	AL-DS	0.5 M NaCl	23	–	10	55 d	6–7 g/L	23	3.9±0.5	Zhang et al., 2012
Side-stream	CTA-FO	HTI	FS	AL-FS	0.5 M NaCl	20±2	10	–	7–8 h	–	5.8	5.1	Cornelissen et al., 2008
Side-stream	CTA-FO	HTI	FS	AL-DS	0.5 M NaCl	20±2	10	–	7–8 h	–	7.1	6.2	
Submerged	CTA-FO	HTI	FS	AL-FS	50 g/L NaCl	23±1	5.5	15	28 d	4 g/L	11	9	Achilli et al., 2009
Submerged anaerobic	CTA-FO	HTI	FS	AL-FS	0.5 M NaCl	25	3.9–4.6	90	155 d	20.5 mS/cm	9.5	3.5	Chen et al., 2014
Submerged anaerobic	CTA-FO	HTI	FS	AL-FS	0.5 M NaCl	35	–	90	120 d	20 mS/cm	10	3.0	Gu et al., 2015
Submerged	CTA-FO	HTI	FS	AL-FS	48.4 g/L MgCl ₂ /49 g/L NaCl	23.2±0.5	7	50	63 /40 d	15.1/33 mS/cm	7.8	6.46/5.62	Qiu & Ting, 2014
Submerged	CTA-FO	HTI	FS	AL-FS	0.5 M NaCl	20–22	–	20	73 d	7.2–8.1 g/L	3.2	2.7	Lay et al., 2011
Side-stream	CTA-FO	HTI	FS	AL-FS	0.5 M NaCl	20±2	5	–	14 d	–	5.5	About 8.0	Cornelissen et al., 2011
Side-stream	CTA-FO	HTI	FS	AL-DS	0.5 M NaCl	20±2	5	–	7 d	–	7.5	About 10	
Side-stream	CTA-FO	HTI	FS	AL-FS	0.5 M NaCl	32±2	4.953	–	150 h	–	7.2	7.2	Qin et al., 2010
Submerged	CTA-FO	HTI	FS	AL-FS	48.4 g/L MgCl ₂	23±0.5	7	50	80 d	14–16 mS/cm	7.8	5.45	Qiu & Ting, 2013

Submerged MFO-MBR	CTA-FO	HTI	FS	AL-FS	1 M NaCl	23±0.5	–	10	45 d	5 mS/cm	10.5	5.5	Wang et al., 2014
Submerged	CTA-FO	HTI	FS	AL-FS	32 g/L NaCl	25	–	70	124 d	20 g/L	4.2	0.5	Holloway et al., 2014
Submerged UFO-MBR	CTA-FO	HTI	FS	AL-FS	36 g/L NaCl	25	1.6–3.6	30/60	125 d	<5 g/L	6	4.8	
Side-stream	CTA-FO	HTI	FS	AL-DS	1.5 M NaCl	22.5±0.1	3.4–3.7	–	7 d	4.13 g/L	12	3	Alturki et al., 2012
Submerged	TFC-FO	Made in NTU	HF	AL-DS	0.5 M NaCl	20–22	–	10	–	Around 15 mS/cm	23	3.8±0.3	Lay et al., 2012

The literature presents many studies on the HTI manufactured Cellulose Tri-Acetate (TCA) FO membranes using many different draw solutes. A relatively high flux of 9.6 LMH was achieved using NaCl at a concentration of 0.6M (Achilli et al., 2010). The same study showed a flux of 8.4 LMH for MgCl_2 at a concentration of 0.36M and 7.3LMH for NH_4HCO_3 at a concentration of 0.67M. Below, it is shown that similar values of flux were obtained in our study for NaCl (6.16LMH) and Na_3PO_4 (5.8LMH) at a draw solution concentration of 0.5M. However, the fluxes obtained for polyelectrolytes with the CTA FO membrane have proven to be quite variable. Indeed, some polymers have shown very high fluxes. PAA-Na (1200) gave a flux of 22 LMH at 0.72g/ml with a hollow fibre cellulose acetate membrane (Get et al., 2012). Moderate fluxes were obtained with polyglycol copolymer, 30-70% solution, which gave a flux of 4 LMH with the HTI CTA FO membrane when 3.5% NaCl was used as a feed solution (Carmigani et al., 2012). Note that similar values for concentration weight percentages to those reported in the literature for polymers as draw solutes were not used in the current study because of the challenges presented by the highly viscous solutions obtained.

Previous studies have investigated the effect of higher molecular weight for draw solutes. In a study (Zhao et al., 2015) investigating polyacrylamide (PAM, $M_w \sim 300,000$) as draw solute for treating dye wastewater (Reactive Brilliant Red K-2BP (RBR) dye solution), the PAM showed a more stable water flux as compared to that for KCl, although the latter flux was higher. It was shown that increasing the temperature increased the flux, due to a decrease in kinematic viscosity and an increase in osmotic pressure, but the effect of temperature on the low reverse solute transport was very small (0.02-0.07 g/m²h). The fluxes obtained using PAM with a TFC membrane were the same in baseline studies, both when using DI water as a feed and when using the dye solution as a feed.

Few studies can be found on the reverse solute transport of the different draw solutes studied in this work. Surfactants have been previously reported to be novel and easy to regenerate, due to micelle formation and the Krafft phenomenon (Nawaz et al., 2013). Although there can be some interaction between the surfactant and the membrane polymer, the main parameter influencing the diffusion is the polymer-free volume fraction of the membrane. A study on a polymeric membrane showed that the water diffusion coefficients are mainly dependent on the polymer density, and no significant effect of the polymeric surface was found (Valente et al., 2005).

Unlike in RO, solutes in FO can diffuse in both directions i.e. both forward and reverse. The reverse diffusion takes place partly because of concentration polarization on the draw side and mostly because of the concentration gradient between the draw and feed sides. In a previous study (Hancock & Cath, 2009), drawn water flux and reverse salt diffusion increased with increasing concentration for both NaCl and MgCl_2 draw solutes. DI was used as a feed and the experiments were run in AL-FS configuration. When both draw solutes were used at similar osmotic pressures, the flux was lower for MgCl_2 (by 25-30%) compared to NaCl; the lower diffusion coefficient of the former would lead to an increased severity of ICP in the support layer on the draw side. The higher viscosity of the MgCl_2 also contributed to an increased ECP on the draw side. Not surprisingly, the RST was also lower for MgCl_2 (by 59-67%). The reverse solute flux for MgCl_2 may be subject to Donnan equilibrium, whereby large Mg^{2+} ions diffuse more slowly and limit the diffusion of counter ions. Draw solute ions (Na and Cl) were shown to reverse diffuse at nearly equal molar proportions in those cases where

MgSO₄, CaSO₄, K₂SO₄, H₃PO₄, and NH₄HCO₃ were applied as feed solutions, but in the case of Ba(NO₃)₂ as feed the chloride ion diffused at a faster rate than sodium.

