Integration of Forward Osmosis Membrane Bioreactor (FO-MBR) and Membrane Distillation (MD) Units for Water Reclamation and Regeneration of Draw Solutions

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Abstract

In the current lab scale study, the two treatment technologies of FO (Forward osmosis) and DCMD (Direct contact membrane distillation) were used in combination to create a continuous treatment system for water reclamation using, inorganic NaCl, surfactant (Tetraethyl ammonium bromide, TEAB) and polyelectrolyte (Polydiallyldimethylammonium chloride, PDAC) as FO draw solutes with both DI water (FO-MD), and monoculture municipal synthetic wastewater with *Bacillus subtillis* inoculum as feed (FOMBR-MD).

Each of the units was optimized separately at bench scale, and then combined to form a Forward Osmosis Membrane Bioreactor – Membrane Distillation (FOMBR-MD) hybrid for water reclamation from wastewater. In this hybrid system, the diluted draw solution was fed to the MD unit for reconcentration. The MD unit was tested at various operating temperatures; for FO-MD, a temperature difference of 15°C was chosen, with a feed temperature of 35°C and a permeate temperature of 20°C. For the FOMBR, the temperature difference was increased to 25°C. When the cross flow velocity was kept constant, the MD flux increased significantly with increasing temperature. Low grade waste heat from industry can potentially be utilised for the FO-MD process. The increase in flux was higher for NaCl and TEAB (60-80%) when compared to PDAC (20-50%), as the temperature difference increased to 35°C. A greater feed flow velocity increased the turbulence in the flow channel, and increased the MD flux. Up to a 60% increase in flux was observed when the feed velocity was increased from 0.12 to 0.17m/s, while the increase in flux was not as high when the flow was increased from 0.17 to 0.21m/s and thus 0.17m/s was chosen as the cross- flow velocity for MD. Higher feed concentrations tended to reduce vapour pressures and hence decreased the MD water fluxes.

The flux for FO-MBR and MD were well balanced for lower molecular weight draw solutes, but lower FO fluxes were observed for higher molecular weight draw solutes (TEAB, PDAC). This greater imbalance reflected their lower diffusivities and greater tendencies toward concentration polarization. Reverse solute transport (RST) values leading to salinity or toxicity were not reflected by the observations, and therefore it was feasible to run an FOMBR-MD Hybrid for extended times. However, a greater decline in flux versus time was observed for NaCl than for TEAB. PDAC showed the lowest but most stable flux, and a lesser fouling tendency compared to that of TEAB. Overall, The FO-MD hybrid enabled pure water production and a non-volatile component rejection of nearly 99%, with an RST of <0.1 GMH for the draw solutions back to the FO feed and a much lower solute transport from the MD feed to the permeate. NaCl and other low molecular weight solutes are recommended when high fluxes and system stability are priorities and where high reverse solute transport (RST), leading to salinity or solute toxicity in the MBR feed tank, is not an issue. Higher molecular weight solutes, such as TEAB or PDAC, are recommended when high flux is less critical and when the sensitivity of the microbial consortium to RST and solute toxicity is a concern. In all cases, some degree of process control is recommended in order to bring the systems more quickly to a stable operating state; periodic membrane cleaning is deemed necessary to maintain this state.

Key words: Tetraethyl ammonium bromide (TEAB), Polydiallyldimethylammonium chloride (PDAC), Water flux, FO-MBR, FO-MBR MD hybrid, Draw solute regeneration, Water reclamation.

1 Introduction

FO-MD is a membrane-based hybrid technology, consisting of FO and MD units where FO draws clean water from a feed such as wastewater and MD re-concentrates the diluted draw solution. This integration provides high product water quality (as the membrane only allows water vapours to pass through), low fouling tendency (because of the membrane being hydrophobic) and the potential utilization of low-grade, industrial waste heat due to the potential for vapour formation at lower temperatures (Ge et al., 2012). Although the FO-MD hybrid has been studied for the concentration of protein solutions (Wang et al., 2007), olive mill wastewater treatment (El-Abbasi et al., 2013), dye wastewater treatment and sewer mining wastewater (Xie et al., 2013), detailed studies on the use of FO-MD for municipal wastewater treatment using novel draw solutions (as opposed to more conventional ones, such as inorganic salts) is rather scarce. The FO-MD hybrid can be an option for water reclamation compared to pressure intensive membrane filtration systems, as it has demonstrated higher and more stable flux and resulted in a high-quality product water (El-Abbasi et al., 2013; Xie et al., 2013). Hybrid setups other than FO-MD require an additional pressure driven system such as nanofiltration (NF), ultrafiltration (UF) or reverse osmosis (RO), which are energy intensive, some have been summarised in **Table 1**.

Table 1. Summary of hybrid FO–MD, FO-NF, and FO-RO processes with different draw solutes, adapted from, (Wang et al., 2015)

Hybrid process	**Feed and draw solute**	**Application**	**FO/MD flux (LMH)**	**Remarks**	**Reference**
FO-MD	2-methylimidazole-based compounds	Desalination	11/7 (Feed: DI water) (MD at 70 °C)	(1) Low reverse draw solute leakage.	Yen et al., 2010
FO-MD	NaCl	Protein concentration	7–9/17 (Feed: Protein solution) (MD at 60 °C)	(1) High water flux; (2)High reverse draw solute leakage	Wang et al., 2011
FO-MD	Polyelectrolytes	Treatment of dye-containing wastewater.	15-38/9-23 (Feed: Dye-containing wastewater) (MD at 80 °C)	(1) Excellent dye rejection; (2)Viscosity increases rapidly with concentration; (3) Potential fouling of MD membranes.	Ge et al., 2012

FO-MD	NaCl	Treatment of sewer mining wastewater	4-8/4-8 (Feed: Sewer mining wastewater) (MD at 40 °C)	(1) ~80% water recovery; (2)Additional granular activated carbon adsorption or ultraviolet oxidation was required to remove the accumulated trace organic contaminants (TrOC).	Xie et al., 2013
FO-MD	$MgCl_2$	Extraction of orthophosphate and ammonium from anaerobically digested sludge	4-10/5-8 (Feed: Anaerobically digested sludge) (MD at 40 °C)	(1) Excellent rejection (2) Accelerated membrane fouling.	Xie et al., 2014
FO-MD	Thermo-responsive co-polymer	Seawater desalination	4/2.7 (Feed: Seawater) (MD at 60 °C)	(1) High FO flux/Low reverse salt flux; (2) Potential risk for membrane fouling.	Zhao et al., 2012
FO-MD	Na_5Fe–CA	Seawater and brackish water desalination	19.2/32 (Feed: DI water) 3.9-6/32 (Feed: Seawater) (MD at 60 °C)	(1) High FO flux/Low reverse salt flux; (2) Low risk for membrane fouling.	Wang et al., 2015
FO-NF	0.8 M NaCl	Tannery wastewater	52-55 LMH at 1.6 bar pressure : Draw solution recovery/ recycling, 12 bar (700L/h)	Rejection: 98.5% of COD 97.2% of Cl 98.2% of Sulphides	Pal et al., 2017
FO-RO	Seawater after UF	coal fired power plant wastewater	Average flux 10.6 LMH, 2 bar transfer pump: RO had an applied pressure of 60 par	FO-RO energy use was 15% less than that of RO; Water recovery rate was fixed at 55%	Choi et al., 2017
FO-MD	4.82M NaCl	Landfill leachate	Flux: 4.65 LMH; temperature of inlet MD, 72.5°C for salt concentration of 60,000 mg/l and 62.5 °C for	Salt rejection rate: 96% TN and TOC rejection rate: 98%	Zhou et al., 2017

			25,000 mg/l NaCl		
FO-MD	NaCl	Dairy wastewater	9.79 LMH	The drop in flux was higher for dairy wastewater compared to DI water due to membrane fouling	Song et al., 2017
FO-MD	20% TDS hypersaline brine	Grain processing wastewater	15 LMH	Brine draw solution outperformed a 20% $MgSO_4$ draw solution due to higher osmotic pressure and a 60% higher water flux	Salih & Dastgheib, 2017
FO-MD	0.5 M TEAB, NaCl and 0.44 M PDAC	Synthetic mucinipal wastewater with a monoculture (*B. subtilis*)	Tested with DI water Wastewater as a food for a period of 3-7 days FO-MD flux: 6-8 LMH FOMBR-MD flux: 2-7 LMH MD at 45°C	> 99% rejection for all the draw solutions that entered the MD as a feed	Current study

FO hybrid systems offer many advantages over running FO or other membrane filtration systems on their own. A study (Xie et al., 2013) claims that such systems can take advantage of the low FO fouling propensity (however, this point is debatable as higher fluxes may lead to cake formation) to pre-treat the feed prior to further treatment by RO, NF, UF or MD. Another advantage of these hybrid systems is that they provide a double barrier to the feed (in terms of contaminants, microorganisms etc.) and therefore ensure high quality product water. Other recovery media, such as magnetic fields and heat, are very specific to suitable draw solutes. Wu et al., studied rejection of Hg, Cd, and Pb and the effect of coexisting metals on Hg removal through Forward Osmosis (FO) and Membrane Distillation (MD) (Wu et al., 2017). More than 97% rejection for each metal was achieved through the FO system. It was observed that Hg^{2+} rejection increased with increase in the concentration of the coexisting metals. Approximately 1–10 ppb Hg from the feed solution transported into the draw solution due to permeation. An FO–MD hybrid system was set in place to allow for complete removal of the heavy metals. Approximately 100% rejection of Hg^{2+} was achieved and a stable water flux was observed.

On the other hand, the term ‘low energy consumption’, long associated with FO systems, is only valid when the regeneration systems are not required or applied. The challenge now facing FO is that the use of FO hybrid systems to allow the regeneration increases the capital cost as well as the energy demand of the overall system (Chekli et al., 2016).

