Forward Osmosis for Water Recovery Using Polyelectrolyte PolyDADMAC and DADMAC Draw Solutions as a Low Pressure Energy Saving Process

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Highlights

- Cationic organic DADMAC and PolyDADMAC were used as draw solutes for FO system.

- Cellulose Triacetate and Aquaporin flat sheet membranes were tested under FO mode.

- Both draw solutions have high electrical conductivity due to strong cation $C_8H_6N^+$.

- Water flux and reverse solute diffusion of DADMAC were higher than PolyDADMAC.

- Diluted draw solutions were reconcentrated by a stirred dead-end Nanofiltration cell.

Nomenclature

CTA	Cellulose triacetate
DADMAC	Diallyldimethylammonium chloride
FO	Forward osmosis
GHM	Grams per square meter per hour $(\frac{g}{m^2}.hr)$
IBMA-Na	Poly isobutylene-alt-maleic anhydride salt
J_S	Reverse solute diffusion $(\frac{g}{m^2}.hr)$
$J_{w_{i+2}}$	Water flux on top of every two hours $(\frac{L}{m^2}.hr)$
LMH	Litres per square meter per hour $(\frac{L}{m^2}.hr)$
M_w	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
OP	Osmotic pressure
Osmol	Osmolality
PAA-Na	Polyelectrolyte polyacrylic acid sodium salt
$Pa.s$	Pascal per second
PAspNa	Poly aspartic acid sodium salt
PESA	Poly epoxysuccinic acid
PolyDADMAC	Poly diallyldimethylammonium chloride
PRO	Pressure related osmosis
PSS	Poly sodium 4-styrene sulfonate
TDS	Total dissolved solids
TFC	Thin film composite

Abstract

Polydiallyldimethylammonium Chloride (PolyDADMAC) is a cationic polyelectrolyte utilised widely in drinking water industry. This study has evaluated the performance of cationic organic polyelectrolyte PolyDADMAC and its monomer DADMAC as osmotic agents in Forward Osmosis (FO) process. The properties of PolyDADMAC and DADMAC draw solutions were initially studied. Thereafter, a series of experiments were conducted to examine the efficiency of these solutions for water recovery using CTA and Aquaporin flatsheet membranes under FO mode. The results show a high electrical conductivity of both draw solutions due to the presence of strong cation electrolyte ($C_8H_6N^+$) in solutions. The obtained water flux and reverse solute diffusion of DADMAC were higher than PolyDADMAC at same concentrations. Factors contributing to the change of water flux and reverse solutes diffusion through membranes were addressed. CTA membranes accomplished higher water flux than the aquaporin membranes, however; the latter was more selective and provided better results of reverse solutes diffusion. Diluted draw solutions were reconcentrated via Nanofiltration-system. High ion rejection of DADMAC (96%) and poor ion rejection of PolyDADMAC (85%) were observed. Lastly, this article introduced a valuable comparison between cationic polyelectrolyte and its electrolyte based on their behaviours as draw solutes in FO process.

Keywords: *forward osmosis; draw solution; cationic polyelectrolyte; aquaporin protein membrane; water recovery; desalination*

1   Introduction

Pressure driven membrane processes, such as reverse osmosis and Nanofiltration, are widely employed to supply both industrial and residential sectors with high quality water [1]. The stand-alone systems of these technologies are challenged by the high energy consumption of operations and irreversible membrane fouling which is limiting their sustainability. Taking in

considerations that low energy consumption and low fouling influent and are central to desalination and water recovery processes, the feasibility of Forward Osmosis (FO) prevails as an integrated promising membrane technology for water recovery [2,3]. FO is an osmotically driven membrane process which be used in conjunction with other pressure driven membrane technologies or stand-alone. It allows movement of water molecules up gradient to an extractable highly concentrated draw solutions composed of natural, artificial or non-degradable solutes. The spontaneous movement of water molecules through a semi-permeable membrane separated two solutions is attributable to the variance of osmotic pressure between those solutions [4–7]. In pressure driven membrane processes, energy loses occur due to the external hydraulic pressure which is required to apply and overcome the osmotic pressure of solution to produce fluxes. Whereas, in the FO process, the osmotic pressure of the solutions themselves operates as drawing force to generate a flux across the membrane. The absence of the external hydraulic pressure in the FO process results in an affordable removable fouling layer [8,9]. The reversible fouling can removed by an accessible physical cleaning and no need to use an intensive chemical cleaning as in pressure driven membrane systems where the fouling layer is irreversible and crosslinked [10,11].

The final products of FO process are diluted draw solutions and dewatered feed solutions. Therefore, an integrated separation process is needed to produce various streams such as a purified water and concentrated draw solution to reuse it in the FO process. An efficient energy separation process is required in reconcentration stage, where the energy loses happen in FO systems, to minimise the overall energy consumption [12,13]. Reconcentration of draw solutions as well as internal polarisation concentration and reverse solute diffusion still pose challenges connecting to the FO efficiency [5,14,15]. Mitigating these challenges can be accomplished by developing and selecting an effective draw solution. The wide range of materials vary from responsive solutes (e.g. inorganic, organic solutes and polyelectrolytes) to

non-responsive solutes (e.g. nanoparticles, hydrogels and volatile compounds) are proposed as a convenient draw solution for the FO process. However, researches are ongoing to study novel materials for this purpose. The current literatures demonstrate that few studies were conducted on using the polyelectrolytes as draw solutions in the FO process compared to other conventional solutes [4,13,16,17]. However, exploring these components has been recently increased due to their merits which meet the requirements to be proper draw solutions. Soluble polyelectrolytes have relatively high osmotic pressure and low reverse solute diffusion due to the expanded structure of their chains. They also have large molecular weights compared to their monomers which enable them to be reconcentrated easily via low pressure driven processes [13,18,19].

The majority of the polyelectrolytes investigations have addressed the viability of using anionic polyelectrolytes as draw solutions, as illustrated in referencing (table 1). The efficiency of the listed anionic polyelectrolytes draw solutions has been defined based on their water flux, reverse solute diffusion, reconcentration method, and ion rejection percentage. In contrast, a lack in the number of studies which exploring the behaviour of cationic polyelectrolytes as draw solutions has been observed. This study aims at answering question whether the appropriateness of PolyDADMAC and DADMAC cationic organic draw solutions may propose feasible draw agents for the FO process.

Table 1: FO Performance Using Anionic Polyelectrolytes Draw Solutions

Draw Solution	Dynamic Viscosity at 25°C	Osmotic pressure	Water flux	Reverse solute diffusion	Reconcentration process, ion rejection %	Ref.
	Pa.s [10^{-4}]	atm.	LMH	GMH		
PAA-Na (1800), 0.48 g/mL	166	37.00	9.70, CTA-FO mode	1.00, CTA-PRO mode	Ultrafiltration,	[19]
PAA-Na (1800), 0.72 g/mL	1050	54.00	12.00, CTA-FO mode	1.50, CTA-PRO mode	(99.00 %)	
PSS(70,000), 0.04 g/mL	20		2.50, TFC-PRO mode	0.80, TFC-PRO mode		
PSS(70,000), 0.12 g/mL	75	Not mentioned	8.50, TFC-PRO mode	2.50, TFC-PRO mode	Ultrafiltration,	[20]
PSS(70,000), 0.24 g/mL	150		12.00, TFC-PRO mode	5.00, TFC-PRO mode	(93.50 %)	
PSS(70,000), 0.48 g/mL	10140		17.00, TFC-PRO mode	15.00, TFC-PRO mode		
PAspNA, 0.10 g/mL	16	8.30	5.00, CTA-FO mode	0.75, CTA-FO mode		
			6.25, TFC-FO mode	1.30, TFC-FO mode		
PAspNA, 0.20 g/mL	26	26.60	6.90, CTA-FO mode	1.50, CTA-FO mode	Nanofiltration,	[21]
			8.25, TFC-FO mode	1.60, TFC-FO mode	(98.90 %)	
PAspNA, 0.30 g/mL	45	51.50	8.40, CTA-FO mode	1.90, CTA-FO mode		
			9.25, TFC-FO mode	2.30, TFC-FO mode		
IBMA-Na, 0.30 g/mL	142	28.00	6.88, CTA-FO mode	0.11, CTA- PRO mode	Distillation	[22]