Size exclusion and electrostatic effects clearly have an important role to play in forward and reverse solute transport (Alsvik & Hagg, 2013). At lower fluxes and trans-membrane flow velocities, the feed solute is concentrated at the membrane surface on the feed side, and the concentration boundary layer on the draw solution side of the membrane is not well mixed and remains diluted. This results in a diminishing chemical potential gradient between the draw solution and the feed solution; retardation in the net diffusion of salts into the feed solution and high cross flow velocity (CFV) has an important role to play in diminishing this (Hancock & Cath, 2009).

By the same token, few previous studies have been performed on draw solute toxicity to bacteria. For *E. coli* toxicity, eight inorganics were tested in one study (Nawaz et al., 2013); sodium chloride [NaCl], calcium chloride [CaCl₂], potassium chloride [KCl], magnesium chloride [MgCl₂], potassium sulphate [K₂SO₄], magnesium sulphate [MgSO₄], sodium sulphate [Na₂SO₄], and ammonium sulphate [(NH₄)₂SO₄]. Four surfactants were also tested; TMOAB, DTAB, MTAB, and SDS. SDS was strongly recommended, based on its ability to generate high fluxes and allow *E. coli* to grow at all concentrations tested, but high fluxes were not observed in this study. Among inorganic draw solutions, MgCl₂, CaCl₂ and ammonium sulphate were highly recommended because of high fluxes and non-toxicity, while sodium sulphate was not recommended because of reduced bacterial growth.

As a follow up to the study cited above by Nawaz et al, a more detailed study was conducted using *P.aeruginosa* monoculture and an activated sludge mixed consortium to see the effect of draw solution concentration on toxicity to the feed consortium (Nawaz et al., 2016). Four surfactants TEAB, TMOAB, SDS, and 1-OSA were tested for toxicity. Reverse solute transport for surfactants as draw solutions was observed to be much lower as compared to that for inorganic draw solutes. Significant bacterial growth was observed in the presence of TEAB and SDS, and therefore these two draw solutions were recommended for future studies.

In the current study, a single active layer nanofiltration membrane was used and compared with a HTI CTA FO membrane. A range of draw solutions were evaluated against biological feed solutions; the hypothesis to be tested was that relatively higher fluxes will be observed for NF membranes, while potentially higher reverse solute transport might be circumvented by the use of higher molecular weight draw solutions. Inorganic draw solutes (NaCl, Na₃PO₄), Surfactants (TEAB, SDS), and Polyelectrolytes (PDAC, PEGBE) were tested as draw solutes. Observations were then made of water fluxes, osmotic pressures using freezing point depression, reverse transport of draw solute, microbial toxicity and viscosity.

The overall aim of this work was to perform an engineering-oriented study to examine the component parts and integrated operation of a continuous and feasible FOMBR system for the treatment and recycle of wastewater. The research question addressed by this work was to ask whether the use of a higher pore- size Nano-filtration (NF) membrane in combination with high molecular weight novel draw solutions for forward osmosis could improve the overall performance of FO-MBR systems; this would be achieved by improving flux without causing excessive reverse solute transport nor

toxicity to the feed bacterial consortium. This study is therefore important, as many studies on FO are run with DI as feed and simple inorganic draw solutes (NaCl, MgCL₂) and show results for ideal systems which are, however, less realistic or practical.

2 Materials and Methods

2.1 FO-MBR Bench-Scale Apparatus

The forward osmosis bench scale apparatus consisted principally of a flat sheet membrane module fitted into an acrylic membrane cell (**Figure 1**). The cells were fabricated with symmetrical flow channels on both sides of the membrane and sealed with a nitrile rubber gasket. Spacers were placed on each side of the membrane as they disrupt the concentration boundary layer and increase the permeation rate (Yun et al., 2011). An ultra-thin, polyamide-based membrane was provided by Dr Chuyang Tang at the Singapore Membrane Technology Centre, with a MWCO of 400-600 Da, and a water permeability of 7.0-11.0 Lm⁻²h⁻¹bar⁻¹. An HTI Cellulose Tri-Acetate (CTA) FO membrane was obtained from the manufacturer with an estimated NaCl rejection of 95%, and a water permeability of 0.7-1.0 Lm⁻²h⁻¹bar⁻¹.

The membrane had an effective surface area of 47.25cm². The water flux was calculated using equation 1:

$$J = \frac{\Delta v}{A \Delta t} \quad (1)$$

Where J (LMH) is the permeate flux, Δv is the increase in volume of permeate water (L); A is the effective surface area of the membrane (m²); Δt is the time period of observation (h).

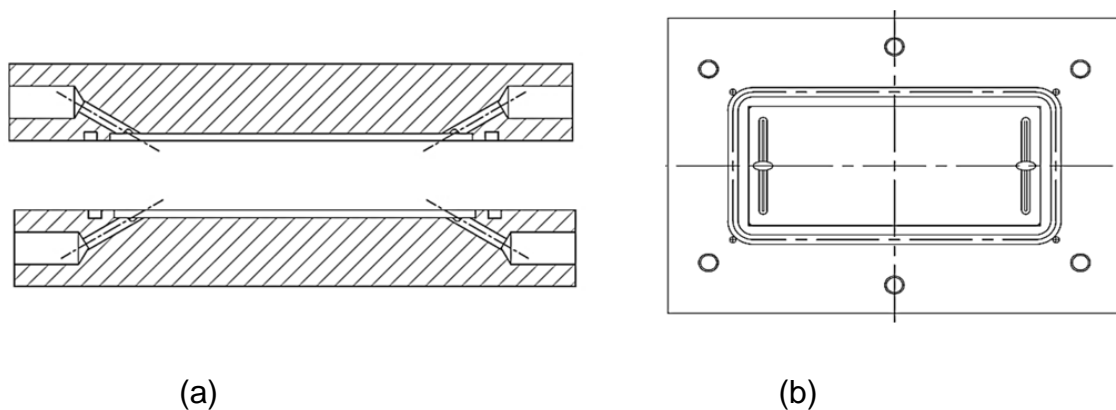


Figure 1: Schematic Diagram for the External Plate and Frame Membrane Cell: (a) Section of Top and Bottom Plate; (b) Plan View of a Single Plate. The length, width, and height of the FO cell was 21cm, 15cm and 0.6cm respectively, and the effective membrane area was 47.3 cm² (10.3 cm x 4.6 cm).

Similarly, reverse solute transport was calculated using equation 2:

$$J_s = \frac{V_t C_t - V_o C_o}{A \Delta t} \quad (2)$$

Where J_s (GMH) is the reverse solute transport for the draw solution, C (g/l) is the concentration of draw solute in the feed tank and V (l) is its volume; subscript 0 indicates zero time and t indicates t hours. The FO apparatus has been described in detail elsewhere (Gadelha et al., 2014).