Research on performance efficiency is previously reported (Parveen & Hankins, 2019). In this paper the focus is more on Hybrid systems and their use in wastewater treatment. Research shows that the performance of FO and FO hybrids decline with time, which is said to be caused due to concentration polarisation (CP) and membrane fouling. Therefore, current research on FO membranes is focused on the development of membranes with antifouling capability, such as hydrogel membranes (Li et al., 2017, Huang et al., 2014). The actual growth in the application of membrane technologies for water treatment in general lies far behind that which was initially projected. One of the major obstacles which remains is the decrease in filtration performance with time (Abdelrasoul et al., 2013). The main causes for the reduction in membrane flux can be separated into concentration polarization and fouling. Concentration polarization leads to an accumulation of particles or solute molecules on the boundary layer adjacent to the membrane surface. Fouling is the build-up of material on or in the membrane surface, and may arise in the form of adsorption, pore blockage, deposition or gel formation (Field, 2010).

Although tested extensively on the bench scale, large scale applications for these systems require expertise in operation and are therefore far from being commercial. Most of the work carried out on bench scale for FO use the same simple inorganic draws such as NaCl and $MgCl_2$ while the feed often remains to be DI water (**Table 2**).

Although membrane fouling in FO has been reported by some workers to be less detrimental and more reversible as compared to RO, it is still one of the major draw backs for implementation of the FO process (Li et al., 2017). Various techniques have been used for fouling analysis in FO. In one study, fouling analysis for forward osmosis has been performed using membrane autopsy, and involved dissection of the membrane to check deposited foulants and surface properties (Darton et al., 2004). Atomic force microscopy (AFM) has also been used for interfacial force measurements between foulants, and between foulants and membrane (Mi & Elimelech, 2010). Mass spectroscopy and ion chromatography (Tijing et al., 2015) have also been used for anion and cation detection in membrane samples. Similarly, X-ray spectroscopy has been used to determine the elemental composition of the fouling layer. These techniques are coupled with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) for imaging and further analysis (Li et al., 2012). For biofouling, the biofilm has been characterised using a direct bacterial count and total organic carbon (TOC) content. Confocal lens microscopy has also been used to record the morphology and thickness of the film (Kwan et al., 2015).

The research to-date on FO fouling has mainly focused on organic fouling of the membrane. The organic fouling is caused by organic macromolecules, such as humic acid, or biopolymers such as proteins (Kwan et al., 2015; Motsa et al., 2014). Alongside the foulant itself, fouling is also highly dependent upon the membrane surface properties and the hydrodynamic conditions under which the membrane is being used (Kwan et al., 2015).

Fouling is also one of the major obstacles in the application of MD (Srisurichan et al., 2005). Fouling causes a progressive wettability of a membrane (El-bourawi et al., 2006) such that the aqueous liquid phase can penetrate the membrane pores and contaminate the permeate. Membrane cleaning is the major technique used to control fouling in MD, particularly for the most commonly used form, direct contact membrane distillation (DCMD) (Gryta, 2006; Srisurichan et al., 2005). It is desirable for the feed water to be pre-treated for fouling control in MD applications. The degree of pre-treatment depends on the nature of the feed solution, the membrane in place, the quality of the product water, and the frequency of the subsequent membrane cleaning (Motsa et al., 2014; Gryta, 2005; Karakulski & Gryta, 2005; Karakulski et al., 2002).

The feed temperature is an important parameter in the membrane distillation process, as it controls the rate of vapour formation. The permeate production rate is proportional to the vapour pressure difference between feed and permeate and increasing the feed temperature will increase the permeate production rate. When the feed temperature and temperature difference across the membrane is low, the vapour pressure at the feed side has a direct linear relationship with the temperature difference across the membrane (Khayat & Matsuura, 2011, Martinez-Diez & Vaquez-Gonzalez, 1999).

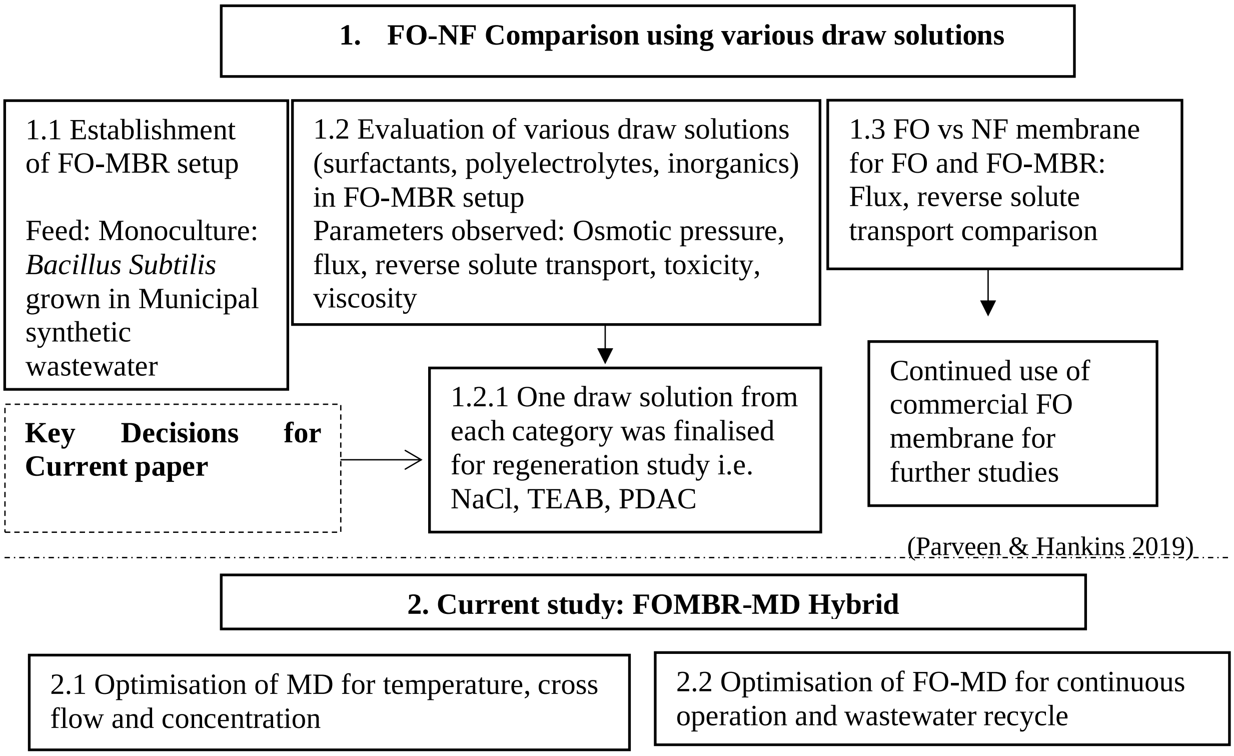
Nearly all studies on MD confirm (Rashid & Rahman, 2016) the positive relationship between an increase in flux and an increase in temperature. For the latter study, at a permeate temperature of 20°C and the varying feed temperatures of 40, 50, 60 and 70°C, the flux increased to 6.5, 8, 10 and 15 kg/m^{2}hr respectively when the cross-flow rate was kept at 0.6 L/min. It was also shown that when the temperature difference was decreased by increasing the permeate temperature, the overall flux then decreased. Thus, the feed temperature should be increased to a level that is easy to handle and can be maintained so that adequate mass transfer can take place across the membrane. The surface tension and viscosity of the feed solution affects the pore wetting and may result in contamination of the permeate by the feed (Chemical Rubber Co, 1970); such leakage is thus a greater potential problem at higher temperatures.

Table 2 Summary of Operating conditions, performance, structural parameter, water and solute permeability for FO membranes adapted from (Kim et al., 2017)

Draw solution	**Feed solution**	**Membrane**	**Water flux, LMH**	**Solute flux, GMH**	**Membrane orientation**	**Ref.**
1.0 M NaCl	DI water	Thin film composite (TFC)	31.1	8.50	AL-FS	Liu & Ng, 2014
1.5 M NaCl	DI water	TFC with lignin additive	27.6	-	AL-FS	Vilakati et al., 2014
2.0 M NaCl	DI water	TFC	11.8	2.5	AL-FS	Luo et al., 2014
1.0 M NaCl	DI water	TFC-nano fiber	15.0	0.5	AL-FS	Huang & McCutcheon, 2014
0.5 M $MgCl_2$	DI water	Silica gel–polyacrylonitrile SG-PAN	28.6	5.8 g/L	AL-FS	Lee et al., 2014
0.5 M NaCl	DI water	Nano TFC	27.24	–	AL-FS	Puguan et al., 2014
0.5 M NaCl	0.01 M NaCl	Thin film nanocomposite (TFN)	17.1	3.97	AL-FS	Emadzadeh et al., 2013
2.0 M NaCl	DI water	TFI (Inorganic)	60.3	11.4	AL-FS	You et al., 2013
0.5 M NaCl	DI water	PSf N-TFC (polysulfone)	21	12.6	AL-FS	Ma et al., 2013
0.5 M NaCl	DI water	TFC-sPPSU (sulfonated polyphenylenesulfone)	22.51	5.49	AL-FS	Zhong et al., 2013

1.5 M NaCl	DI water	Nylon-TFC	6	1	AL-FS	Huang & McCutcheon, 2014
0.5 M $MgCl_2$	DI water	poly(amide-imide) - polyethersulfone - polyethyleneimine PAI-PES/PEI	20.8	6.448	AL-FS	Setiawan et al., 2013
0.1 M $MgCl_2$	DI water	Layer by layer (LbL)	20.66	0.138 g/L	AL-FS	Liu et al., 2013
2.0 M NaCl	DI water	TFC-PES	32.1	6.15	AL-FS	Sukipaneerit & Chung, 2012
0.5 M $MgCl_2$	DI water	LbL	8	16.8	AL-DS	Su et al., 2012
1.0 M $MgCl_2$	DI water	LbL	28.7	17.136	AL-FS	Saren et al., 2011
3.0 M NaCl	DI water	PES	30	8.766	AL-FS	Liu &Ng, 2014

The overall aim of the current work was to perform an engineering-oriented study of the component parts and integrated operation of a continuous and feasible FOMBR-MD system. Therefore, an MD setup was established at bench scale and optimized for reconcentrating the draw solution continuously to produce clean water downstream of the FOMBR. This hybrid setup was used to develop a continuous and self-regenerating FOMBR-MD system to study flux, permeate quality, the reverse transport of solute, toxicity, and fouling of the membrane over a week, representing the longer term observation. None of the studies conducted on such systems has been observed continuously for a longer period of time. Therefore, this study will help future research in looking at the issues and challenges associated with such operations.