IBMA-Na, 0.35 g/mL	215	36.00	8.80, CTA-FO mode	0.13, CTA-PRO mode	(99.90 %)	
IBMA-Na, 0.40 g/mL	1112	63.00	10.80, CTA-FO mode	0.20, CTA-PRO mode		
PESA, 0.05 g/mL	10.50	7.70	7.00, TFC-FO mode	3.00, TFC-FO mode		
PESA, 0.10 g/mL	13.50	14.70	11.00, TFC-FO mode	6.00, TFC-FO mode	Nanofiltration	[23]
PESA, 0.15 g/mL	16.50	22.30	13.00, TFC-FO mode	8.00 TFC-FO mode	(97.80 %)	
PESA, 0.20 g/mL	19.60	30.50	14.00, TFC-FO mode	9.00, TFC-FO mode		
Carboxylate polyelectrolyte, 0.03 g/mL	33.75	3.30	2.50, CTA-FO mode	0.06, CTA-FO mode		
Carboxylate polyelectrolyte, 0.06 g/mL	36.25	7.13	3.50, CTA-FO mode	0.20, CTA-FO mode		
Carboxylate polyelectrolyte, 0.12 g/mL	44.50	15.30	4.50, CTA-FO mode	0.28, CTA-FO mode	Ultrafiltration, (93.70 % ion rejection)	[24]
Carboxylate polyelectrolyte, 0.15 g/mL	46.25	18.40	5.60, CTA-FO mode	0.54, CTA-FO mode		
Carboxylate polyelectrolyte, 0.18 g/mL	53.75	22.25	6.70, CTA-FO mode	0.75, CTA-FO mode		

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PolyDADMAC was the first polymer to be permitted for the use in potable water treatment by Food and Drug Administration of U.S.A [25]. It has also been used in industrial applications such as flocculation, dewatering, coagulation, separation processes [26,27], and other applications [28,29]. The study is mainly covered three points: (1) examining the physiochemical properties of PolyDADMAC and DADMAC draw solutions with various concentrations. (2) investigating the performance of FO process under different operation conditions including two draw solutions, four concentration of each draw solution, and two types of FO membranes. (3) studying the efficacy of a stirred dead-end stainless steel NF membrane cell in reconcentration the diluted draw solutions.

2   Materials and Methods

2.1   Membranes

Cellulose Triacetate (CTA) and Aquaporin flat sheet membranes were employed in FO set up. CTA commercial membrane, supplied by Hydration Technology Innovation (USA), is an anisotropic membrane with thickness less than 50 μm. It consists of cellulose triacetate thin layer casted over embedded polyester mesh layer forming a two-layer membrane. Aquaporin flat sheet membrane, supplied by Sterlitech Corporation (USA), is a thin film composite TFC membrane [30] composed of two layers with thickness equals 110 μm (±15μm). It is formed by a thin polyamide active layer comprising aquaporin protein water channels casted on a porous support layer.   The support layer material is unspecified in the data sheet of manufacturer, however; some materials e.g. a polyethersulfone [31] or polysulfone [32] were found in the literatures.

In addition, a negatively charged Nanofiltration flat sheet membrane (NF90), purchased from Dow FilmTec, USA, was employed in the reconcentration setup of diluted draw solutions. NF90 membrane is a stable and durable TFC polyamide membrane used widely in commercial and industrial applications. It operates successfully as a low net driving pressure membrane

with low energy and at maximum operating pressure 41 bar. (Table 2) indicates the characteristics of the NF90 Nanofiltration membrane [30].

Table 2: Characteristics of the NF90 Nanofiltration membrane

Membrane	Flux LMH/bar	Rejection %	MWCO Daltons	pH range	Pore size nm	Surface charge
NF90	78.2-102/8.96	99.0 % $MgSO_4$	~200-400	2-11	0.73/0.68	Negative

2.2 Draw and feed solutions

Stock solutions of DADMAC (M_w = 161.67 g/mol with concentration 65 wt. % in H_2O), and PolyDADMAC (M_w < 100,000 g/mol with concentration 35 wt. % in H_2O) were purchased from Sigma-Aldrich. Water still unit (WD-2008F, Daihan LabTech) was used to produce distilled water with an electrical conductivity of about 1.3μS/cm. The distilled water was utilised to prepare the draw solutions with different concentrations meanwhile it was also used as feed solutions in all the FO experiments. Figure 1 illustrates the chemical structure of DADMAC and PolyDADMAC, respectively. The hydrophilic high charged quaternary ammonium groups enhance the solubility of PolyDADMAC in water and grant it the properties of strong polyelectrolyte solutions [40]. The synthesization steps of DADMAC and PolyDADMAC are provided in figure S1 in the Supplementary Information.
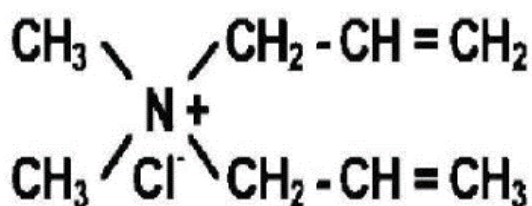
(a)   **(b)**
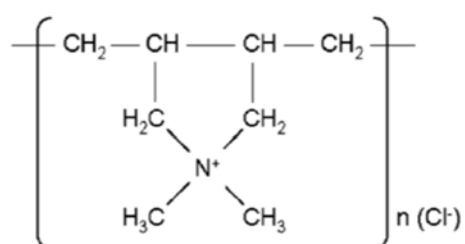
Figure 1: The chemical structure of (a) DADMAC, (b) PolyDADMAC [25]

2.3   Measurements and analytical methods

2.3.1   Preparation of draw solutions

Four draw solutions at concentrations 0.035, 0.085, 0.120 and 0.155 g/mL were prepared from each DADMAC and PolyDADMAC stock solutions using distilled water as a solvent. The final volume of each diluted draw solutions was 2000 mL. The required volumes of stock solutions and distilled water were calculated by the general mass equation. The equation and the required volumes to prepare 2000 mL of draw solutions with various concentrations are provided in Equation S1 and Table S1 in the Supplementary Information.

2.3.2   Determination of osmotic pressure

Freezing point depression Osmometer (Osmomat 030, cryoscopic osmometer, Gonotec) was utilised to measure the osmolality (Osmol / Kg) of draw solutions at various concentrations. The osmolality of draw solutions was converted to osmotic pressure (atm) at a temperature of $(22°C \pm 1°C)$ by using equation (1).

$$OP = RTc \tag{1}$$

where OP (atm) is the osmotic pressure. RT (kg . atm /mol) = 24.22 at 22 ℃. And c (moles/ Kg) is the draw solution osmolality.

2.3.3   Determination of dynamic viscosity

The dynamic viscosity of draw solutions at each concentration was tested at $22°C \pm 1°C$ via MCR 301 rheometer (Anton Paar) linked to Rheoplus 3.0X software. The instrument utilises air bearing instead of mechanical bearing which reduces the friction impact and therefore enhances the sensitivity of viscoelastic measurement. An enough drop of the draw solution was occupied a 1mm gap between the instrument base and 50 mm parallel plate spindle. After running the instrument, the plate spindle dropped down and the sample was exposed to shear

rate increased from $0.1 \, S^{-1}$ to $100 \, S^{-1}$ on logarithmic scale. Dynamic viscosity readings were collected from the desktop Rheoplus 3.0X software.

2.3.4 Determination of electrical conductivity

The electrical conductivity of draw solutions at each concentration was measured by using handheld conductivity meter (FG3-FiveGo, Mettler Toledo) connected with LE703 robust conductivity probe.

2.3.5 Scanning Electron Microscopy

A scanning electron Microscopy (SEM) was used to investigate the surface morphology of NF90 membranes before and after reconcentration the diluted PolyDADMAC draw solutions. Zeiss Crossbeam 540 FEG-SEM (Carl Zeiss Microscopy, Munich, Germany) was used to for this purpose. The membranes were stored 48 hours in clean place to dry, followed by coating with carbon. The images were taken at three different scale bars namely 20 μm, 2 μm, and 200 nm.

2.4 Experimental set up

Two separated bench-scale of FO and NF systems were built and ran at 22°C±1°C. The FO system was utilised to draw water molecules through FO membranes from the feed solution, results in diluting the draw solution meanwhile concentrating the feed solution. The NF system was used later to reconcentrate the diluted draw solutions via a stirred dead-end filtration cell for reusing it in FO process.

2.4.1 Forward osmosis system

The schematic diagram of bench-scale FO set up is displayed in (Figure 2). The core element of the FO set up is the cross-flow membrane cell with two different sized channels for the draw solution and feed solution flows. The draw solution channel is with dimensions of 4 cm in width, 20 cm in length and 0.3 cm in depth. The feed solution -distilled water- channel has the

same surface area however the depth was 1 cm. A mesh spacer was inserted into the feed channel to increase the crossflow turbulence and minimise the external concentration polarisation. The effective area of FO membrane was fixed at 80 cm^2. Both CTA and Aquaporin flat sheet membranes were used during the experiments under FO mode, where the support layer faces the draw solution. Two pre-calibrated peristaltic pumps (Masterflex L/S, Model 77201-60) were used to pump the draw and feed solutions in counter clockwise loop and in clockwise loop, respectively with flow rate of 60 L/hr. The increase of draw solutions weight was recorded by electronic scale (Radwag Model PS 4500/C/2) every two hours, and used to calculate the water flux, J_w $(L/m^2.\,hr,$ cited to as LMH) across the membrane using equation (2).