Solute concentrations were obtained from electrical conductivity measurements of their solutions using a conductivity meter (YSI Hydrodata, UK). The conductivity meter had a probe that was calibrated using standard solutions of the solute to be analysed. Concentration values for the solute were then obtained directly by placing the probe in the solution to be analysed.

A forward osmosis membrane bioreactor was established for the treatment of synthetic wastewater. To establish a bioreactor, *Bacillus subtilis* was grown overnight in an incubator at 30°C and inoculated in a 1000ml flask containing municipal synthetic wastewater, **Table 3** (Khan et al., 2013). *B. subtilis* is known for its ability to aid in digesting waste matter in a septic system and was readily available in the lab; it was therefore chosen as a monoculture in the FO-MBR. Note that a full bacterial consortia, as present in activated sludge, was not employed in this work, due to health and safety restrictions in the lab.

The inoculation flask was placed in a shaking incubator at 120 rpm for 24 hours and the final contents used as a feed solution for the FO-MBR. The draw solution was selected from amongst those in **Table 4** and was circulated from a 1000 ml tank. A mechanical mixer (100 rpm) was placed in the bioreactor to ensure the solution always remained homogenous and to ensure uniform distribution of bacterial species. The bioreactor was operated at room temperature over a period of several days.

Table 3: Composition of Municipal Synthetic Wastewater.

Component	Formula	Quantity (mg/L)
Glucose	$C_6H_{12}O_6 \cdot H_2O$	514
Ammonium Chloride	NH_4Cl	190
Potassium di-Hydrogen Phosphate	KH_2PO_4	55.6

Calcium Chloride	CaCl_2	5.7
Magnesium Sulphate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	5.7
Ferric Chloride	FeCl_3	1.5
Manganese Chloride	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	1
pH buffer	NaHCO_3	142.8

2.2 Chemicals and Solutions

All chemicals were of lab grade and purchased from Sigma Aldrich, the majority for use as draw solutes. The organic and inorganic draw solutes of varying molecular weight were chosen to understand the performance of the FO-MBR for treatment of synthetic wastewater, with “Active Layer to Draw Solution” (AL-DS) configuration employed when DI water was used as a feed (to avoid ICP in the support layer), and “Active Layer to Feed Solution” (AL-FS) configuration employed when synthetic wastewater with live bacteria was used as a feed (to avoid fouling by the feed within the support layer). A summary of the draw solutions employed is given in **Table 4**.

Unfortunately, it was not physically possible to measure the osmotic pressure of SDS at the required concentration using the freezing point depression method; due to the Krafft phenomenon, the solute crystallizes out of solution above the freezing point. However, it may be expected based on previous measurements that SDS has osmotic pressure values which are lower than that of TEAB (Gadelha et al, 2014) .

Table 4: A Summary of the Draw Solutions Used in the Current Study; * denotes molecular weight of each monomeric unit, ** denotes average molecular weight of the polyelectrolyte solution.

Draw Solutes (Chemical formula)	Type	CMC (mol/L)	Mol. Wt. (g/mol)	Abbreviation	Osmotic Pressure (MPa)
Sodium dodecyl sulfate: $[C_{12}H_{25}OSO_3Na]$	Anionic-Surfactant	0.008	288.38	SDS	-
Tetraethyl ammonium bromide: $[(C_2H_5)_4NBr]$ or $[C_8H_{20}NBr]$	Cationic-Surfactant	0.16	210.14	TEAB	1.61 (at 0.5M)
Polydiallyldimethylammonium chloride $(C_8H_{16}ClN)_n$	Anionic-Polyelectrolyte	-	161.67*	PDAC	0.2 (at 0.61M)
			200,000-350,000**		
Poly (ethylene glycol) butyl ether $(CH_3(CH_2)_3(OCH_2CH_2)_nOH)$	Cationic-Polyelectrolyte	-	118.17*	PGBE	0.63 (at 0.42M)
			400,000**		
Sodium chloride (NaCl)	Inorganic	-	58.4	NaCl	2.13 (at 0.5M)
Sodium phosphate (Na_3PO_4)	Inorganic	-	141.96	Na_3PO_4	2.13 (at 0.5M)

Sodium chloride (NaCl) was selected as a model draw solute as it has been well studied (Roach et al., 2014), and sodium phosphate (Na_3PO_4) was also considered in the inorganic draw solution category. The surfactants sodium dodecyl sulphate (SDS) and tetraethylammonium bromide (TEAB) were selected because of their ability to form a distribution of aggregates known as micelles at concentrations above their critical micellar concentration (CMC), with the larger molecular size of the micelles causing a lower RST as compared to inorganic draw solutions of smaller molecular size (Nawaz et al., 2013).

Recently, polyelectrolytes have been proposed and applied as draw solutes for the following reasons; they are soluble and non-toxic in water, have a larger molecular size and flexibility in structural configuration (**Figure 2**), and possess a lower critical solution temperature to aid solute recovery (Roach et al., 2014). The polyelectrolytes Polydiallyldimethylammonium chloride (PDAC, often used as a coagulant aid in conventional water treatment) and Poly (ethylene glycol) butyl ether (PEGBE) from Sigma Aldrich were used as received, in different solution percentages.

Draw solutes were formulated at 0.5 M concentration, see **Table 5**. The concentration in **Table 5** is reported in estimated monomeric units for surfactants and polyelectrolytes; the latter values were later adjusted to account for the non-symmetric

molecular weight distribution of the polyelectrolyte. The osmotic pressure of draw solutes was measured using an osmometer (Micro-osmometer 13/13DR Roebling, Germany). The instrument measured the osmolality, based on the freezing point depression of the solution. Distilled water, which has a zero osmotic pressure, and phosphate buffer saline were used for calibration. The osmolality of the solution was then converted to osmotic pressure, using the Van't Hoff equation (Gadelha et al., 2014).

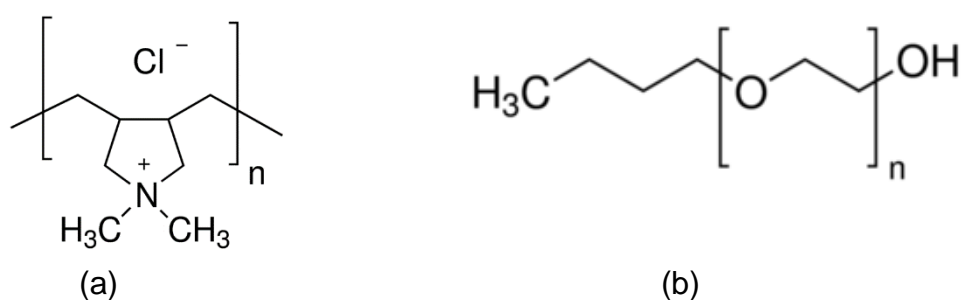


Figure 2: Molecular Structure for Polyelectrolytes Used in the Current Study (a) PDAC ($\text{C}_8\text{H}_{16}\text{Cl N}$)_n, (b) PGBE ($\text{CH}_3(\text{CH}_2)_3(\text{OCH}_2\text{CH}_2)_n\text{OH}$).