Parameters observed: Flux for FO and MD, permeate quality in MD, Membrane cleaning

Based on performance all draw solutions finalised in 1.2.1 were studied further for FOMBR-MD continuous hybrid for treatment of wastewater.

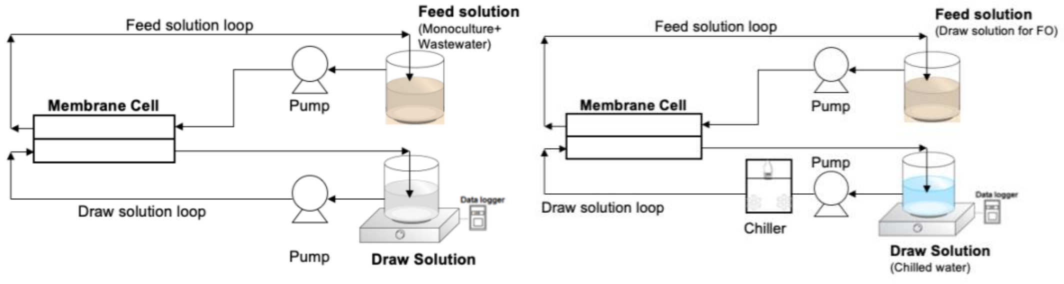
Feasibility study for scaling up the system

Figure 1: Summary of work presented previously and its contribution to current work

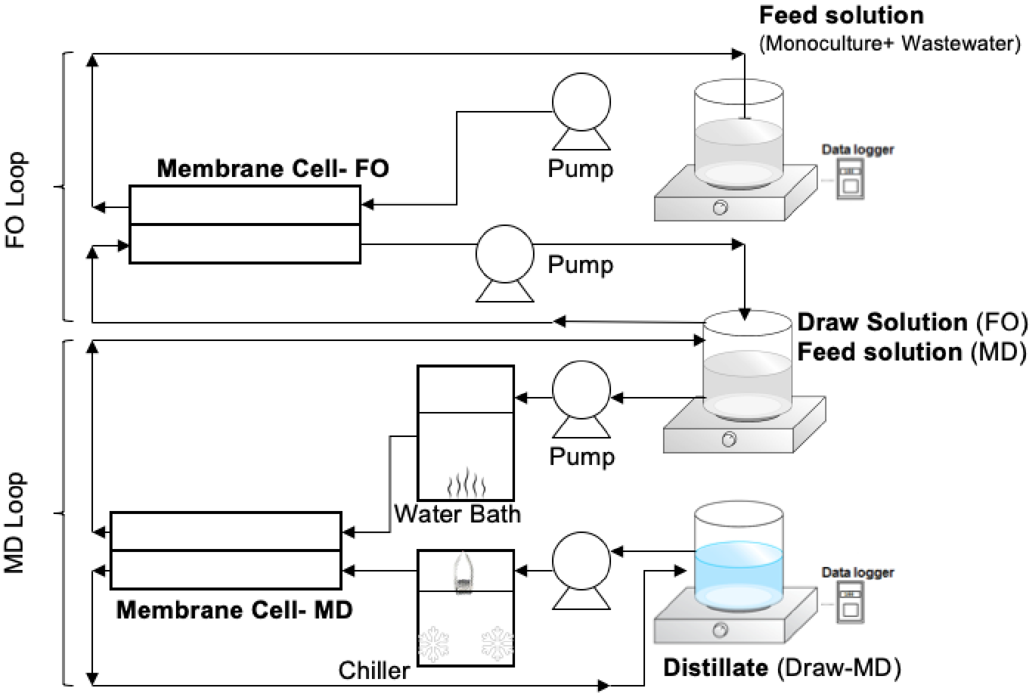
Methodology

2.1 Chemicals and Membranes

The selected draw solutes (NaCl –inorganic/baseline, PDAC-polyelectrolyte, TEAB-surfactant) and their performance in FO-MBR have previously been presented (Parveen & Hankins, 2019). The membrane module for MD was purchased from Membrane Solutions (Shanghai, China). The hydrophobic membrane was made of Polytetrafluoroethylene (PTFE) with a Polypropylene (PP) woven support layer and had a pore size of 0.22μm and nearly 100% rejection to water. The cellulose triacetate (CTA) HTI membrane for FO, already tested in previous work (Parveen & Hankins, 2019), was used in these FO-MD hybrid studies. A summary of the work done and follow up work in the current paper is presented in **Figure 1 and 2.**



(a) (b)



(c)

Figure 2: Setups established to develop an FOMBR-MD hybrid; (a) FO-MBR (Parveen and Hankins., 2019), b) MD setup, c) FOMBR- MD hybrid

2.2 Benchscale Setup

Both setups (FO and MD) principally consisted of a flat sheet membrane module fitted into an acrylic membrane cell (**Figure 2**, **a and b**) similar to those presented previously (Wang et al., 2015). The effective surface area of the membrane was 36 cm^2 for MD and 47.25 cm^2 for FO. Water flux was calculated for both setups. The draw solution exiting the FO was the feed for the MD (**Figure 2, c**). Initially, the membrane cell for FO had a DI water feed loop and the draw solution loop faced the active layer (AL). For MD, this same draw solution entered the MD feed loop, which faced the AL side of the membrane and was immersed in a water bath (Grant, UK) to control its temperature; the permeate loop, which was immersed in the chiller (Grant, UK) to control its temperature, was facing the support layer (SL) of the MD membrane.

Each loop was provided with a circulation pump (Longer pump, China). For the MD unit, the water bath and chiller were connected to pumps (Longer Pump, China) that circulated the feed and permeate streams co-currently within the membrane cell. Conductivity for the permeate and feed was measured using a conductivity meter (YSI, USA), and this was converted into solute concentration by plotting a standard calibration curve for conductivity of a solute against concentration.

2.3 FO-MD Hybrid Experiments

For MD, a preliminary experiment was performed using DI water as both a distilland (feed - at warm temperature) and a distillate (permeate - at cold temperature). Direct contact membrane distillation (DCMD) experiments were then conducted in batch mode, which resulted in the re-concentration of the feed (the diluted FO draw) solution and produced clean water (for which conductivity was measured) in the permeate stream. Temperature differences of 15 degrees (feed temperature at 35°C and permeate temperature at 20°C), 25 degrees (feed temperature at 45°C and permeate temperature at 20°C) and 35 degrees (feed temperature at 55°C and permeate temperature at 20°C) were chosen for optimisation of the MD process. A lower temperature difference was preferable for final operation based on the principle that low-grade waste heat is available on-site in many industrial sites or in homes, and is thus convenient to use for membrane distillation, as is solar power (Qtaishat & Banat, 2012; Chang et al., 2010).

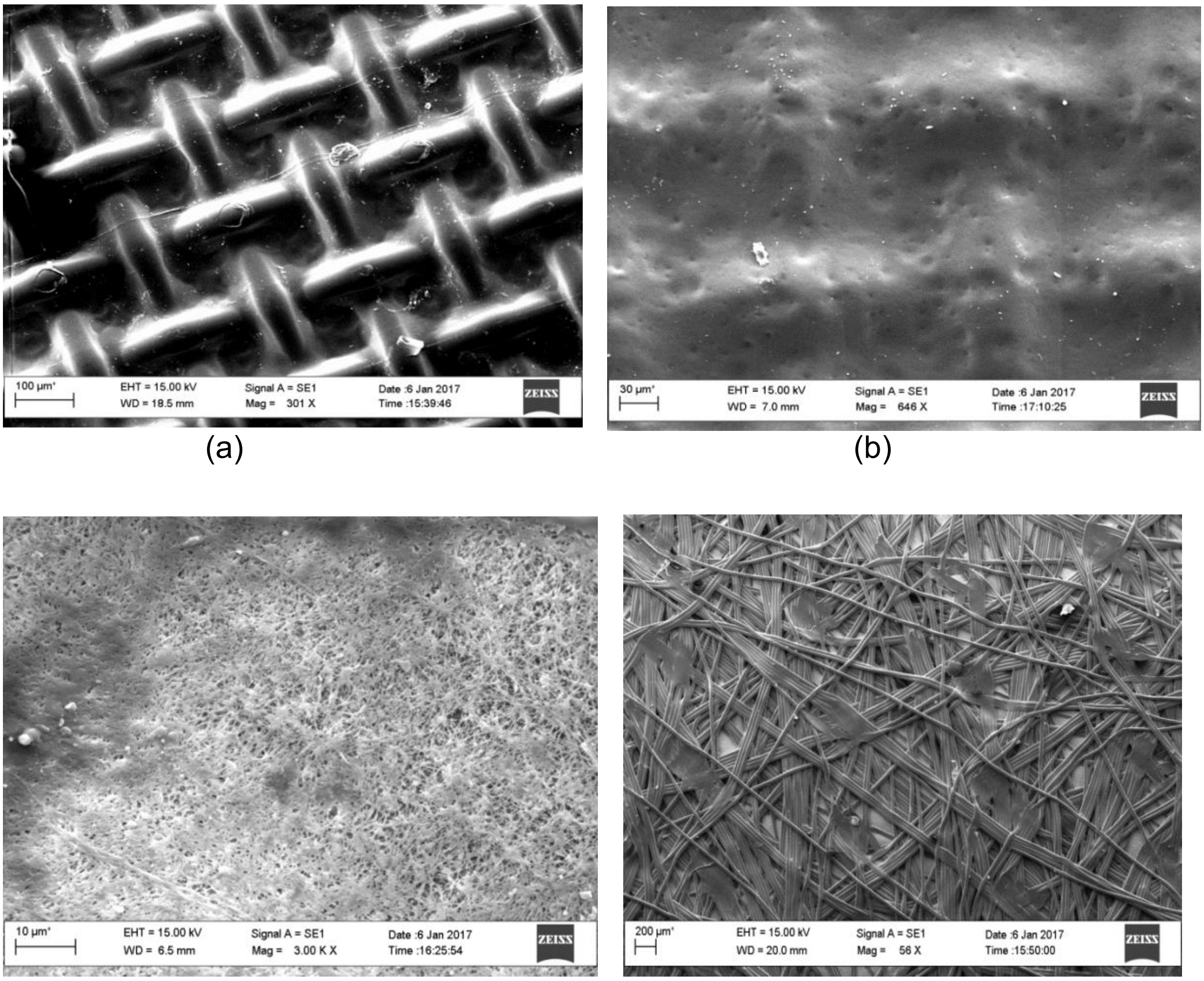
Three different flow-rates (0.12, 0.17, and 0.21 m/s) were tested for cross-flow velocity optimisation. The various draw solutions which had been studied in detail previously for a forward osmosis process (Parveen & Hankins, 2019) were tested for the performance of the DCMD process. The draw solutes included TEAB, PDAC, and NaCl. These draw solutes were dissolved in DI water to formulate the initial draw solutions, all at a concentration of 0.44 - 0.5M. The experiments were run over several days (3-7) to understand the effects of draw solute dilution and concentration polarization on the flux of the FO and MD membranes. Note that for simple FO the membrane orientation was AL-DS; this latter was because DI water was used as feed for these optimisation experiments, and thus internal concentration polarisation in the support layer would be negligible.