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

where $J_{w_{i+2}}$ $(L/m^2.\,hr)$ is the water flux on top of every two hours. $W_{i+2} - W_i$ (g) is the weight change of the draw solution every two hours. ρ_{water} (g/L) is the water density. A (m^2) is the effective membrane area, and $t_{i+2} - t_i$ (hour) is the time change.
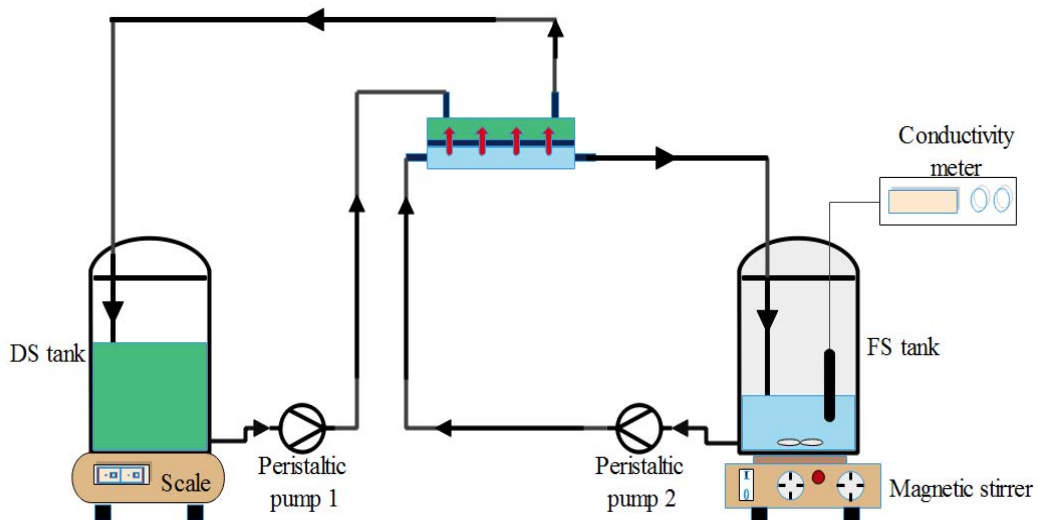
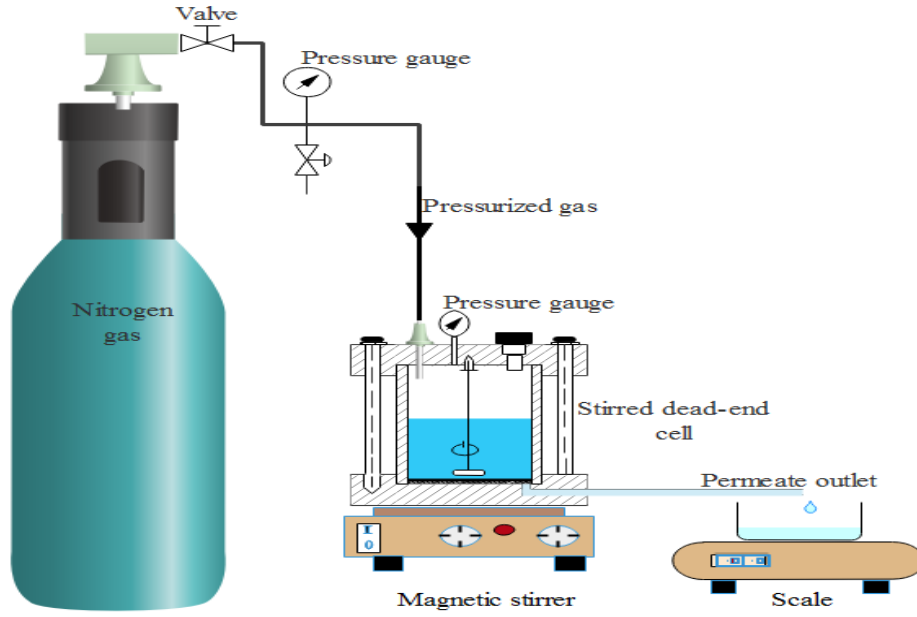**Figure 2:** Schematic diagram of the bench-scale FO set up

The reverse diffusion J_S $(g/m^2 \cdot hr,$ cited to as GMH) of DADMAC and PolyDADMAC solutes through FO membranes was observed by measuring total dissolved solids (TDS) in the feed solution tank. The TDS was measured using a handheld conductivity meter (FG3-FiveGo, Mettler Toledo) every two hours successively for 24 hours. J_S was calculated by using equation (3).

$$J_s = \frac{(C_t \times V_t - C_0 \times V_0)}{A \times t \times 1000} \tag{3}$$

where C_t (mg/L) & V_t (L) are the TDS and the feed solution volume at time t, respectively. C_0 (mg/L) & V_0(L) are the initial TDS and the initial volume of feed solution at time zero. A (m^2) is the effective membrane area, and t in hours.

2.4.2 Nanofiltration system

The schematic diagram of bench-scale Nanofiltration set up is displayed in (Figure 3). The core element of the Nanofiltration set up is a stirred dead-end stainless steel cell, purchased from Memcom Pty. Ltd, South Africa. The cylindrical container of the cell fitted with a magnetic stirrer bar. A magnetic stirrer was employed to disperse the accumulative solutes on the membranes surface, results in minimising the effect of external concentration polarisation. The top plate of the cell is connected to a pressurized nitrogen gas operated as an external pressure source. Using nitrogen gas instead of compressed air to avoid the large pH shifts due to dissolution of carbon dioxide. The external applied pressure was adjusted every two hours to retain a constant difference between the external pressure and the internal osmotic pressure of the draw solution.

Figure 3: Schematic diagram of the bench-scale Nanofiltration set up

The solute rejection of NF90 membrane was calculated by equation (4). The solute rejection of Nanofiltration membrane in dead-end cell is defined as minus the ratio of solute concentration in permeate for the initial concentration of the solute.

$$R = (1 - {C_P}/{C_F}) \times 100 \tag{4}$$

where C_P (g/mL) is the concentration of solute in cumulative permeate. C_F (g/mL) is the initial concentration of the solute.

The concentrate concentration inside the dead-end cell at any time was calculated using the mass balance equation (5).

$$C_C = \frac{C_F V_F - C_P V_P}{(V_F - V_P)} \tag{5}$$

where V_F (L) is the initial volume of diluted draw solution, and was constant (1 Litre). V_P (L) is the volume of cumulative permeate at any time. C_F (g/mL) is the initial concentration of solute, and was constant (0.035 g/mL). C_P(g/mL) is the concentration of solute in cumulative permeate at any time.

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Samples of the cumulative permeate were collected every 2 hours to measure the osmolality of permeate by OSMOMAT instrument. The experiment was run until the concentration of concentrate inside the dead-end cell reached 0.092 g/mL (optional concentration).