2.3. Toxicity

Toxicity of the draw solutes is a very important issue, whether with reference to reverse solute transport to the biologically-active feed side of the bioreactor or to the draw solutes remaining in the permeate after draw solution recovery. Toxicity issues may affect the biological functioning of the FO-MBR. Toxic compounds in the permeate may cause environmental and health issues, and will increase the cost of FO treatment since a polishing stage will be required to remove them.

Toxicity of all the draw solutes was evaluated using a microbroth dilution test; for this, a bacterial culture of *Bacillus Subtilis* was allowed to grow in an incubator at 32°C overnight. This culture was then added to individual eppendorfs and centrifuged at 10,000rpm for 15 minutes. The pellet was then filled with 500μl of M9 media (Sigma Aldrich) and 500μl of individual draw solutions to observe possible sudden shocks to bacteria. A range of concentrations that included both observed RST levels and higher levels were tested.

2.4. Viscosity

In addition to osmotic pressure and diffusivity, viscosity plays an important role in draw solution characteristics (Xie et al., 2013a). This characteristic might be more important for polyelectrolytes as compared to other draw solutions, as high viscosity often prevents polyelectrolytes from being used as practical draw solutes at ambient conditions (Nawaz et al., 2016). Viscosity was evaluated for all the draw solutions, using an Anton Paar rheometer with a cone plate of diameter of 24.946mm and at a constant shear rate of 100/s.

3 Results and Discussion

3.1 Forward Osmosis Membrane versus Nanofiltration Membrane

Figures 3, 4 and 5 show the initial fluxes for FO and NF membranes for the draw solutions studied, with both DI water (run in AL-DS mode) as a control feed and live monoculture bacterial feed in the FO-MBR (run in AL-FS mode). Note that, whichever feed was used, we were comparing the draw solutions in the same orientation.

Observation of the initial flux allows a straightforward comparison of the different membranes, draw solutions and feeds, but without the interfering effects of membrane fouling which causes a decline in the flux. In general, it can be observed that the presence of live feed greatly influenced the flux for all draw solutions for both membranes, tending to reduce it compared to DI feed. It is to be noted that the live feed was associated with cake formation on the feed side of the membrane. It can also be observed that the fluxes for the FO membrane were, in general, lower than that for the NF. A gradual decline in initial fluxes was also observed in live bioreactor configuration for both NF and FO membranes. This can be related to biofilm/cake formation at the active layer of the FOMBR process (in AL-FS configuration).

3.1.1 Polyelectrolytes

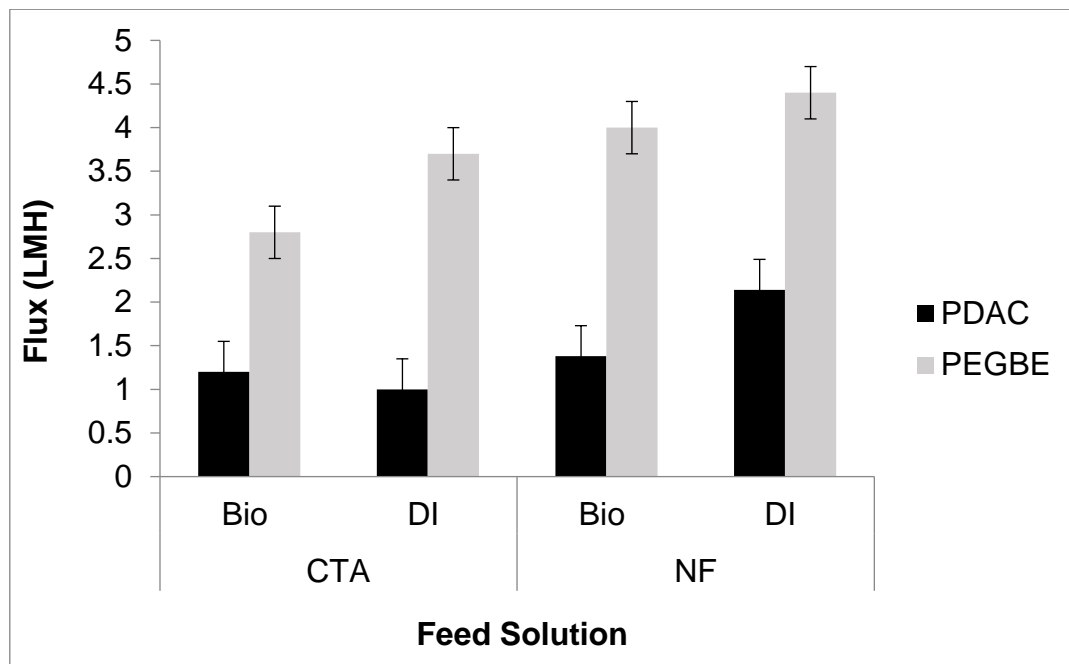


Figure 3: Initial Fluxes for Polyelectrolytes PDAC and PGBE with NF and FO (CTA) Membranes Using both DI Water as Feed (AL-DS) and a Live Monoculture FO-MBR 'Bio' feed (AL-FS mode) at 0.44 and 0.67 Draw Solute Concentrations, Respectively (Cross Flow Velocity, CFV: 0.12m/s).

The molecular weight for draw solutes used in this study (e.g. PDAC: M_w 200,000-350,000 and PGBE: 200,000-400,00) were high and were chosen to yield stable flux

and reduced RST. However, as shown in Figure 3, the initial fluxes were relatively low for polyelectrolytes (relative to the other draw types in figures 4 and 5), presumably due to lower diffusivity and higher viscosity (the latter as shown in section 3.3). The flux for PGBE was 2 or 3 times higher than for PDAC; the monomeric concentration for PGBE was 1.5 times higher and the molecular weights broadly similar, so that molecular configuration and other non-ideal solution behavior must play a role.

Unfortunately, many of the previous studies conducted using polyelectrolytes are not consistent with each other (Zhao et al., 2015, Jun et al., 2015). High molecular weight PAM gave a reasonable flux (M_w 3,000,000; flux 14-17 LMH) with FO and PRO configurations (Zhao et al., 2015). However, in our study as well as in a few others, it was shown that the flux at a given monomeric concentration for higher molecular weight polyelectrolytes was lower than that for lower molecular weight polyelectrolytes, with PEI having a higher molecular weight and performing poorly (Jun et al., 2015). Again, non-ideal solution behavior seems to be more important at high molecular weight.