2.4 FOMBR-MD Hybrid

The FOMBR hybrid was run for the same draw solutes using the same optimised conditions as presented previously in section 2.3. In short, the same membranes had first been used for the FO-MD process; the feed had been DI water, and was now biological feed in the FOMBR-MD hybrid. The membranes were then cleaned using various cleaning agents, and observed under the microscope to make further conclusions; since the post-experiment membranes were cut into pieces to perform the microscopic observation, the flux after cleaning was not observed.

Biological feed with synthetic wastewater and a *B.subtilis* inoculum was set in place for the MBR. The feed was topped up with synthetic wastewater and autoclaved DI water daily during long-term operation. Bacterial count of the feed was taken daily to check the health of bacteria after fresh food addition and under the effect of possible reverse solute transport (RST). A temperature difference of 25 degrees (feed temperature at 45°C and permeate temperature at 20°C) was chosen for the FOMBR-MD hybrid.

For SEM imaging, membrane samples were dried. Appropriate size samples were cut so they could be fixed onto a specimen holder (stub) to be placed in the SEM chamber. The surface to be analysed was mounted upwards on the aluminium, SEM stub. A Scanning Electron Microscope (Carl Zeiss Evo LS15 VP, with SE (secondary electrons) detector was used for imaging at varying working distances.



(a) (b)

(c) (d)

Figure 3 SEM images for a nascent forward osmosis cellulose triacetate membrane (a) Active layer (b) Support layer, and a PTFE MD membrane (c) Active layer (d) Support layer

The samples were gold coated beforehand for better quality imaging, using a SC7620 Mini Sputter Coater. It contained an Au/Pd insert and a plasma current of 18mA; with a coating time of 120s, it gave a thickness of 10nm. Images for nascent membranes are given in **Figure 3**

3 Results and Discussion

3.1 Establishment of MD setup

3.1.1 Effect of Temperature on MD Flux

The draw solutions NaCl (0.5M), PDAC (0.44M) and TEAB (0.5M) were tested against the three temperature differences at a cross flow velocity of 0.12m/s, and the results are shown in **Figure 4**.

MD involves simultaneous heat and mass transfer processes, and therefore heat and mass transfer profiles are involved simultaneously, as shown in **Figure 5.**

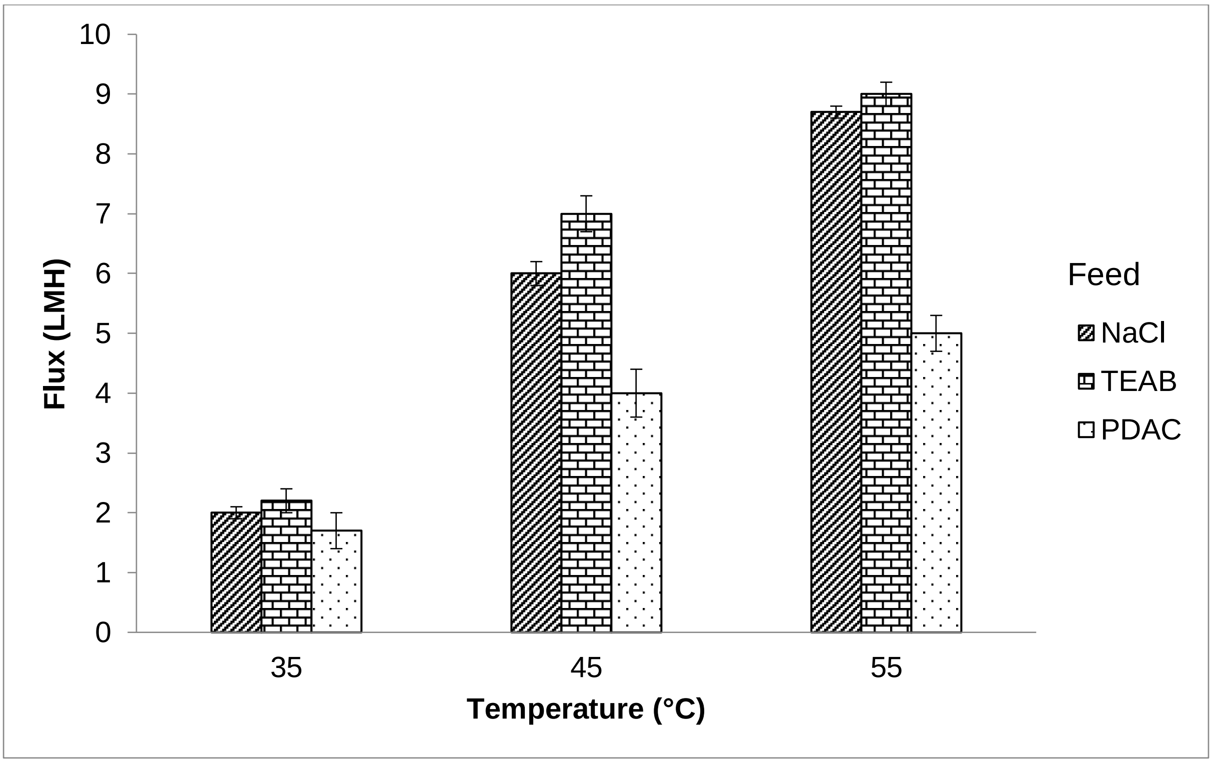


Figure 4 MD water flux at different temperatures with CFV of 0.12 m/s at feed temperatures of 35°C, 45°C and 55°C and a draw temperature of 20°C, respectively (AL-FS mode).

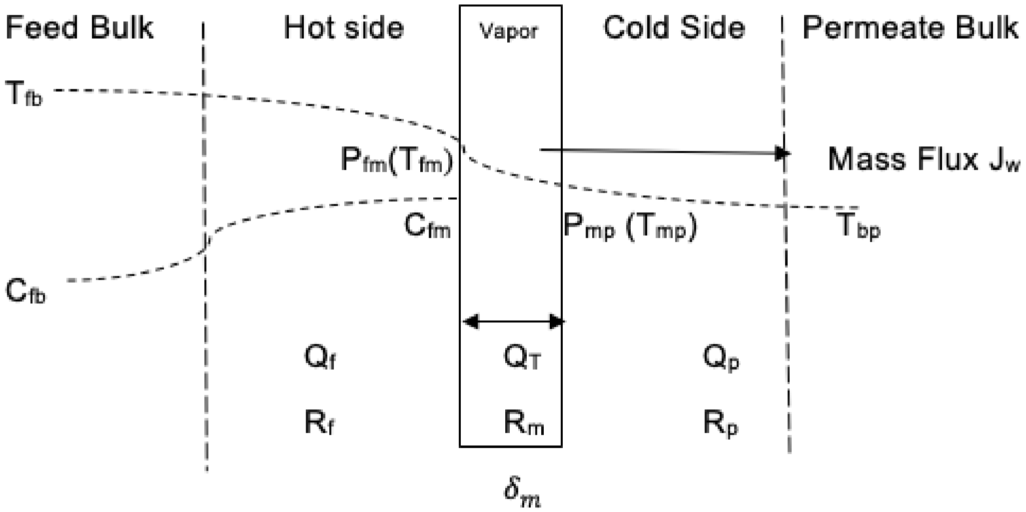


Figure 5 Heat and mass transfer profiles during membrane distillation

It was observed that, as the feed temperature increased, the MD flux increased significantly; as expected over the modest temperature range, the flux increases were approximately linear with the temperature difference increases (from 15 to 25 to 35°C). A small fluctuation in the heating temperature was observed; it was caused by an inefficient internal temperature controlling system. Nevertheless, the small oscillation did not influence the overall results, as the mean values were almost constant. It is also worth noting that the extra heating demand at higher temperature increases the power consumption in the heating bath.

The increase in temperature may also increase the forward transport of the solutes in the feed solution by increasing the fluid-phase movement of these molecules, due to wetting of the membrane (the latter because of an increase in diffusion with temperature). In the current studies, conductivity in the permeate (at 20ºC) increased as the feed temperature was increased, indicating a solute leakage across the membrane. In addition to the availability of waste-heat at low temperature, this is another reason for preferring a lower temperature difference for the FO-MD hybrid.