3   Result and discussion

3.1   Electrical conductivity of PolyDADMAC and DADMAC

The electrical conductivity of PolyDADMAC and DADMAC solutions at the various concentrations are illustrated in (Figure 4). The electrical conductivity of both cationic components are quite high due to the quaternary ammonium group ($C_8H_6N^+$) which is considered as a strong cation electrolyte. It is observed that the electrical conductivity of both components increases with the increase of concentration. The electrical conductivity of DADMAC ranges from 17.96 mS/cm at 0.035 g/mL to 52.63 at 0.155 g/mL, whereas the one of PolyDADMAC rises from at 13.20 at 0.035 g/mL to 44.00 at 0.155 g/mL. (Figure 4) also shows that the electrical conductivity of DADMAC is higher than the PolyDADMAC at same concentration, which may occur as a result of the dissociation degree of electrolyte. The dissolved DADMAC gives more free cations than the dissolved PolyDADMAC, where cationic groups of PolyDADMAC tend to bond the long backbone in aqueous solutions. The increase of electrical conductivity leads to rise the osmotic pressures of draw solutions. Therefore; the monomer DADMAC is anticipated to achieve a higher water flux in FO experiments than its polymer.
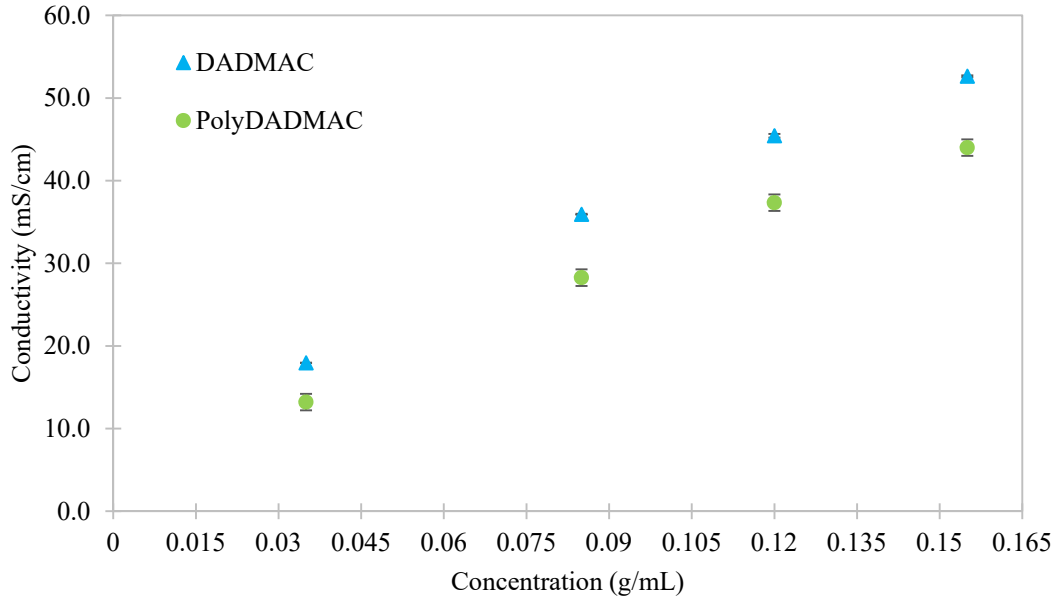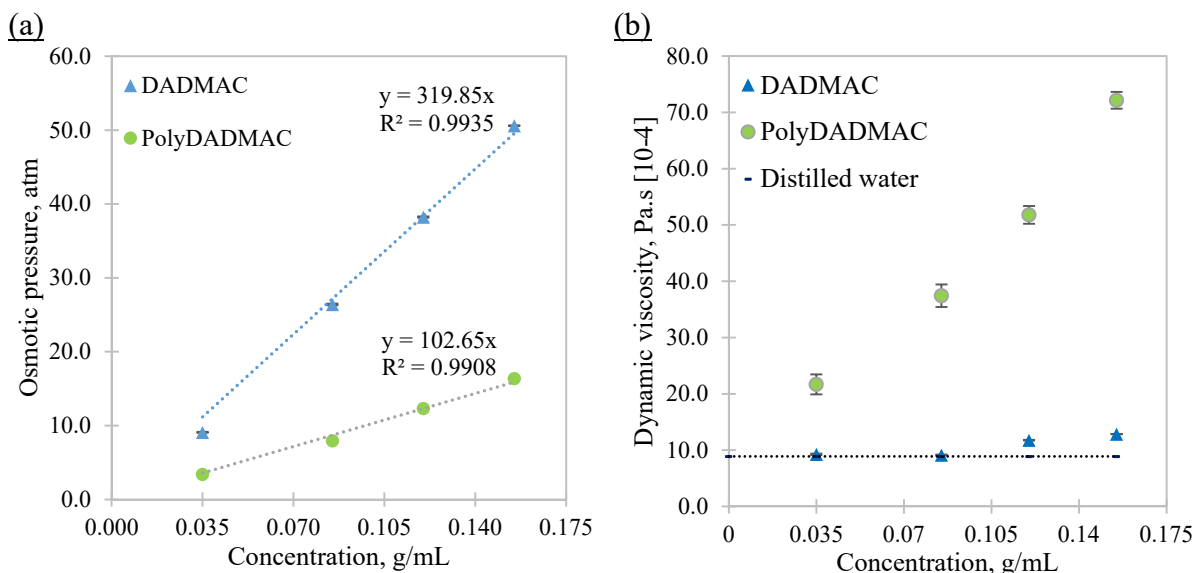
Figure 4: Electrical conductivity of DADMAC and PolyDADMAC as a function of concentration. Error bars represented the standard deviation of experiments calculated in triplicate measurements. In case of DADMAC, the variations are smaller than the marker size.

3.2   Effect of draw solution concentration on osmotic pressure and dynamic viscosity

The osmotic pressure and dynamic viscosity of each draw solutions were investigated before the bench-scale of FO was setup. Both characteristics have considerable influence on water flux and reverse solute diffusion through FO membranes. Firstly, the osmotic pressure of DADMAC and PolyDADMAC draw solutions at different concentrations are illustrated in (figure 5: a). The figure shows that the osmotic pressure of DADMAC and PolyDADMAC draw solutions increases linearly with increasing the concentration. However, the osmotic pressure of DADMAC solutions is higher and sharper than the one of PolyDADMAC. For instance, DADMAC draw solution at 0.085 g/mL demonstrated 26.41 atm of osmotic pressure, whereas a 7.95 atm was measured for the same concentration of PolyDADMAC.

Secondly, the dynamic viscosity of DADMAC and PolyDADMAC draw solutions at different concentrations are recorded in (figure 5: b). It is observed that the dynamic viscosity of DADMAC solution at various concentrations is quite similar and close to the dynamic viscosity

of distilled water (9.8×10^{-4} Pa. s). However, the dynamic viscosity of PolyDADMAC increases dramatically with the increase in the concentration. It increases from 20.74×10^{-4} Pa. s at 0.035 g/mL to 72.15×10^{-4} Pa. s at 0.155 g/mL. The preliminary results of osmotic pressure and dynamic viscosity also illustrate that DADMAC draw solutions with high osmotic pressure and low dynamic viscosity will give better performance as a draw solution than PolyDADMAC. Draw solutions with low viscosity enhance the efficiency of FO process by minimising the required energy consumption for pumping it, and minimising the impacts of internal concentration polarisation inside membranes structure.

Figure 5: Characteristics of the DADMAC and PolyDADMAC draw solutions. (a) Osmotic pressure, and (b) Dynamic viscosity. Error bars represented the standard deviation of experiments calculated in triplicate measurements. Some of these variations are smaller than the marker size.
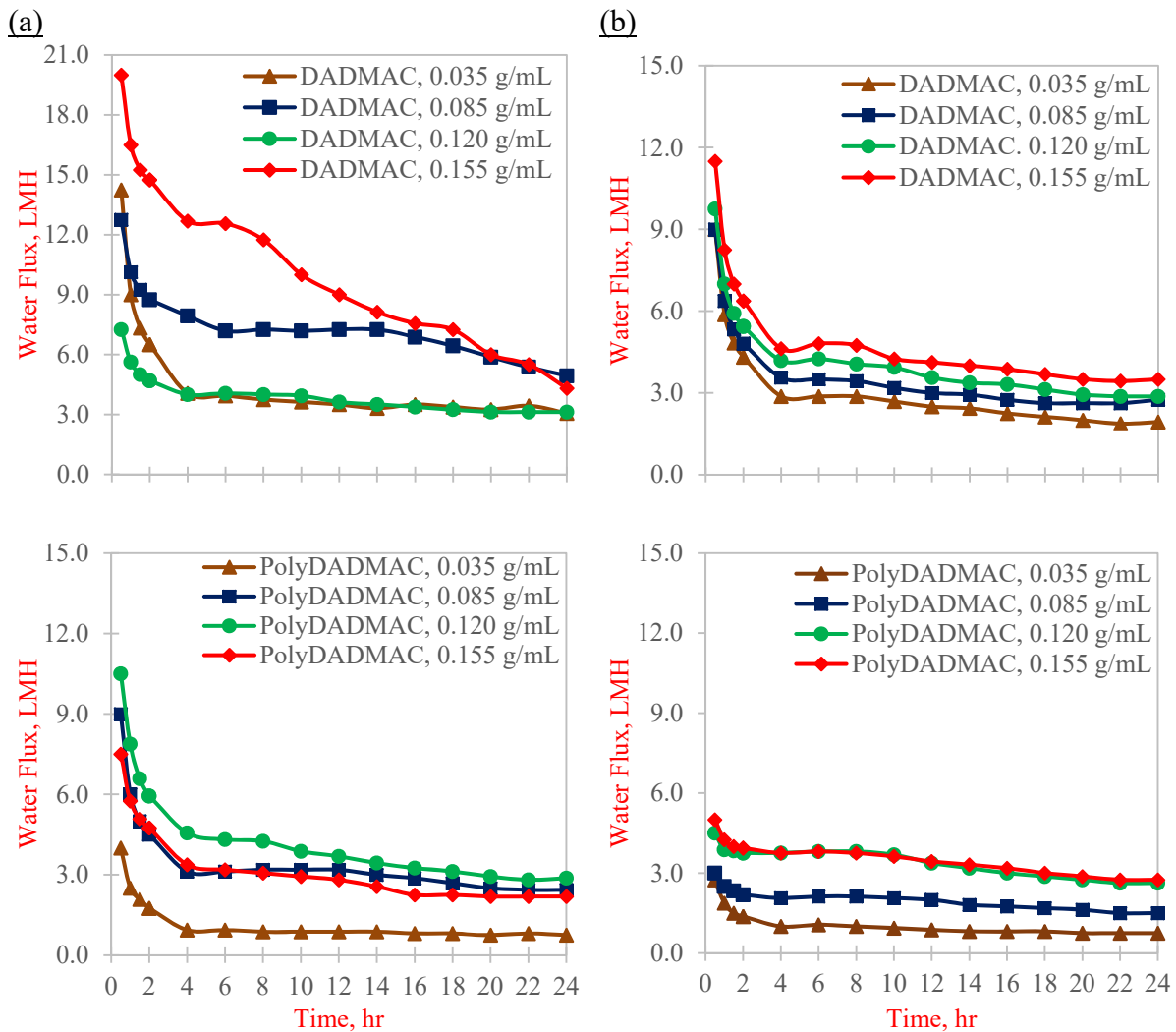
3.3   Variation of water flux over operation time