3.1.2 Surfactants

A similar pattern of reduced flux was observed for surfactants (**Figure 4**) when the NF membrane was replaced with an FO membrane. The flux was consistently higher for the cationic surfactant (TEAB), and lower for the anionic SDS. The flux values in general were higher than those observed for the polyelectrolytes, and lower than those observed for inorganic draw solutes in Figure 5, but nevertheless compared favourably. Note that there was a lot of foam formation in the SDS solution, depending on how freshly the solution was prepared, and this seemed to affect the flux as well as the reverse solute transport. SDS has a higher molecular weight than TEAB, and yet the reverse solute transport values were higher for SDS for both membranes (see Table 4).

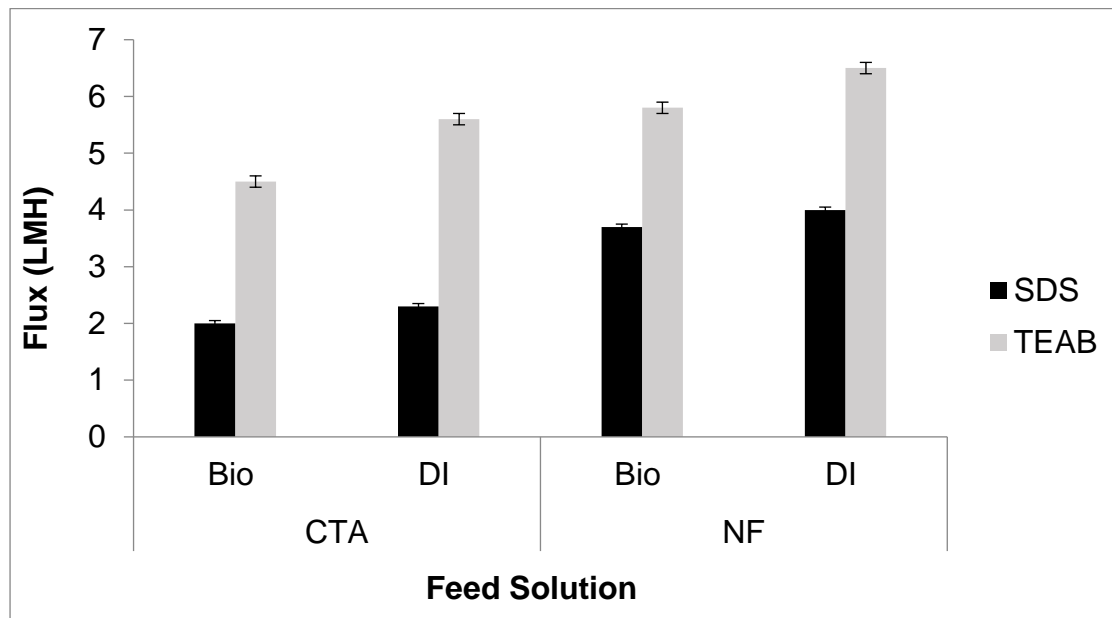


Figure 4: Initial Fluxes Using SDS and TEAB as Draw Solutes against Both DI Water (AL-DS) as Feed and a Live Monoculture FO-MBR ‘Bio’ Feed (AL-FS Mode) for FO (CTA) and NF Membranes at 0.5 M Draw Solute Concentration (CFV: 0.12m/s).

Surfactants have been previously reported (Hoyer et al., 2016) to produce high osmotic pressures per unit molar concentration. But the dilution of surfactant in the membrane support layer can lead to a lower osmotic pressure difference across the membrane. This effect of internal concentration polarization (the draw solute cannot diffuse back into the support layer rapidly enough) was reported in the same work to be higher for surfactants than for inorganic draw solutes, and was assumed to be because of higher viscosity and lower diffusivity of the surfactant solution.

If the hydrocarbon chain length is sufficiently long, then a microscopic phase separation can appear at high enough concentration i.e. micelles will be formed. Longer chain hydrocarbons have a lower CMC and thus fewer monomers in solution and lower osmotic pressure (as in the case of SDS). Both of the membranes used in the current study would certainly prevent the passage of micelles, but they seemed to allow for the passage of individual surfactant monomers and thus allow for some reverse transport of solute, which is a disadvantage compared with the polyelectrolytes.

As noted above, higher fluxes were observed for TEAB as compared to SDS, but the decline in flux with time was also higher. Conversely, lower fluxes were achieved with SDS but the decline in flux for the bio feed was also lower over time; presumably, lower fluxes lead to a lower rate of fouling.

3.1.3 Inorganic Draw Solutes

Initial fluxes for the inorganic draw solutes are shown in **Figure 5** for the FO membranes. They were not tested against the NF membrane because of the ability of monovalent draw solute ions to pass directly through the membrane. It can be observed in general that the flux values observed were higher than those for polyelectrolytes and surfactants, but that the flux for Na_3PO_4 was lower than that for NaCl for both DI water and MBR as feed. This is because draw solutions with divalent ions in general yield lower fluxes than monovalent ions even at the same concentration, which is due to the lower diffusivity coefficients of the divalent ions in comparison with those of the monovalent ions (Holloway et al., 2015) and the consequently higher effects of concentration polarisation on effective osmotic pressure. Higher diffusivity is another reason why NaCl is widely studied for FO processes in the literature.

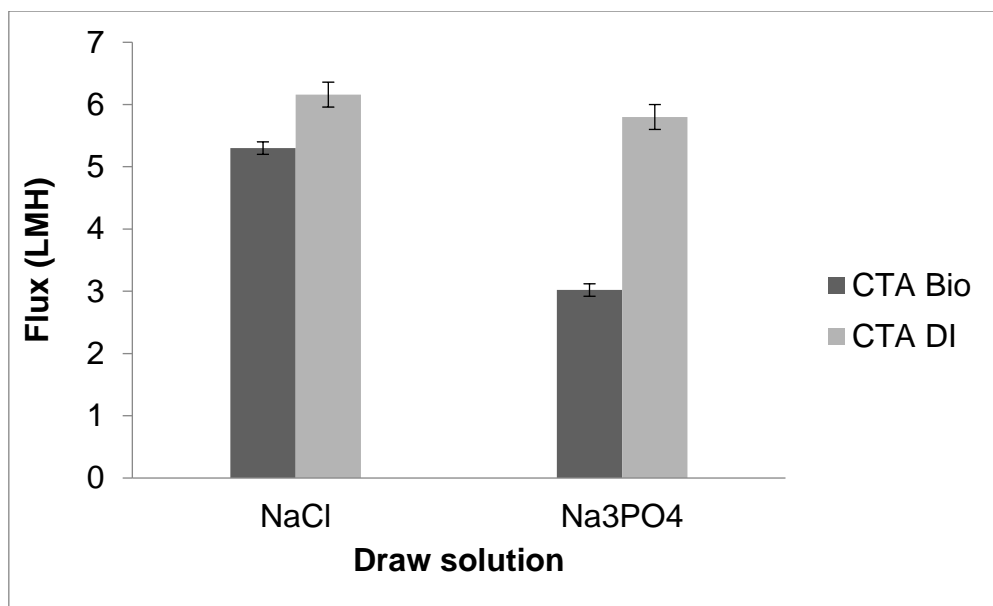


Figure 5: Initial Fluxes for NaCl and Na₃PO₄ as Draw Solutes Using the FO (CTA) Membrane and Both DI water (AL-DS) as Feed and a Live Monoculture ‘Bio’ FO-MBR Feed (AL-FS Mode) at 0.5M Draw Solute Concentration (CFV: 0.12m/s).