In terms of the safety and permissibility of the draw solutes, PDAC is used in drinking water as a coagulant and is not considered a hazard either by contact or ingestion. It is also important to note that, as a part of the manufacturing process, NaCl is a constituent of the PDAC product solution. There are currently no permissible limits for PDAC in drinking water, but there are references to a regulated residual concentration of 50µg/L (NSF, 2002). Similarly, the limits for TEAB in drinking water are not defined. Note, however, that food-grade (i.e. consumable in small quantity) surfactants are available as an alternative to non-food grade surfactants. NaCl is commonly found in drinking water but the WHO suggests that adults should limit their potable water sodium consumption to 2g per day.

3.1.2 Effect of Feed Cross-Flow Velocity on MD Flux

Optimization of the MD process with respect to temperature is not straight-forward because temperature polarization is a non-linear process and thus difficult to predict. In addition, because of concentration polarization, cross flow velocity and the concentration of the feed must also be considered during optimisation. Therefore, various feed cross-flow velocities

(0.12, 0.17, and 0.21m/s) were tested to optimize the feed cross-flow velocity for the MD process. The results of this experiment are shown in **Figure 6.**

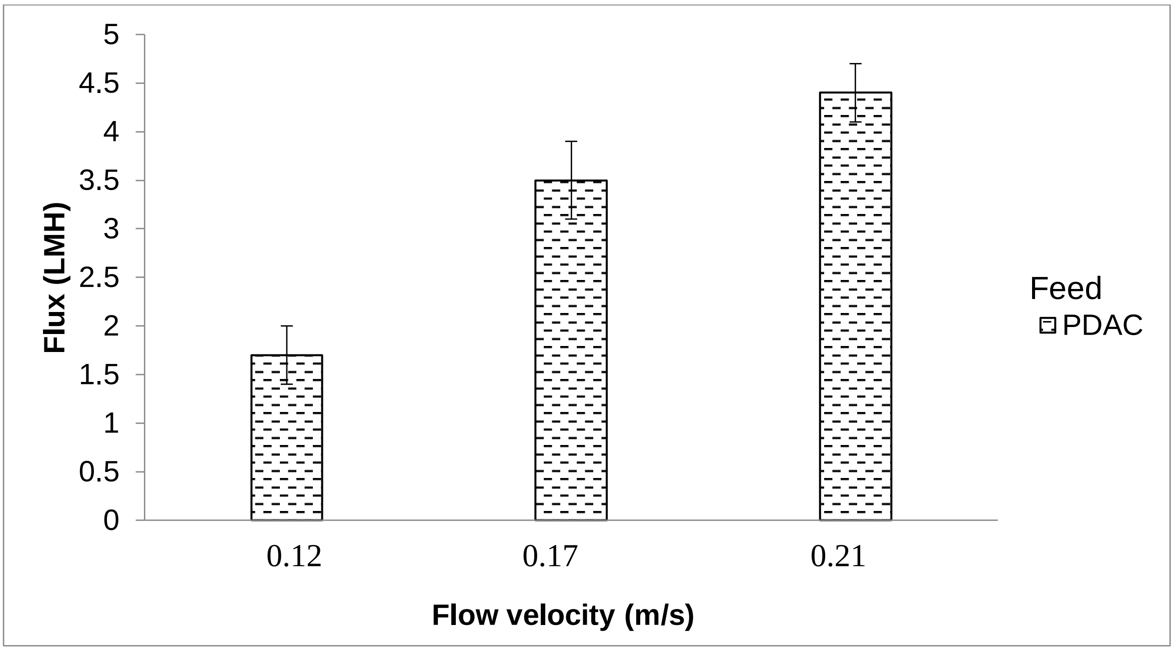


Figure 6 Effect of Feed cross-flow velocity on flux performance with the feed temperature at 35°C using PDAC as MD feed (AL-FS mode)

A large feed flow-rate and hence cross flow-velocity will increase the turbulence in the flow channel, decrease the thickness of the temperature and concentration boundary layers, and thus enhance the heat and mass transfer. Normally, a higher feed flow rate will lead to a higher flux rate. In the current study, a 60% increase in permeate flux was observed as feed flow velocity was increased from 0.12 to 0.17m/s (42 %); however, there was a minimal increase in fluxes between feed flow rates of 0.17 and 0.21m/s (30%), so the effect of cross-flow velocity approached an asymptote. It was apparent that while the feed temperature had a steady influence on the permeate flux, the feed flow velocity had a declining effect. Nevertheless, the effect of the velocity should not be ignored, particularly at low values (Martinez-Diez & Vaquez-Gonzalez, 1999).

Dimensionless correlations for heat and mass transfer generally involve power-law relationships with Reynold’s number of fractional index. Increasing the feed velocity results in an increase in the Reynolds number, which decreases the mass and heat transfer boundary layer thickness and increases the mass and heat transfer coefficients (Boubakri et al., 2014) but at a slower than linear rate of increase.

3.1.3. Effect of Feed (Draw Solute) Type and Concentration on MD Flux

Like temperature polarization, concentration polarization also leads to a reduced effective driving force for transport. Concentration polarization is primarily governed by the flux level. Concentration polarization at a membrane surface is quantified using the parameter ς and is presented in equation 1 for a feed to the membrane:

$$\varsigma = \frac{C_{mf}}{C_{bf}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where, C_{mf} and C_{bf} are the feed concentration at the membrane surface and the bulk, respectively (Martinez-Diez & Vaquez-Gonzalez, 1999).

Since the feed for the MD unit in the FO-MD hybrid is the diluted draw solution exiting from the FO unit, the effect of feed concentration for MD was also studied in the current study. The FO flux was high for simple draw solutes such as NaCl (2.1LMH), followed by slightly lower values for TEAB (1.9LMH) and then PDAC (1.8LMH) using AL-DS mode at 0.12m/s.

An increase in concentration of the solute in the feed can slightly decrease the heat transfer coefficient; at higher solute concentrations, the solution becomes more viscous and the thermal conductivity also becomes lower and reduces the convective heat transfer. Slower rates of heat transfer from bulk flow to the membrane surface increase the temperature polarization.

An increased solute concentration will also lower the effective vapour pressure of water. The vapour pressure of a non-volatile solution is governed by Raoult's law, given in equation 2:

$$P_{solution} = (X_{solvent})\ (P^{\circ}_{solvent}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

where P is the vapour pressure, $X_{solvent}$ is the mole fraction of the solvent and P° is the vapour pressure of the pure solvent. In this work, water was used as a solvent and has a vapour pressure of 3.16 KPa at room temperature, while 0.5 M NaCl solution has a vapour pressure of 2.6 KPa (the room temperature in the lab was regulated at 25°C).

In a previous study (Boubakri et al., 2014), NaCl solution was used as an MD feed and it was shown that the fluxes reduced significantly compared to when only distilled water was used as a feed. Feed fluxes for NaCl solutions between 4.5 and 10 wt% have been studied (Naidu et al., 2017) and the study demonstrated that permeate flux decreased with increasing concentration. This was attributed to a reduction in the driving force to transport the vapour through the membrane pores. This study also showed that an addition of $MgCl_2$ and $MgSO_4$ had an additional fouling tendency on the PTFE membrane. Nevertheless, the PTFE membrane was used in the current study and has been reported for its durability and higher solute rejection compared to that of polyvinylidene fluoride (PVDF), which is the second most widely used MD membrane (Cheng et al., 2010).

3.2 Performance of FO-MD Hybrid with the Draw Solutions

FO-MD hybrid results with DI water as a feed solution are presented in **Figures 7, 8 and 9.** As noted previously, relatively simple draw solutes such as NaCl, which are more soluble at a higher temperature and give rise to a higher osmotic flux, also lead to a greater lowering of vapour pressure at higher concentration (and vice versa). As a consequence, when these draw solutes become more dilute because of the drawn FO flux, the MD flux on the other side of the draw tank tends to increase, leading to reconcentration of the draw solution. Consequently, the rate at which water is drawn from the draw solution as MD permeate tends to track and balance the rate at which it is drawn from the FO feed (note a similar self-correct mechanism occurs if there is a change in feed solution concentration; an increase/decrease in osmotic driving force will change the FO flux from the feed tank and thus change the draw tank concentration in the direction of a decrease/increase (respectively) in osmotic driving force). However, it was observed that the fluxes were much less balanced with the higher molecular weight draw solutes TEAB and PDAC; in these cases, the MD flux was always higher. This was partly due to the lower associated FO fluxes, but they demonstrated a much lower level of the tendency to self-balance observed with the NaCl.

The decline in FO flux for NaCl as draw solute, as presented in **Figure 7,** indicates that the fouling in the FO membrane is significant; in the present case with draw regeneration, and since FO and MD fluxes are fairly balanced, the dilution is not at all significant and cannot explain the flux decline. The MD flux, on the other hand seems somewhat more stable, and the percentage decline in flux is lower for MD as compared to FO.

The steadier flux for MD may have been because the temperature of the latter process was more carefully controlled. It should be noted that, over the days of the experiment, controlling the temperature at a steady value using the water bath and chiller was not straightforward due to changes in both the ambient temperature and the water level decrease in the water bath (due to evaporation). Because of this, some variation in fluxes can be expected. The MD flux suggests that a change in temperature during the operation of a continuously running experimental setup may affect the flux, but not as severely as for FO. The temperature fluctuates but the magnitude of this wasn't measured in the current study.

The fluxes observed throughout a single day were very stable, and a decline of less than 25% in flux was observed even after the end of three days of operation. It would certainly be recommended that the membranes be cleaned at the end of daily operation or at least after two days of operation, in order to keep them clean and to avoid the effects of membrane fouling which apparently leads to a steady decline in flux.

