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# Transport of trace organic contaminants (TrOCs) in pressure-assisted forward osmosis (PAFO)

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## ABSTRACT

Pressure-assisted forward osmosis (PAFO) tests were conducted in lab-scale by applying hydraulic pressure to the feed side to evaluate the rejection of trace organic contaminants (TrOCs) using a cellulose triacetate (CTA) forward osmosis membrane. The test results showed a clear difference in transport mechanisms of TrOCs depending on their physicochemical properties; neutral compounds were rejected predominantly by steric hindrance mechanism while charged compounds showed unique rejection patterns depending on the charge of the compounds implying the change of their rejection mechanisms by hydraulic pressure. To statistically find the mechanistic effects of hydraulic pressure on the rejection of TrOC, improvement ratio, *IR* ($J_{w,PAFO}/J_{w,FO}$), reverse solute diffusion ($J_{sw} = J_s/J_w$)and solute diffusion ratio, *SDR* ($J_{sw,PAFO}/J_{sw,FO}$) were computed for Pearson correlation analysis with solute rejection ratio, *SRR* ($R_{PAFO}/R_{FO}$). The Pearson correlation analysis for the rejection of neutral compounds showed the strongest correlation with *SDR* suggesting that the transport of neutral compounds with sizes bigger than the pore size of the membrane were significantly affected by the combined effect of both permeate water flux and reverse solute flux in association with steric hindrance. Negatively charged compounds showed a distinguishing rejection pattern suggesting the critical pressure point of which the rejection is the highest. Unlike the rejections of neutral and negatively charged compounds, positively charged compounds showed a clear decreasing rejection pattern in high correlation with *IR* and *SDR* indicating the facilitated diffusion of positively charged compounds. To sum up, additional hydraulic pressure in FO (i.e. PAFO) does not alter the transport mechanism for neutral compounds but significantly affect the TrOC rejection mechanisms of charged compounds depending on physicochemical properties of TrOCs.

*Keywords:* Pressure-assisted forward osmosis; Hydraulic pressure; Trace organic contaminants

## 1. Introduction

Forward osmosis (FO) process has drawn lots of attention in desalination research fields for its potentiality of utilizing lower energy than reverse osmosis (RO) process. FO process utilizes osmotic pressure difference across a semipermeable membrane for water transport while most ions and solute molecules are rejected [1]. Practicality of the FO process has been intensively studied and two most important hurdles were identified: 1) lower permeate water flux than RO and consequent use of draw solutions with high concentration and 2) loss of draw solutes resulting in continuous needs of replenishment of draw solutes. When it comes to seawater or brackish water desalination, the osmotic pressure of the draw solution must be higher to induce water transport across the membranes and to selectively collect water molecules from the source waters. However, this in turn causes a technical issue of retrieving water from the draw solutions with higher salinity than the source waters, which potentially raise the operation cost. Direct water retrieval from seawater as the feed water source using FO process alone is far from reality.

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In that, FO-RO hybrid process has been suggested and widely studied in both lab-scale [2] and pilot scale operations [3] utilizing secondary wastewater effluent as the feed water source and seawater as the draw solution. In the conceptual combination of water reuse and desalination, FO can be used as a pretreatment step for desalination. Seawater is diluted and acts as the feed stream to the following RO operation thus reduce the production cost. However, it was suggested that the total membrane area would increase approximately 8 folds compared to the conventional 2-pass RO operation at 40% total system recovery [4]. Further improvements are required in reducing the total membrane area and enhancing the total system recovery. Pressure-assisted forward osmosis (PAFO) was suggested to overcome these hurdles for its capability of enhancing permeate water flux and reduce reverse solute flux thus improve system stability and reduce total membrane area and foot print for construction with little expense of additional energy cost for pressurization.