Yet another reason for the wide usage of NaCl is that it is inexpensive, costing around 15\$/kg, and is highly soluble (315g/l at 25°C). A study (Achilli et al., 2010) evaluating various inorganic draw solutes for cost and performance ranked NaCl low for its performance but high for its inexpensive cost. On the other hand, divalent ions of inorganic compounds such as Ca²⁺, Ba²⁺, Mg²⁺, SO₄²⁻ and CO₃²⁻ are expected to cause mineral salt scaling. However, Mg(OH)² only precipitated out at a pH greater than 9; therefore, MgCl₂ was recommended for use in FO without the risk of scaling.

Increasing flux via higher solute concentration also results in a larger reverse solute transport, and it was found here that 50% or more of the reverse solute transport took place in the first 24 hours of the FO process. This could be because a viscous layer of draw solute forms on the membrane surface hindering further reverse transport or perhaps because the membrane pores got blocked. In addition to higher diffusivities, draw solutions with smaller ions have other advantages. As solute radii decrease, the peak hydration density of the ion increases. Therefore, the strongest osmosis would be expected to occur for the smallest ions, which pull on the water strongly (Cannon et al., 2012). NaCl yielded the highest water flux amongst all the draw solutes tested in this study. On the other hand, a small solute radii will not be ideal for RST; NaCl showed the highest RST amongst all the draw solutes tested (see **Table 6**).

Table 5: Flux with FO and NF Membranes After 1h and 8h Time Intervals with Percentage Decline in Flux using DI Water as Feed (AL-DS mode) and FO-MBR as Feed (AL-FS mode) at a CFV of 0.12m/s.

Draw Solution	HTI CTA FO Initial Flux - DI water Feed (LMH)	HTI CTA FO flux after 8 Hours -DI water Feed (LMH)	NF Initial Flux -DI water feed (LMH)	NF Flux after 8 hours -DI water feed (LMH)	HTI CTA FO Initial Flux - Bioreactor Feed (LMH)	HTI CTA FO flux after 8 Hours - Bioreactor Feed (LMH)	NF Initial Flux - Bioreactor Feed (LMH)	NF Flux after 8 hours - Bioreactor Feed (LMH)
0.5M NaCl	6.16	3.8 (38.31%)	-	-	5.3	3 (43%)	-	-
0.5M SDS	2.3	2 (13%)	4	3.5 (12.5%)	2.1	1.8 (14.2%)	3.8	2.5 (34%)
0.5M TEAB	5.6	4 (28.57 %)	6.5	3.8 (41%)	4.5	3 (33.3 %)	5.8	4.5 (22.41 %)
0.44M PDAC	1.1	0.8 (27%)	1.4	0.6 (57%)	0.9	0.6 (33%)	1.1	0.4 (63%)
0.67M PGBE	3.7	3 (18.9 %)	4.4	3.5 (20.45%)	2.8	2.2 (21.4%)	4	3 (25%)
0.5M Na ₃ PO ₄	5.8	3.2 (44.8 %)	-	-	3.02	2.1 (30.4%)	-	-

3.1.4 Comparison between Fluxes for the FO Membrane and the NF Membrane

The use of NF membranes for FO is promising, as NF membranes generally have a much higher water permeability than FO membranes; in this work, it is an order of magnitude higher (see section 2.1). Therefore, the osmotic fluxes can reasonably be expected to be higher for an NF membrane as compared to an FO membrane for the same draw solution. **Table 5** shows the initial fluxes, and the flux after eight hours of operation, for both FO and NF membranes and for both DI water and bioreactor feed. Indeed, fluxes were higher for NF than for FO for all those draw solutes which were compared. The fluxes were highest for the inorganic draw solutes, followed by the surfactants and finally the polyelectrolytes. The tables also show the percentage decline in flux. The decline in flux over a period of time and the decline in initial flux with the change in feed were both significant. For the biological feed and the FO membrane after 8 hours of operation, the decline was greatest for 0.5 M NaCl (43%), followed by TEAB (33.3%), PDAC (33%), Na₃PO₄ (30.4%), PGBE (21.4%), and finally SDS (14.2%). The percentage decline in flux also varied with draw solute for the NF membrane. For the NF membrane, the initial flux was already very low for PDAC (1.1 LMH) and the percentage decline in the bioreactor was highest (63%), followed by SDS (34%), PGBE (25%), and TEAB (22.5 %), respectively. In the case of PDAC, the lowest initial flux actually yielded the highest rate of decline, but in general higher initial fluxes were seen as compared to FO. A greater relative decline in flux for both membranes when biological feed was used rather than DI water demonstrated the importance of fouling cake formation on the feed side of the membrane.

In general, for both CTA FO and NF membranes, a decline in flux was observed over time due to the dilution of the draw solution. For biological feed (with AL-FS configuration), initial fluxes were generally lower due to ICP in the support layer of the membrane, and flux decline was greater due to cake formation on the active layer of the membrane. A draw solute reconcentration system would be necessary in order to subtract the draw dilution effects and thus understand the decline better.

3.2 Reverse Solute Transport

Reverse solute transport of ions from the draw solution (DS) to the feed is a potential problem with forward osmosis (FO). RST is reduced when divalent ion salts, such as MgCl₂ and MgSO₄ with a larger hydrated radius, are used instead of salts with monovalent ions only, such as NaCl (Holloway et al., 2015). The observed reverse solute transport is reported for all draw solutes tested with NF and HTI membranes in **Table 6**. As mentioned previously, tests were not performed for the inorganic draw solutes versus the NF membrane, but values of RST for monovalents with NF can be expected to be perhaps an order of magnitude greater than for the FO membrane.