The operation time of each experiment was kept constant at 24 hr. (Figure 6) describes the water flux produced by DADAMAC and PolyDADMAC solutions at different concentrations using CTA and Aquaporin flat sheet membranes. Similar behaviour of water flux trends of DADAMAC and PolyDADMAC solutions through both CTA and Aquaporin flat sheet membranes are observed. Water flux trends decrease sharply during the first four hours,

following by a relatively slow decrease along the remaining time of experiments. The highest water flux (20 LMH) is produced through CTA flat sheet membrane using DADMAC draw solution at 0.155 g/mL. The water flux of DADMAC at 0.155 g/mL drops dramatically from 20 LMH to 12.69 LMH during the first four hours then decreases slightly to 4.31 LMH after 20 hours. Whereas, the lowest initial water flux (2.75 LMH) is recorded through the Aquaporin membrane when PolyDADMAC at 0.035 g/mL is used as a draw solution.

The highest water transmission for CTA and Aquaporin flat sheet membranes were observed during the first 4 hours. This fast water transmission to the draw solution side causes a reduction in its osmotic pressure, leading to decrease in the driving force across membranes and sharp declination in the flux. Furthermore, the sharp decrease of water flux during the first 4 hours can also be attributed to the dilutive internal concentration polarisation impact. When the high permeate goes through the support layer of membranes, the DADMAC or PolyDADMAC solutions which occupy the porous structure dilute quicker and consequently the effective osmotic pressure difference decreases. The observed results of high dilutive internal concentration polarisation in FO mode were in line with previous results of the literatures [4,6,31,32].

It also illustrates that water flux across CTA membranes (with thickness of 50 μm) are higher than water flux across the Aquaporin membranes (with thickness of 110 μm). The hydrophilicity merit and the low thickness of CTA membranes result in low ICP; consequently higher water fluxes are achieved. In addition, CTA and Aquaporin membranes are asymmetric where the water molecules can diffuse with less resistance through the support layers. However, the polyester-mesh support layer of CTA membranes contains macro voids while the layer of Aquaporin membranes has a sponge structure which causes the latter to be denser [33].

Figure 6: Variation of water flux of DADMAC and PolyDADMAC using (a) CTA flat sheet membrane, and (b) Aquaporin flat sheet membrane over the operation time

Although, the scope of this study is focused on the investigation of PolyDADMAC and its monomer DADMAC performance as osmotic agents in FO process, it is worth to mention that an unexpected behaviour resulting from DADMAC draw solution at 0.120 g/mL was noticed. Figure 6 exhibits that the water flux achieved by 0.120 g/mL is lower than that of 0.085 g/mL, which contradicts the general hypothesis stating that increasing the concentration of a solution will increase the osmotic pressure and increases the generated water flux accordingly. Another two trails were conducted under same laboratory conditions to confirm the unusual results of

DADMAC at 0.120 g/mL, however; a two years gap is to be noticed between trails 2 and 3, and previous experiments. CTA membranes stored in cold water at 4 °C was flushed by warm pure water and reused. It has been observed that there is a certain improvement in water flux as shown in figure 7. This does not exclude the fact that the unusual behaviour can be observed where the water flux of DADMAC at 0.120 g/mL in three trials is still not proportionally higher than that of 0.085 g/mL.

These low water flux results at 0.120 g/mL might be attributed to the interaction between the cations of DADMAC solution and the surface negative charge of CTA membranes. The density of positive ions found in DADMAC solution at certain concentration might have serious impacts on the surface of CTA membranes, subsequently affects the function of membranes. In this regards, more studies are needed to be conducted in future works investigating the effect of various ions density presented in draw solutions on the charged surface of FO membranes.
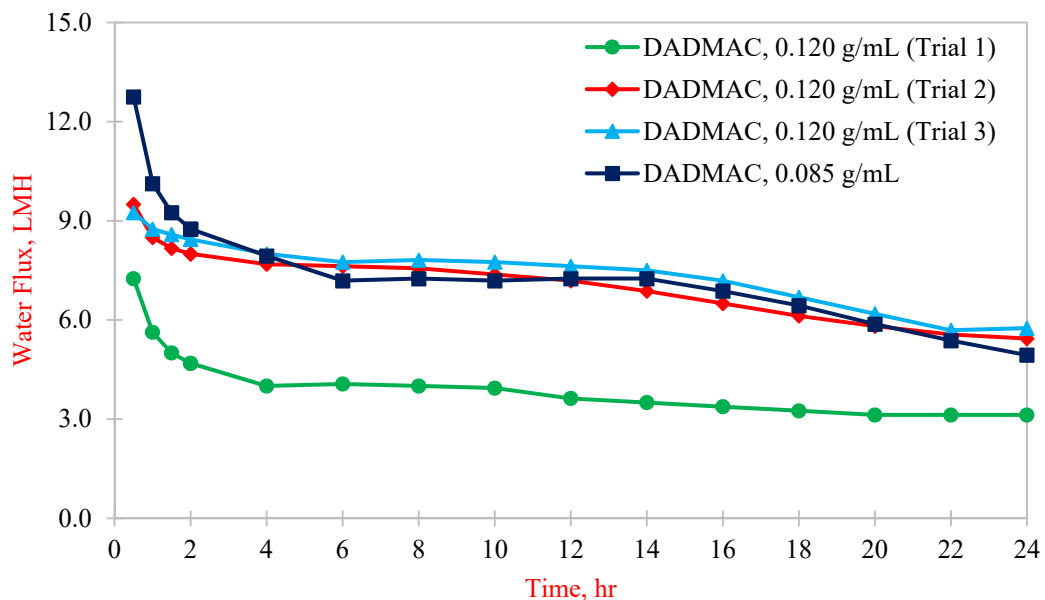

Figure 7: Comparison between water flux of DADMAC at 0.085 g/mL and 0.120 g/mL (in triplicates) using CTA flat sheet membrane.

The effect of viscosity on FO performance is not seen when DADMAC solutions at various concentrations are used because of its low viscosity, however; the effect is observed when

PolyDADMAC solution is used at high concentration (0.155 g/mL). Water flux produced by high viscosity PolyDADMAC at 0.155 g/mL is lower than the one at 0.120 g/mL. This decrease of water flux occurs due to the sharp increase of PolyDADMAC viscosity coincided with the concentration increase. Severe concentration polarization creates near the surface of membranes when PolyDADMAC with high viscosity is used, thus water flux is declined. Similar observations were recorded in literatures when other anionic polyelectrolytes were used as draw solutions at high viscosity (Ge et al. 2013; Tian et al. 2015).