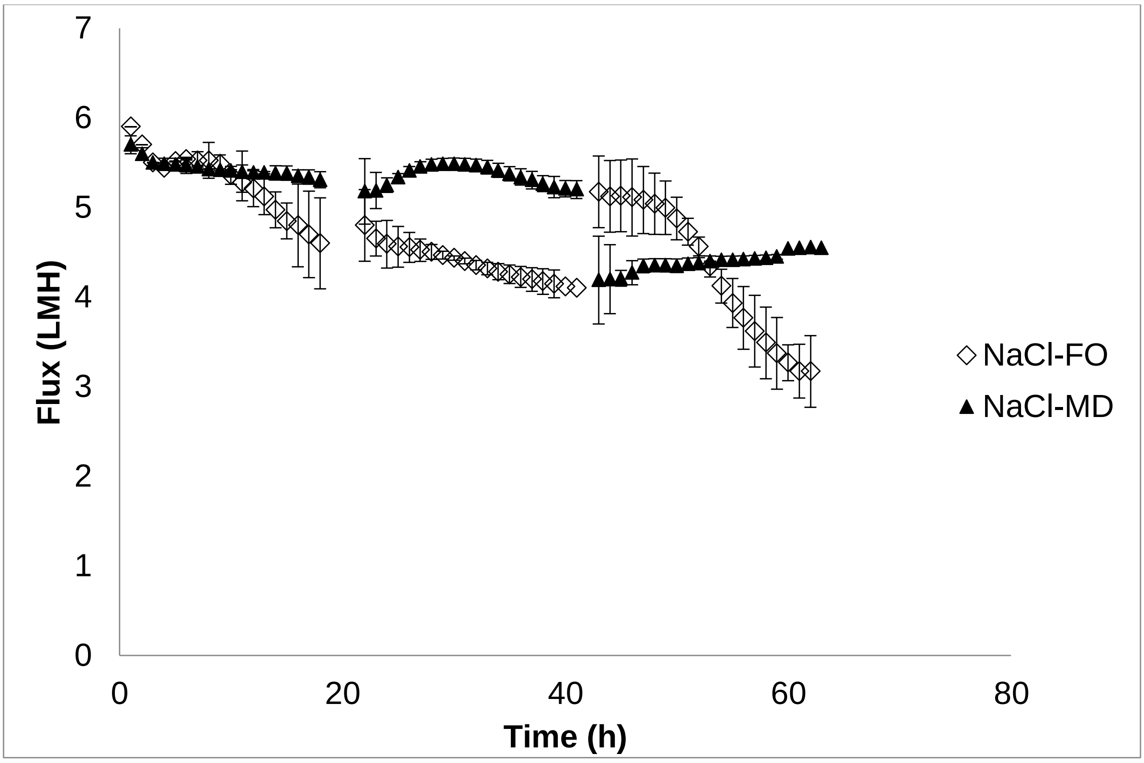


Figure 7 MD and FO flux over three days with NaCl as a draw solution and DI water as a feed at a CFV of 0.12m/s (FO: AL-DS, MD: AL-FS)

An increase in temperature increases the solubility of the draw solution; however, due to the increase in diffusion and Brownian motion, the solute molecules and ions are more likely to diffuse across the membrane as compared to the case with no heating system in place for the draw solution (note that the same heated draw solution enters both FO and MD loops). The RST for NaCl was also linked in part with a decline in flux; the FO feed becomes more concentrated due to both FO flux and RST, causing a decline in the driving force for FO.

On the other hand, the MD solute concentration in the permeate remained very low. Up until the end of day three of operations, only 0.1GMH (g/m^2h) was lost. There results show that neither FO nor MD membranes are able to demonstrate 100% rejection for the NaCl draw solute ions, but the FO unit performs far worse in this regard. For this reason, it is thus appropriate to consider and evaluate higher molecular weight draw solutes; one can reasonably expect their rates of diffusion and RST to be lower.

Literature suggests that the Na^+ ion has a covalent radius of 0.157nm and an ionic radius of 0.095nm, while the Cl^- ion has a covalent radius of 0.099nm and an ionic radius of 0.181nm. As these ions are very small in size, and since the MD membranes have a porosity which is on the microscale (0.1-0.22μm), their permeation into some, if not all, membrane pores is highly likely upon wetting. The draw solutes could then readily diffuse or even leak into the permeate. Therefore, the experimental setup should always be monitored for any wetting changes by continuous permeate conductivity monitoring. However, the low permeate conductivity observed indicates that under non-wetting conditions the diffusion of ions through the solid matrix of the membrane is negligibly small. Conversely, the hydrated size of the two ions means it is possible that they could diffuse backwards through a dense FO membrane which has an effective pore size in the nanometer range.

The TEA cation has a hydrated radius of 0.45nm and an ionic radius of 0.385 nm and is more likely to be retained by the FO membrane than NaCl; however, the Br^- anion has an ionic radius of 0.196nm. This means that, depending on the membrane size, the smaller ions might be able to pass through.

Examining the fluxes for TEAB as draw solute in **Figure 8**, it can be seen that in this case the flux is somewhat steadier for FO than for MD, which is contrary to the case with NaCl. This suggests that, as the draw solute increases in molecular weight and becomes more complex in molecular structure, the decline in flux for MD is more obvious as compared to the case of the simple solutes such as NaCl (see below). A variety of reasons are possible, including in particular a greater tendency to foul the MD membrane. At the outset of the experiment, it should be noted that the system was less balanced with respect to FO (lower) and MD (higher) fluxes than was the case with NaCl, while the overall decline in FO flux for TEAB is lower. The lower FO fluxes for the higher molecular weight draw solute at similar concentrations probably reflects both a lower diffusivity (and hence greater tendency towards CP) and a lower activity (due to non-ideal solute-solvent interactions).

The results above demonstrate that both the FO and MD membrane should be cleaned, with the procedure being adapted to the type of draw solute being used. Because in **Figure 8** the MD flux exceeds the FO flux, the draw solution in the draw tank is being concentrated at a higher rate than it is being diluted and the flux for FO would therefore be expected to increase. In fact, due to the large tank sizes it remains relatively constant up until day two and then reduces slightly on day three, which is therefore indicative of fouling. This also suggests that very high concentrations of surfactants should be avoided as a draw solution, due to an increased fouling tendency.

The overall decline in MD flux can be related to the gradual increase in the draw solution concentration previously noted, and the consequent decrease in vapour pressure driving force. The persistent imbalance in fluxes suggests that the MD flux needs to be more carefully controlled for the higher molecular weight draw solutes, such as via reduction of feed temperature; indeed, at the outset of the experiment, the MD flux was too high, while dynamic self-balancing of the system was too slow to be effective.

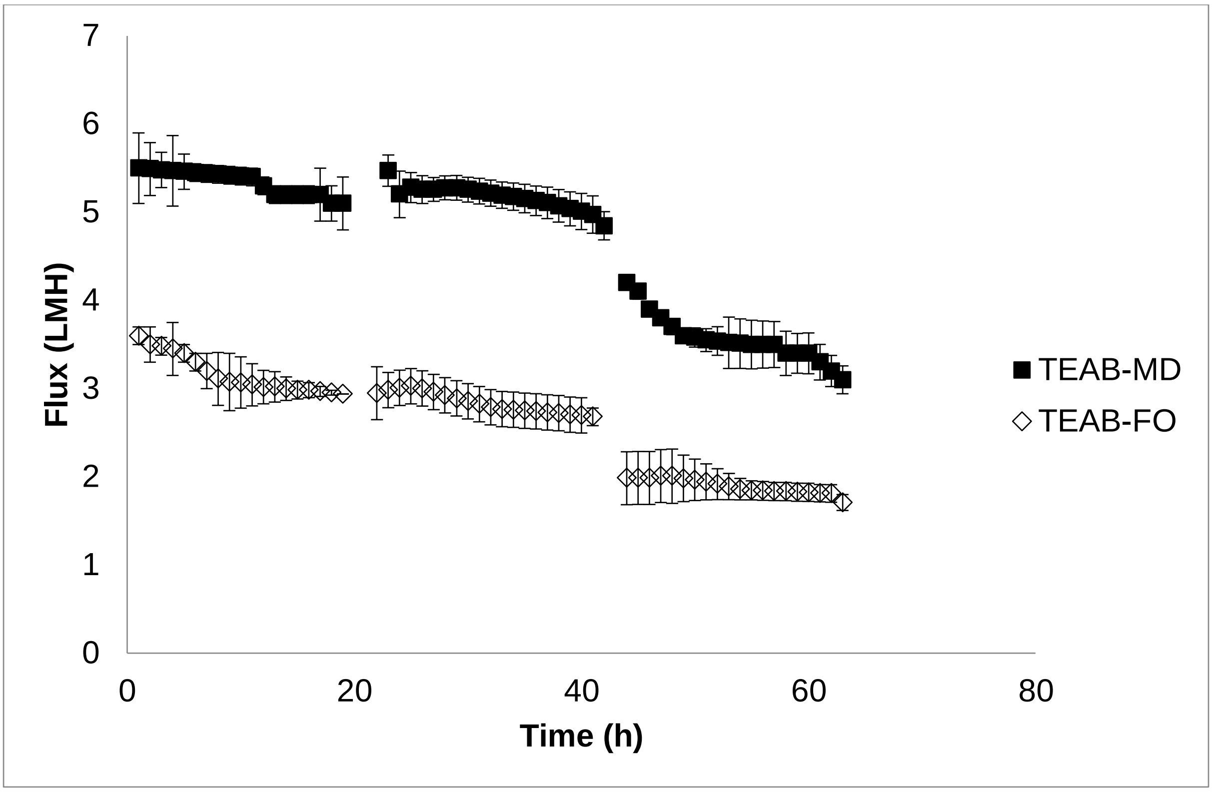


Figure 8 MD and FO flux over three days, with TEAB as a draw solution and DI water as a feed at a CFV of 0.12m/s (FO: AL-DS, MD: AL-FS)

The RST values for TEAB increased from 0.2 GMH on day 1 to 0.45 GMH at the end of day 3. The concentration of solute in the MD permeate was very low. To evaluate the exact permeate concentration of TEAB, liquid chromatography analysis was performed to separate out the other ionic species (bromide) present, but the presence of TEAB could not be detected as the detection signal remained below the baseline.

To better understand the previous observations and effects, higher molecular weight draw solutes should be evaluated. The polyelectrolyte PDAC was thus investigated.