For the FO membrane, the following order in RST was observed:

NaCl > SDS > Na₃PO₄ > TEAB > PGBE > PDAC

For the NF membrane, the following order in RST was observed:

SDS > TEAB > PDAC > PGBE

It can first be observed that the reverse solute transport was related to the charge of the draw solute. For example, for NF, the anionic surfactant showed a slightly higher RST value than the cationic surfactant, while RST for the sodium chloride (monovalent salt) was higher than for sodium phosphate (with a trivalent co-ion) for the FO

membrane. It can also be seen clearly from the values reported that solute molecular size was an important factor to determine the reverse solute transport of a draw solution. The RST values were consistently lowest for the highest molecular weight draw solutes (polyelectrolytes).

In general, values for reverse solute transport were slightly higher for NF than those for FO but were still of comparable magnitude, and the issue of RST should not prevent the use of NF as an FO membrane when paired to the draw solutes tested, particularly those of larger molecular weight. This issue is explored further below with respect to toxicity to the bioreactor.

Table 6: Reverse Solute Transport (grammes per m² per hour, GMH) for Draw Solutes used in the Study after 24 Hours of FO Operation when Run in the Absence of a Draw Re-concentration System (AL-DS mode, CFV: 0.12m/s).

Draw Solution	Formula weight (g/mol)	Reverse solute Transport	
		FO Membrane (GMH)	NF Membrane (GMH)
		DI water feed	DI water feed
TEAB	210.14	6.3	7.07
SDS	288.372	7.66	8.07
NaCl	58.44	9.33	-
Na ₃ PO ₄	163.94	7.2	-
PDAC	161.673	1.14	1.86
PGBE	118.17	1.2	1.56

SDS showed a relatively high RST for both membranes. Micelles will not pass through the membrane but monomers will. The latter may also enhance the hydrophilicity of the membrane, and allow further monomers to pass through. The hydrophilicity could also result in cake formation on the membrane layer, due to surfactant adsorption (Zhao et al.,2015), thus enhancing surface concentration on the draw side.

Based on the high RST values measured in this work, the use of SDS was not recommended for future studies. Use of NaCl was continued as a baseline for comparison with literature.

Viscosity and toxicity values were looked at for a final comparison of draw solutes in the following sections.

3.3 Viscosity

The viscosity of the polyelectrolyte solution is an important factor for its use as a draw solute in FO, and it plays a key role in determining water fluxes. The viscosity

measurements for draw solutes are reported in **Table 7**. As can be seen, the viscosities followed the order:

PDAC > SDS > PGBE > Na₃PO₄ > TEAB ≥ NaCl

Table 7: Viscosities of Draw Solutions at Operational Concentrations.

Draw solution	Concentration (M)	Viscosity (cP)	Osmotic pressure (MPa)	Flux with DI water (LMH)
NaCl	0.5	1.2	2.13	6.16
Na ₃ PO ₄	0.5	1.5	2.13	5.8
SDS	0.5	2	-	2.3
TEAB	0.5	1.2	1.61	5.6
PDAC	0.44	2.5	0.2	1.1
PGBE	0.67	1.7	0.43	3.7

As expected, viscosities were highest for the polyelectrolyte solutions, but it is also interesting to note that the viscosity of SDS was comparable with that of the polyelectrolytes.

The water flux created by a draw solution is inversely proportional to its viscosity, at similar osmotic driving force. This can be understood in terms of basic fluid mechanics, where Poiseuille's law for the laminar flow of viscous liquids in pipes implies an inverse relationship between velocity (leading to flux) and viscosity at constant hydraulic driving force.

One of the negative impacts of the higher viscosity associated with larger molecules could be a reduction in the water flux from feed to draw solution (Jun et al., 2015). This can, at least in part, explain the lower fluxes obtained for PDAC and SDS with viscosity ≥ 2cP as compared to the other draw solutes.

Increasing the molar concentration of the draw solute is an option to increase flux, and a positive relationship between the two is mostly observed in studies in the literature. However, increasing the solute weight fraction also increases the solution viscosity which yields the opposite effect; it leads to limited function in the process of dialysis (Daniels et al., 1988).

3.4 Toxicity

A bacterial monoculture was able to grow in the presence of all the draw solutions tested, as shown in **Figure 6**; all the bacteria were able to grow in the presence of draw solutions at a concentration ranging from 0.005 to 0.05 M. The concentrations observed in the feed tank as a result of RST were one or two orders of magnitude lower. The growth curve presented here is that at a very high concentration of 0.5M to examine how well *B.subtilis* was able to thrive in the presence of all draw solutions. Na₃PO₄ showed higher growth close to that of the control; conversely, as a surfactant, SDS hampered bacterial growth slightly at the high concentration tested. The former was likely to be because of the availability of phosphate in the solution, which is a source of phosphorus for bacteria and a constituent of nucleic acids, nucleotides,

phospholipids, LPS, teichoic acids, and so on. SDS in particular is known to be toxic to bacteria, but the gram negative bacteria chosen here survived well in view of the higher concentration tested.

The study by Nawaz et al (Nawaz et al,2013) has been extended here to demonstrate that the draw solutes tested were not toxic to bacteria even at higher concentrations, and would be safe for use under the conditions arising as a result of RST to the feed bioreactor. Inorganic draw solutions were least toxic, followed by polyelectrolytes and surfactants.

In view of the higher associated bacterial growth, PDAC and TEAB are recommended as draw solutes. On the other hand, PEGBE and TEAB perform best when higher flux is important, while PDAC and PEGBE confer the lowest RST. For all criteria, both NaCl and Na₃PO₄ are suitable as benchmark draw solutes for future studies, but of course their relatively low molecular weight will lead to high RST values.