3.4   Variation of reverse solute diffusion draw over operation time

(Figure 8) displays the reverse diffusion of DADMAC and PolyDADMAC solutes at various concentrations across CTA and Aquaporin flat sheet membranes. It demonstrates that the reverse diffusion of draw solution increases by increasing the concentration. Increasing the electrolytes in draw solutions generates more osmotic pressure and therefore higher reverse solutes diffusion. The reverse solute diffusion of DADMAC through both FO membranes was higher than PolyDADMAC at same concentration. This observation is attributed to the high electrical conductivity and relatively small molecular weight of DADMAC compared to its polymer. DADMAC and PolyDADMAC have different configuration in their aqueous phase. When the PolyDADMAC dissolved in water, the positively charged branches repel each other and force the backbone chain to expand which increases the solution viscosity and consequently causes a low reverse solute diffusion in FO process [34]. Generally speaking, membranes surface charge has a big influence on the reverse diffusion of solutes. High reverse diffusions of the used cations were observed compared to the aforementioned anionic polyelectrolytes. The lack of repulsion between cation solutes and the negatively charged FO membranes allows the solutes to diffuse to the feed solution side easily and thus higher reverse solution diffusion [35,36].
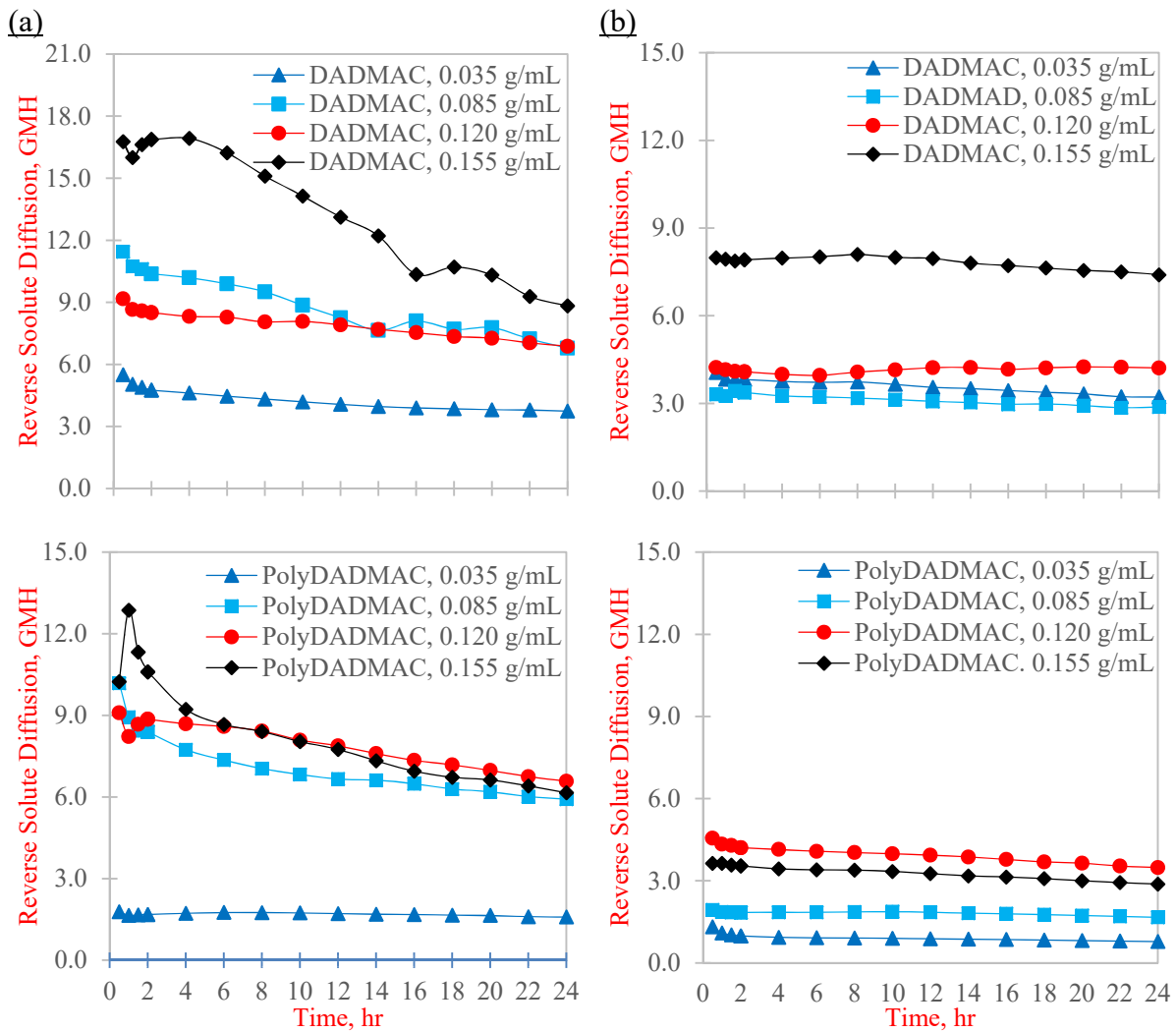
Figure 8: Reverse diffusion of DADMAC and PolyDADMAC solutes at various concentrations across (a) CTA flat sheet membrane, and (b) Aquaporin flat sheet membrane

Furthermore, (figure 8) also shows that the reverse diffusion of both draw solutions through Aquaporin flat sheet membrane is less than that through CTA membrane. The reverse solute diffusion through Aquaporin flat sheet membrane is nearly constant along experiments time. Nevertheless, the reverse solute diffusion through CTA flat sheet membrane changes gradually with time, especially reverse diffusion of DADMAC at high concentration. The stability and low reverse solute diffusion of Aquaporin membranes is imputed to the well-structured polyamide active layer which comprised aquaporin protein channels. The water transport across Aquaporin membranes is commonly governed by these narrow aquaporin protein

channels which causes the Aquaporin membranes to have a low water flux, while solutes will be rejected highly [37].
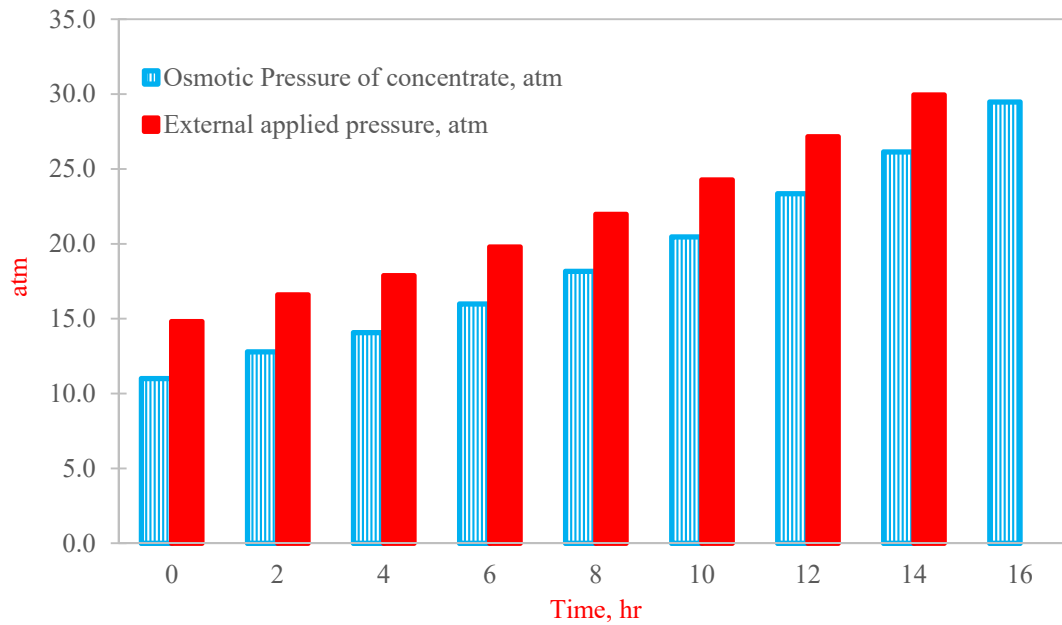
3.5   Draw solution reconcentration

Reconcentrate diluted draw solutions by an efficient process stands as a key factor of the FO technology viability. In this work, Nanofiltration process (NF90 membrane with molecular weight cut-off = 200-400 Daltons) is chosen to reconcentrate the diluted DADMAC and PolyDADMAC solutions. The external hydraulic pressure applied on the diluted solutions must be higher than the internal osmotic pressure of the solutions itself to create a proper water flux. The reconcentration process results in a highly concentrated draw solutions, inside the dead-end cell, which will be reused in the FO process.