It can clearly be observed in **Figure 9** that both the FO and MD fluxes are lower for such a higher (in this case, polymeric) molecular weight compound. The flux remains more stable over a period of days. A stable flux, alongside a reduced reverse solute transport in FO and less or no forward transport in MD, can render higher molecular weight draw solutes preferable for the FO-MD hybrid.

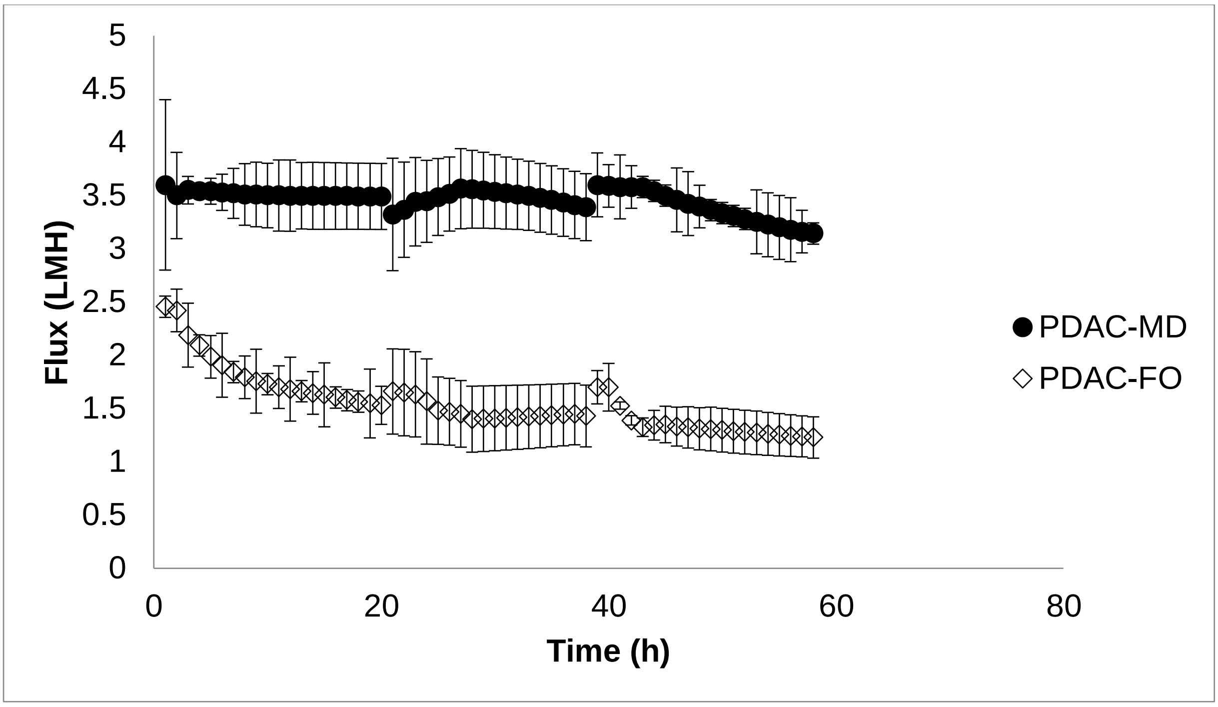


Figure 9 MD and FO flux over three days with PDAC as a draw solution and DI water as a feed at a CFV of 0.12m/s (FO: AL-DS, MD: AL-FS).

PDAC has a hydrodynamic diameter of 38.5nm. This effective value of molecular size is very high compared to that of the other draw solutes, NaCl and TEAB. The much larger size of PDAC renders it less likely to diffuse and pass through the membrane. The chances of chloride ion escaping from the draw solution side and crossing the FO membrane seem less likely as well because of the requirement of charge neutrality. However, it may still escape through an adjustment of the hydrogen ion-hydroxyl ion equilibrium, and thus lead to a change in pH. Although a slight decrease in pH was observed, the same was true for all other draw solutes as well and therefore this phenomenon seems unlikely.

As was observed with TEAB, a misbalance is observed between FO and MD fluxes; the initial MD flux exceeds the FO flux, unlike the case with the simple inorganic draw solute NaCl. As before, this may be due to a weaker dissociation of the polyelectrolyte molecule and hence a reduced depression of the vapour pressure (for the MD side) and an increased concentration polarisation and a reduced activity due to non-ideal solution effects (for the FO side). Again, feed temperature control is called for to avoid gradual concentration of the draw solution. The decline in both FO and MD flux is reduced relative to TEAB; since the fluxes themselves are lower than other draw solutes, the dynamic increase in the draw solution concentration over the duration of the experiment is reduced, and at the same time a lower fouling tendency is observed for the polyelectrolyte. Regarding the latter observation, the much larger molecule may be less able to fully occupy the adsorption sites of the membrane.

The RST values towards the feed of the FO and towards the permeate of the MD exhibit higher values for lower molecular weight draw solutes and lower values for higher molecular weight draw solutes, in broad agreement with the earlier hypothesis e.g. the RST value for NaCl on day 1 was 0.09 GMH followed by 0.13 GMH and 0.587 GMH on Day two and day 3 respectively. The very high RST on the third day of the continuous FO-MD setup reflects the fact that the forward water flux reduces drastically for FO as well. It shows that if the membrane is not cleaned properly, the solute can transport at a very high rate. The RST values for PDAC and TEAB were lower than NaCl and didn't go beyond 0.3 GMH after 72 hours of operation.

While the NaCl exhibits the highest RST, it is also the least expensive of the draw solutes and gives the highest water flux. Therefore, if the priority of a large-scale application is such that no salinity/draw solute build-up is permitted in the bioreactor (presumably due to toxicity issues), then TEAB can be preferred, but if high water flux is needed and RST can be tolerated (e.g. where the microbial toxicity is low) then simple inorganic draw solutions like NaCl could be preferable. In all cases, the solute transport into the MD permeate is low (less than 0.05 GMH) and the latter can be expected to remain uncontaminated by draw solute.

3.3 Performance of FO-MBR Hybrid with the Draw Solutions

The FO-MBR hybrid flux for 0.5 M NaCl, 0.5 M TEAB and 0.44 M, PDAC as draw solutes is shown in **Figure 10.** After this set of experiments, the membranes were taken out of the cell and cut into samples for cleaning analysis.

At the beginning, the flux plots for NaCl show that the NaCl draw solute with its high osmotic potential was able to draw water at high flux from the wastewater tank. During this time, the MD process was acclimatizing to the experimental conditions and temperature, and was stabilising as time passed. The increasing concentration polarization (due to a gradual increase in feed concentration) and gradual dilution of the draw solution caused a rapid decline in flux for the forward osmosis until day two. On the other hand, the MD flux gradually increased before decreasing and then finally became steady by day two up to day four. When compared with the FO-MBR hybrid for TEAB and PDAC as a draw solute, it can also be observed that with a small molecular weight draw solute like NaCl (**Figure 10**) FO membrane fouling occurs in the first two days and subsequently the FO-MBR becomes a balanced and self-sustainable system. Fluxes for both FO and MD remain the same after a certain amount of time and fouling. For larger molecular weight compounds, on the other hand, a different pattern was observed.

In a particular and related study (Aimar et al., 1989), it was observed that in the first two days the membrane fouled and permeate flux declined, partly because the hydrodynamic conditions at the membrane surface changed with time. The decline in flux was accounted for by overall internal concentration polarisation (ICP), and external concentration polarisation (ECP) and membrane fouling on the membrane surface. The results also suggested that critical flux for osmotic and vapour pressure-driven membrane systems is reached later than for pressure driven membrane systems.

Because of the higher flux evident for regeneration than for FO in the case of TEAB, the draw solute for the FO process in this case might become more concentrated than its initial concentration, and this higher concentration might have led to the greater chemical fouling of the membrane. This can be seen clearly in the SEM images presented in **Figure 11 (b**), where the fouling on the support layer persists even after basic cleaning.

When PDAC was used as a draw solution in the FO-MBR hybrid setup, the fluxes for both the FO and MD processes were steadier in the first three days and started to decline more rapidly on the fourth day. In this hybrid setup, it could be observed that once the draw solute was more concentrated (due to the MD flux being greater than that for FO), the flux for forward osmosis started to increase by day 4, confirming the self-balancing process described above. However, in relative terms, the FO fluxes observed remained rather too low to recommend using these draw solutes on a larger scale (values between 10-20 LMH or above are preferred).