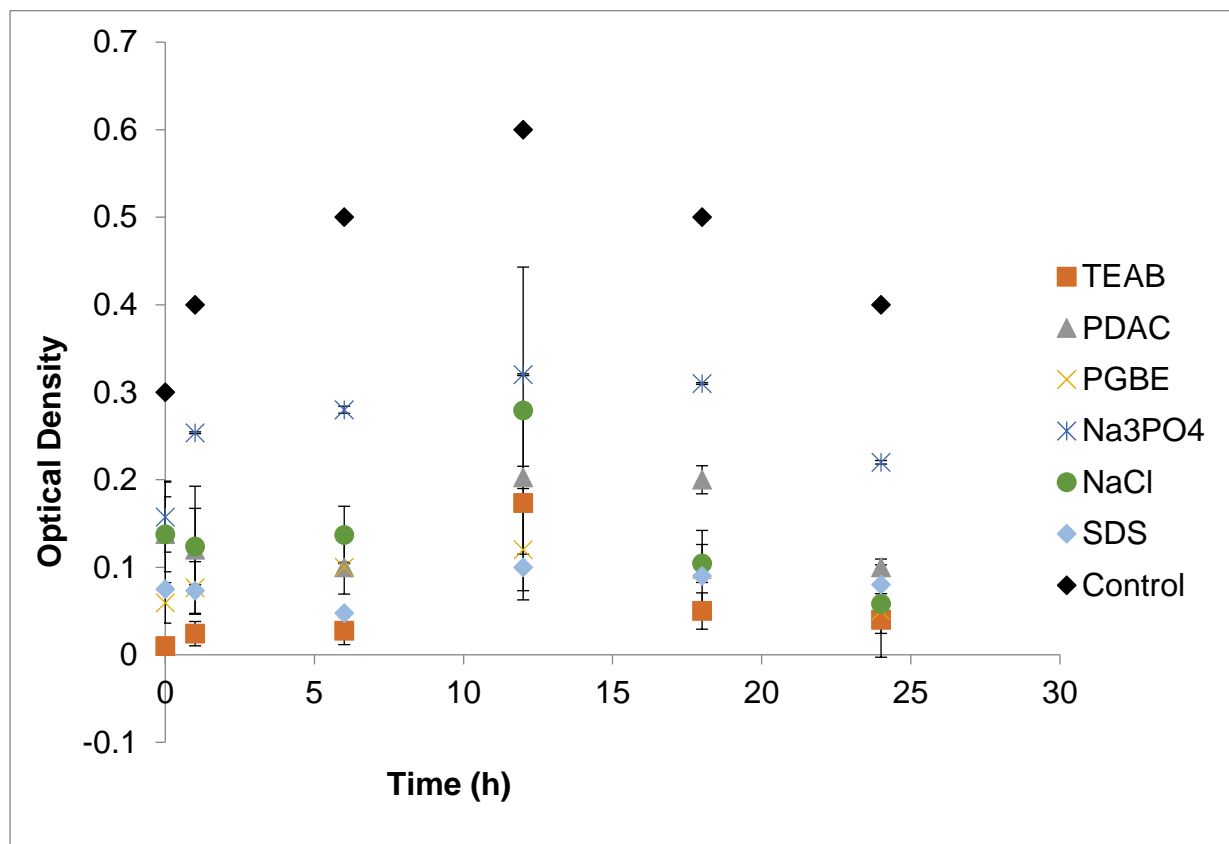


Figure 6: Optical Density of Bacterial Solution Using Microbroth Dilution Test in Minimal Media with Draw Solutes (Error Bars included).

4. Conclusions

The differences in osmotic pressure between low and high molecular-weight draw solutes at similar molar concentrations of charged solutes or monomeric units arose from solution non-idealities; these differences were also reflected in the values for water flux for different draw solutes.

The experimental results confirmed the hypothesis that an NF membrane in the FOMBR yields higher fluxes as compared to the CTA FO membrane for the same draw solute. However, for both FO and NF membranes, the initial fluxes were lower when the DI water feed was switched to a live bioreactor feed and the flux decline was greater. The higher permeability NF membrane led in general to a greater rate of biofouling and/or cake formation and hence flux decline.

Typical levels of reverse solute transport (RST) observed under operational conditions were slightly higher for the NF membrane than for the FO membrane, but were not toxic to the bacterial monocultures present in the bioreactor and the use of these draw solutes with a biologically live feed is supported by this study. However, draw solutes that exhibited higher viscosity also exhibited lower fluxes, and the viscosity of a draw solution is important in draw solution selection.

Flat sheet/hollow fibre NF membranes in combination with high molecular weight draw solutes can provide potentially attractive working systems for the FOMBR, because the fluxes are higher when an NF membrane is in place. On the other hand, the reverse solute transport values, although slightly higher, are still comparable to an FO membrane. However, fouling mitigation will be a more important issue for the NF membrane.

In this study, the regeneration of draw solutions has not been considered. Nevertheless, it will be important to study the performance of membranes and draw solutions for the FOMBR at steady-state in the presence of a continuous regeneration system, in order to examine and optimize the process when running under continuous and long-term operation. The long-term, steady-state buildup of draw solute in the feed tank, and its effect on process operation and viability, cannot be predicted from these short-term, semi-batch lab experiments.

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Figure 1: Schematic Diagram for the External Plate and Frame Membrane Cell: (a) Section of Top and Bottom Plate; (b) Plan View of a Single Plate. The length, width, and height of the FO cell was 21cm, 15cm and 0.6cm respectively, and the effective membrane area was 47.3 cm² (10.3 cm x 4.6 cm).

Figure 2: Molecular Structure for Polyelectrolytes Used in the Current Study (a) PDAC (C₈H₁₆Cl N)_n, (b) PGBE (CH₃(CH₂)₃(OCH₂CH₂)_nOH).

Figure 3: Initial Fluxes for Polyelectrolytes PDAC and PGBE with NF and FO (CTA) Membranes Using both DI Water as Feed (AL-DS) and a Live Monoculture FO-MBR 'Bio' feed (AL-FS mode) at 0.44 and 0.67 Draw Solute Concentrations, Respectively (Cross Flow Velocity, CFV: 0.12m/s).

Figure 4: Initial Fluxes Using SDS and TEAB as Draw Solutes against Both DI Water (AL-DS) as Feed and a Live Monoculture FO-MBR 'Bio' Feed (AL-FS Mode) for FO (CTA) and NF Membranes at 0.5 M Draw Solute Concentration (CFV: 0.12m/s).

Figure 5: Initial Fluxes for NaCl and Na₃PO₄ as Draw Solutes Using the FO (CTA) Membrane and Both DI water (AL-DS) as Feed and a Live Monoculture 'Bio' FO-MBR Feed (AL-FS Mode) at 0.5M Draw Solute Concentration (CFV: 0.12m/s).

Figure 6: Optical Density of Bacterial Solution Using Microbroth Dilution Test in Minimal Media with Draw Solutes (Error Bars included).

Table 1: A Summary of the Removal Efficiencies of FO-MBRs for Organic Compounds, Nitrogen and Phosphorus. (Wang et al., 2016).

Table 2: Summary of Operational Data for Forward Osmosis Membrane Bioreactors (FO-MBRs) in the Literature (Wang et al., 2016).

Table 3: Composition of Municipal Synthetic Wastewater.

Table 4: A Summary of the Draw Solutions Used in the Current Study; * denotes molecular weight of each monomeric unit, ** denotes average molecular weight of the polyelectrolyte solution.

Table 5: Flux with FO and NF Membranes After 1h and 8h Time Intervals with Percentage Decline in Flux using DI Water as Feed (AL-DS mode) and FO-MBR as Feed (AL-FS mode) at a CFV of 0.12m/s.

Table 6: Reverse Solute Transport (grammes per m² per hour, GMH) for Draw Solutes used in the Study after 24 Hours of FO Operation when Run in the Absence of a Draw Re-concentration System (AL-DS mode, CFV: 0.12m/s).

Table 7: Viscosities of Draw Solutions at Operational Concentrations.