(Figure 9) illustrates the change in both external applied pressure and osmotic pressure of DADMAC, and PolyDADMAC inside the dead-end cell. As demonstrated in the figure 9, the external hydraulic pressure was adjusted every two hours to keep the difference between it and the internal osmotic pressure of draw solution constant. The reason for that to keep the water flux through Nanofiltration membrane as constant as possible along the experiment. It also shows that diluted PolyDADMAC solution needs low external hydraulic (atm) compared to DADMAC solution due to its low osmotic pressure.
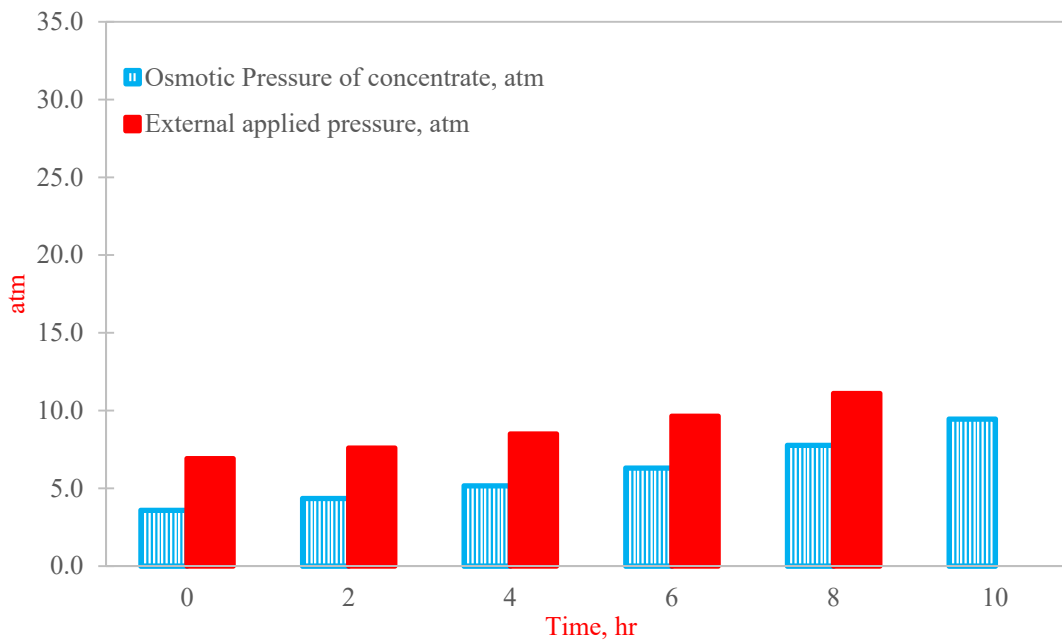
Figure 9: Change in the external applied pressure and osmotic pressure of (a) DADMAC, and (b) PolyDADMAC solutions inside the dead-end cell during reconcentration experiments

In addition, (table 3) indicates the findings of reconcentration experiments of diluted DADMAC and PolyDADMAC draw solutions. These findings include the change in volume, osmolality, cumulative permeate concentration, cumulative concentrate concentration as well as ions rejection. It is observed that the ion rejection percentage of DADMAC and

PolyDADMAC solutions decreases by increasing the solutions concentration inside the dead-end cell. The average rejection percentage of DADMAC is 96.00% and higher than the average of PolyDADMAC which is 85.00%.

Table 3: Concentration of permeate and concentrate, and rejection percentage of DADMAC and PolyDADMAC solutes

Time	Volume of cumulative permeate		Osmolality of cumulative permeate		Concentration of cumulative permeate, C_p		Concentration of cumulative concentrate		Rejection $\left(1 - \dfrac{C_p}{C_f}\right) \times 100$	
hr	mL		Osmol/Kg		g/mL		g/mL		%	
	DADMAC	Poly DADMAC	DADMAC	Poly DADMAC	DADMAC	Poly DADMAC	DADMAC	Poly DADMAC	DADMAC	Poly DADMAC
0						0.035, (C_f)				
2	117	172	0.0120	0.0170	0.00091	0.0040	0.040	0.041	97	89
4	207	334	0.0140	0.0190	0.00106	0.0045	0.044	0.050	97	87
6	304	470	0.0150	0.0220	0.00115	0.0052	0.050	0.061	96	85
8	392	583	0.0157	0.0250	0.00119	0.0059	0.057	0.076	97	83
10	461	666	0.0160	0.0270	0.00121	0.0064	0.064	**0.092**	97	82
12	528	---	0.0180	----	0.00136	----	0.073	----	96	---
14	582	---	0.0190	----	0.00144	----	0.082	----	96	---
16	630	---	0.0190	----	0.00144	----	**0.092**	----	96	---

The poor rejection of cationic PolyDADMAC ions has been also observed in the literature of [38] when Ultrafiltration system were used to recover the PolyDADMAC solutes. The electrostatic attraction between solute and membrane surface plays a significant role in regards to this poor rejection [35]. The positive charged ions of PolyDADMAC can be attracted by the anions NF membrane, leading to smaller rejection. The chemical structure of cationic PolyDADMAC, described in (figure 1) can also be a factor contributing to reduce the ions rejection. It has the ability to deform the pores of Nanofiltration membranes. The high charged cationic pendant groups located on stretched backbone have the tendency to hook the surface

of anionically charged Nanofiltration membranes [34]. Consequently, the mechanism of pore size exclusion rejection is deformed, results in high water flux and poor ionic rejection [39].