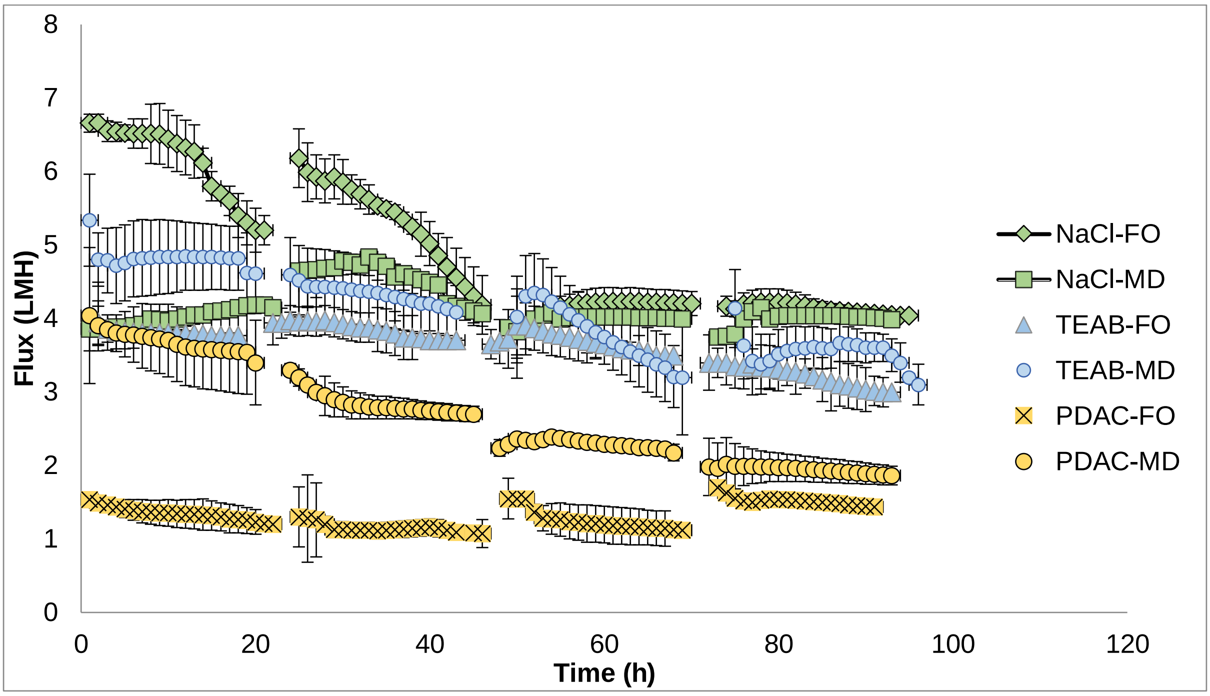
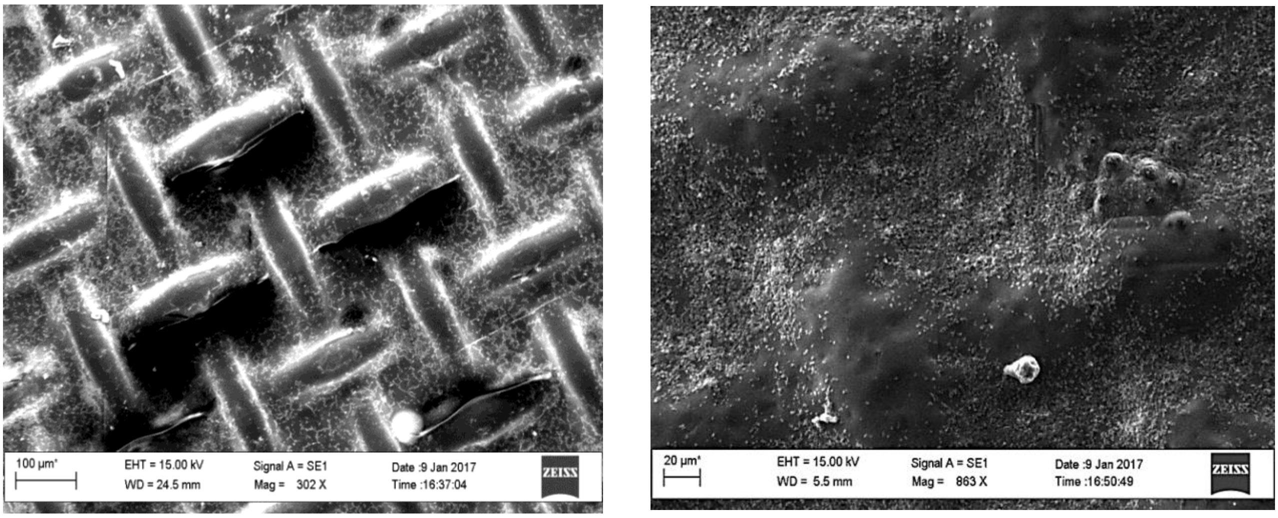


Figure 10 MD and FO flux over three days with NaCl, TEAB and PDAC as the FO draw solution and synthetic wastewater with bacterial inoculum as the FO feed in an FOMBR-MD hybrid at a CFV of 0.12m/s (FO: AL-FS, MD: AL-FS)

It is worth noting that, for all the draw solutes investigated in **Figure 10**, the FO and MD fluxes tend towards equalisation despite initial differences, so that a stable operating point is always reached, regardless of the type of draw solute. The position of this operating point will be influence by the draw solute characteristics, the degree of concentration polarisation and fouling of each membrane, and the operating temperatures of the MD unit. The rate at which it is approached can be accelerated by appropriate use of process control. The dynamics of this self-balancing process (without such control) are more evident here than they were for the FO-MD experiments, presumably because of the longer duration of the experiments. As stated already, the fluxes tend in general to be lower for higher molecular weight and more complex draw solutes.



(a) (b)

Figure 11 SEM image when TEAB was used as a draw solute after basic cleaning (a) AL-FS FO (b) SL-DS FO

Because of the complexity of the feed, the reverse solute transport could not be calculated in the FOMBR unit. However, the bacterial count of the MBR was checked daily to observe any decline in the bacterial viability. It was noted that the overall health of the MBR remained very good, suggesting that the reverse solute transport (even though not measured) did not have a deleterious effect on the microbial consortium.

Only the forward solute transport to the MD permeate was examined using electrical conductivity, to analyze the quality of the product water. It was observed that the forward solute transport was less than 0.1 GMH at the end of day 7 of the FOMBR-MD hybrid for all draw solutions.

The RST was, however, measured for the simple FO-MD and is presented in **Table 3**.

Table 3 Draw solution RST loss in FOMBR-MD hybrid

Draw solute	Total Draw solute (kg) for 500L feed	RST (FO-MD bench scale hybrid after 24 hours, GMH)	Total RST/day in grammes (RST*24*Membrane area)	Percentage loss in one day (%)	Cost of RST loss/day (£)
NaCl (1M)	29.2	0.22	0.327	1.12	0.1[a] 8[b]

TEAB (0.5M)	52.5	0.268	0.398	0.75	0.12[a] 34.6[b]
PDAC (0.44M)	40.4	0.148	0.220	0.54	0.3[a] 5.9[b]

[a]: cost assumed is that of industrial-grade material [b]:cost assumed is that of lab grade material. Economy of manufacturing scale means the industrial cost would be much lower than the lab-scale, so these latter figures are extremely pessimistic.

Using the RST values obtained from the FO-MD hybrid, the RST loss and the material cost incurred per day was calculated and is presented in Table 3. It can be observed from this Table that there is a significant amount of RST per day for all the draw solutions. The highest percentage loss was observed for the NaCl, with the lowest molecular weight, and the lowest percentage loss was observed for PDAC, with the highest molecular weight. This increases the associated material costs. Other issues, such as long term salinity in the case of NaCl and toxicity in the case of TEAB during very long-term operations of the hybrid systems will need to be taken into account.

In the current lab scale study, the two treatment technologies of FO and DCMD were used in combination to create a continuous treatment system for water reclamation using NaCl, PDAC and TEAB as FO draw solutes with both DI water, and monoculture municipal synthetic wastewater as feed. When using NaCl as the draw solute, the individual fluxes for FO and MD were both more balanced and higher overall as compared to the other draw solutes. On the other hand, there was a tendency for the flux to decline, which resulted from both fouling and a high RST back to the FO feed loop. In the case of TEAB and PDAC draw solutes, the fluxes for FO were mostly lower than that for MD, leading to a rising concentration in the draw solution tank which was in turn passed to the MD and caused a subsequent decline in MD flux as a result of feed-side vapour pressure reduction. The concentration of the draw solution had less impact on the FO flux itself, though in the case of TEAB the fouling eventually caused a decline. These effects were observed to give rise to a self-balancing effect for the fluxes, which was more observable over the longer duration of the FOMBR experiments. For the PDAC, the fluxes were both respectively lower and this tended to diminish the observed dynamic effect of the draw concentration. The greater imbalance in fluxes (MD higher than FO) for the higher molecular weight draw solutes at equal concentrations as compared to the lower molecular weight draw solutes partly reflected their lower diffusivities and hence greater tendency towards CP, and partly reflected their lower osmotic activity. This could be compensated, for example, by a decreased MD feed temperature, but the imbalance highlights the fact that the higher molecular weight draws might require more careful process control in practice.

4 Conclusions

In the current laboratory study, the two treatment technologies of FO and DCMD were used in combination to create a continuous treatment system for water reclamation. When the FO-MD hybrid was running in a continuous mode, the flux was more stable and steady as compared to FO when run on its own, due to the regeneration of the draw solution by the MD unit. When using NaCl as the draw solute (Feed: 20°C; Permeate: 35°C and feed velocity of 0.17 m/s), the individual fluxes for FO and MD were both more balanced and higher overall as compared to the other draw solutes. On the other hand, there was a tendency for the flux to decline, which resulted from both fouling and a high RST back to the FO feed loop. In the case of TEAB and PDAC draw solutes, the fluxes for FO were mostly lower than that for MD, leading to a rising concentration in the draw solution tank which was in turn passed to the MD and caused a subsequent decline in MD flux as a result of feed-side vapour pressure reduction. The concentration of the draw solution had less impact on the FO flux itself, though in the case of TEAB the fouling eventually caused a decline. These effects were observed to give rise to a self-balancing effect for the fluxes, which was more observable over the longer duration of the FOMBR experiments. For the PDAC, the fluxes were both respectively lower and this tended to diminish the observed dynamic effect of the draw concentration. The greater imbalance in fluxes (MD higher than FO) for the higher molecular weight draw solutes at equal concentrations as compared to the lower molecular weight draw solutes partly reflected their lower diffusivities and hence greater tendency towards CP, and partly reflected their lower osmotic activity. This could be compensated, for example, by a decreased MD feed temperature, but the imbalance highlights the fact that the higher molecular weight draws might require more careful process control in practice. The FO-MD hybrid enables pure water production and a non-volatile component rejection of nearly 99%, with an RST of <0.1 GMH for the MD feed to the permeate. Overall, the FO-MD hybrid can be used in combination with the draw solutes studied to ensure long-term operation and clean water production. NaCl and other low molecular weight solutes are recommended when high fluxes and system stability are priorities and where high RST, leading to salinity or solute toxicity in the MBR feed tank, is not an issue. Higher molecular weight solutes, such as TEAB or PDAC, are recommended when high flux is less critical and when the sensitivity of the microbial consortium to RST and solute toxicity is not a concern; however, process control becomes more critical for these solutes in long term operation. Application of FO-MD hybrid process in wastewater treatment requires prototyping the technology and testing for long term with real wastewater in the environment to make its application possible. The major recommendation for future work would be to test such hybrid systems at pilot scale to make sense of economy of operation and scale alongside steady operation of the system.

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