The cumulative water flux and the increase of draw solutions concentration inside dead-end cell are illustrated in (figure 10). The cumulative water flux of DADMAC decreases from 6.76 to 4.55 LMH while the concentration increases from 0.035 to 0.092 g/mL. Whereas, the cumulative water flux of PolyDADMAC decreases from 9.93 to 7.69 LMH while the concentration increases from 0.035 to 0.092 g/mL. It can be seen that the reconcentration of DADMAC and PolyDADMAC takes 16 and 10 hours respectively to reach the 0.092 g/mL concentration. During reconcentration of diluted PolyDADMAC solution, the water flux was high and quick because of the pores deformation in Nanofiltration membrane, results in faster reconcentration, see figure 11. The figure clearly shows the deformation of the surface and pores of NF 90 membrane after the reconcentration experiment. The figure 10 also illustrates that the water flux declines even though the difference between the hydraulic and osmotic pressures was constant along the experiments. The declination of water flux occurs due to the external concentration polarization and membrane compaction. By the time, a concentrated layer of solutes with high osmotic pressure forms near or atop of the NF membrane surface. This layer opposes the external hydraulic pressure and contributes to decline the water flux. Besides that, the external hydraulic pressure may compact the NF membrane structure leading to decrease the pores size and increase the hydraulic resistance of the membrane.
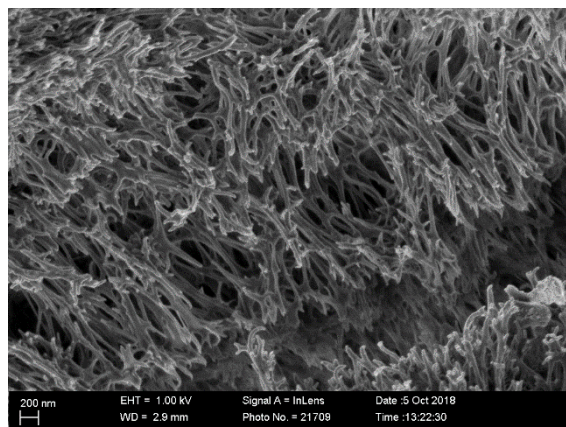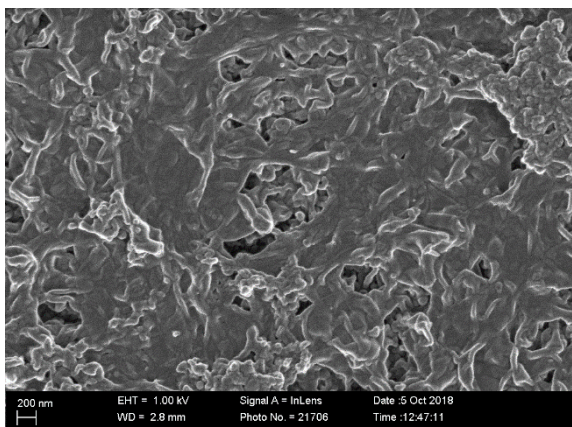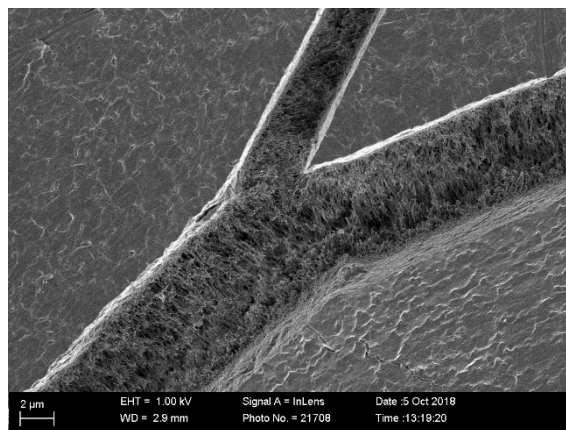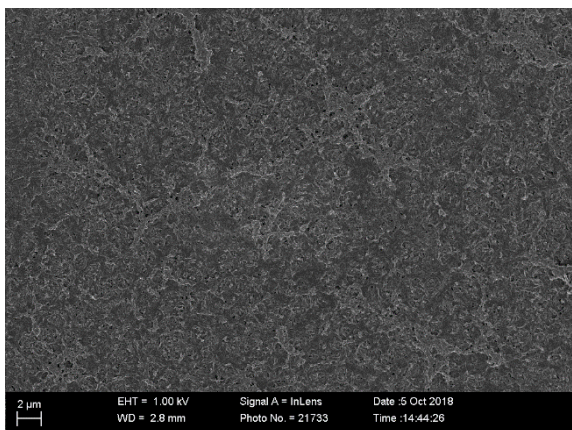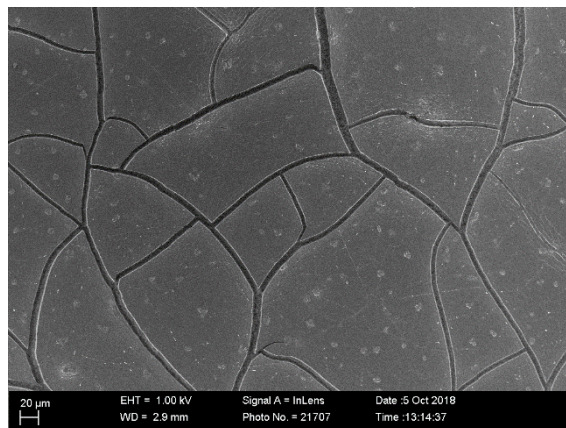
(a)
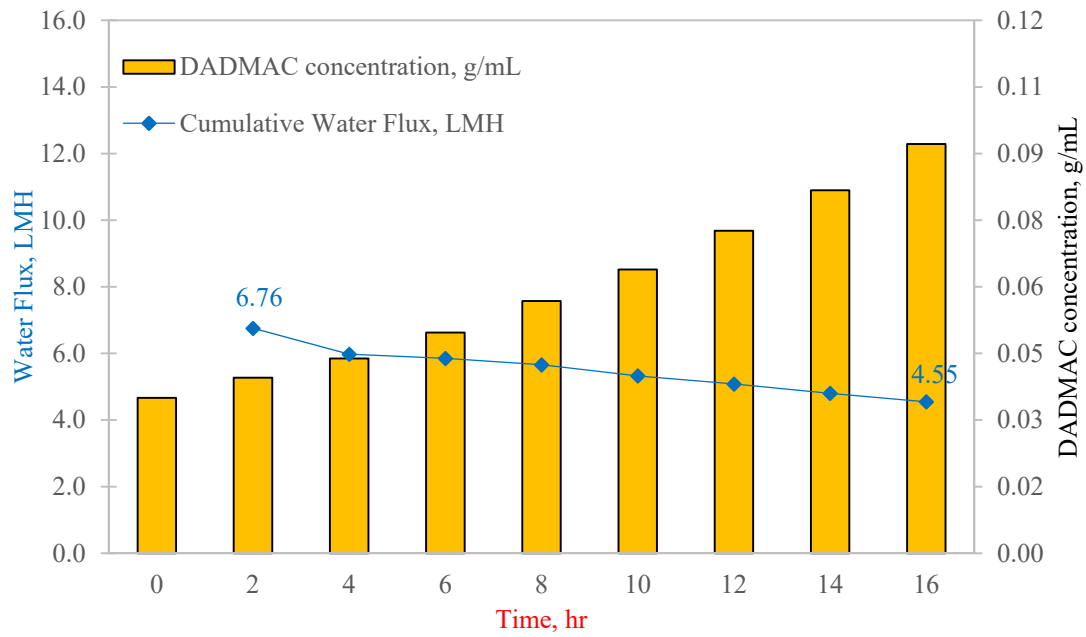
(b)
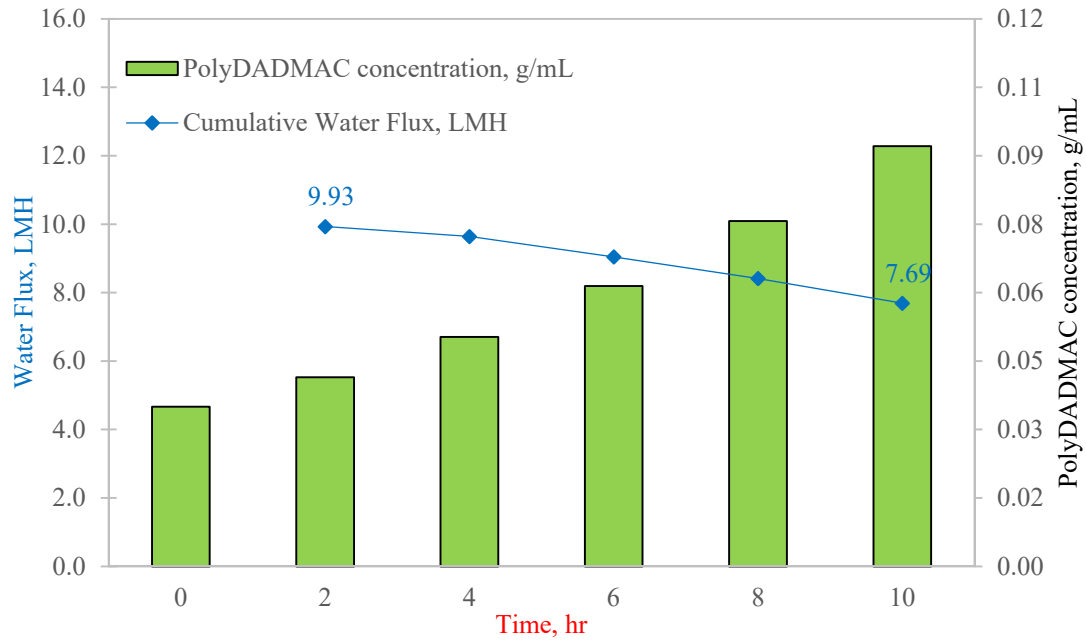
Figure 10: Cumulative water flux across NF membrane and concentration increase of (a) DADMAC, and (b) PolyDADMAC solutions inside the dead-end cell during reconcentration experiments

(a)   (b)

Figure 11: SEM images of the top surface of NF 90 membrane (a) before the use, (b) after reconcentration the diluted PolyDADMAC draw solution at $20\ \mu m$, $2\ \mu m$, and $200\ nm$ scale bars.

4   Conclusions

Cationic organic polyelectrolyte PolyDADMAC and its monomer DADMAC at different four concentrations of each have been evaluated as draw solutes in FO process. The study can be summarized by the following conclusions:

1. Water flux and reverse solute diffusion were affected by the concentration and proprieties of draw solutions i.e. electrical conductivity, viscosity and osmotic pressure, as well as characteristics of FO membranes. The FO experiments illustrate that CTA membranes provide better results of water flux than Aquaporin membranes, however; the latter have more selectivity and lower reverse solutes diffusion.

2. The presence of a strong cation electrolyte, such as quaternary ammonium group ($C_8H_6N^+$), grants both cationic draw solutions with high electrical conductivity, results in high osmotic pressures. The electrical conductivity of draw solutions increases with increasing the concentrations. Furthermore, the dynamic viscosities of PolyDADMAC solutions are much higher than DADMAC solutions and increases sharply with the increase in concentration.

3. Water flux trends of DADAMAC and PolyDADMAC draw solutions are behaved similarly across both CTA and Aquaporin flat sheet membranes. The water flux trends decrease sharply during the first four hours, following by a relatively slow decrease along the remaining time of experiments. DADMAC and PolyDADMAC draw solutions have achieved initial water fluxes up to 20 and 10.50 LMH, respectively. However, high reverse diffusion of both cationic draw solutes has been observed compared to anionic polyelectrolytes. Reducing the reverse diffusion of cationic draw solutes may be achieved by using a positively charged FO membranes, where the cationic ions are repelled and thus reduce solutes flux reversely across the membranes.

4. The Nanofiltration system indicates good performance of DADMAC reconcentration with rejection percentage (96.00%), whereas poor ion rejection of PolyDADMAC with rejection percentage (85.00%) is observed.

Lastly, this study contributes to the emerging body of works indicating energy saving and environmentally solutions for dealing with the global water scarcity problems.

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