Utilizing secondary wastewater effluent as the feed stream has been widely conducted and a number of problematic issues are found such as presence of trace organic contaminants (TrOCs) in the secondary wastewater effluent. The effluents from the wastewater treatment plants (WWTPs) are known to be the major source of the input of TrOCs to the water bodies and no legal requirements are set for the discharge of the effluents to the water bodies [5,6]. In recent years, the attention to the occurrence of organic contaminants in aquatic systems has increased at trace level [7]. The existence of such contaminants in water bodies can be a potential threat to public health. For example, pharmaceuticals are designed to be bio-active thus unintentional intake of such compounds might cause adverse health issues. Carbamazepine (CMZ), for instance, may cause birth defects that include cardiovascular, urinary tract anomalies, sedation, ataxia, confusion and bone marrow suppression [8,9]. Furthermore, the effect of long-term intake of mixed TrOCs is not clearly known [10]. Advanced treatment technologies such as AOP processes have been employed solely or coupled with brackish water reverse osmosis (BWRO) to remove small carcinogens such as NDMA, a disinfection byproduct typically found in drinking water treatment. Electrochemical AOP processes are advantageous in this aspect but, in regards of TrOC removal, AOPs can generate toxic byproducts during the oxidative degradation [11]. Furthermore, it has been reported that AOP processes can be costly in both capital and operating expenditures due to OH radical scavenging [12–14]. Implementation of advanced water treatment technologies such as membrane treatment processes is in need to help prevent health risks and FO-RO hybrid process can be a plausible option as a non-destructive means of TrOC removal by offering dual barriers.

In this sense, removal of TrOCs using membrane-based-processes has been the subject of recent studies. Pressure-driven membrane processes, such as nanofiltration (NF) and RO, have been widely studied but shown incomplete rejection of some TrOCs depending on their physicochemical properties [15,16]. In general, the rejection of positively charged compounds is lower than neutral and negatively charged compounds in pressure-driven membrane processes [17]. In FO process,the rejection mechanisms vary such as steric hindrance, electrostatic interactions and hydrophobic interactions between compounds and membranes [18]. One of the most influencing factor in transport of TrOCs in FO is the electric charge of TrOCs [17]. Neutral compounds are strictly governed by steric hindrance, while negatively charged compounds were primarily governed by electrostatic repulsion and partly by steric hindrance. For positively charged compounds, electrostatic attraction to the negatively charged membrane surface and the hydrophilic/hydrophobic interactions actively engage in the rejection [19]. Also, the rejection of TrOCs has been analyzed with varying solution pH and membrane orientation in FO and they affect the transport of TrOCs through FO membranes [20].

PAFO can enhance the membrane performance with the additional hydraulic pressure far lower than RO and has a high potential benefit to treat the secondary wastewater effluent as feed water. In the co-presence of hydraulic and osmotic pressures, the driving forces of different origin, a previous study reported that, at 4 bar of hydraulic pressure on the feed using one cellulose triacetate (CTA) and two thin-film composite (TFC) membranes with different backing spacer types (i.e. fine and coarse), the rejection of TrOCs generally deteriorated with the additional pressure regardless of membrane types but the coarse backing spacer [21]. Notwithstanding, to date, no study has reported the rejection of TrOCs in PAFO with a variation of hydraulic pressure on the feed side. The objective of this study is to find the relationship between the flux behaviors with the rejection of TrOCs by conducting Pearson correlation and to see the change of rejection mechanisms due to additional hydraulic pressure considering the physicochemical properties of TrOCs.

## 2. Materials and methods

### 2.1. FO membrane and characterization

The FO membrane used in this study was Hydration Technology Innovations, LLC (HTI) OsMemTM CTA-ES membrane. The abbreviated term, ES, stands for embedded support and a polyester support mesh was embedded in the membrane's support layer. The acceptable operating pH is ranging from 3 to 8 given by the manufacturer. The cross-section of the membrane was examined by an FE-SEM (Scanning Electron Microscopy)/EDX (Model S-4700, Hitachi, Japan) and 7 membrane coupons were analyzed to determine the membrane thickness. The membrane has an asymmetric structure with a thickness of 50.42 ± 9.04 µm. Also, membrane surface zeta-potential at pH 6.5 was measured using zeta potential and particle size analyzer (ELS-Z, Otsuka Electronics, Japan) and streaming potential method was utilized for measurement. The membrane coupons were cut into 3 cm by 2 cm dimension and pre-soaked in 10 mM NaCl solution titrated using HCl (0.1 N) and NaOH (0.1 N) at pH 6.5 for 30 min prior to each measurement. For all measurements, the same solution of 10 mM NaCl at pH 6.5 was used as the background electrolyte solution. The membrane surface zeta-potential of the CTA-ES membrane was obtained to be –5.79 ± 1.17 mV at pH 6.5 showing that the membrane is negatively charged.

### 2.2. Trace Organic Contaminants (TrOCs)

Target TrOCs were purchased from Sigma-Aldrich Co. (Saint Louis, MO, USA). The tested compounds were selected based on varying molecular weight (MW), Stokes radius, and solute charge. General physicochemical properties of the TrOCs are summarized in Table 1.

The hydrophobicity of the solutes can be determined by referring to the logarithm of the octanol-water partitioning coefficient (i.e. $log\ K_{ow}$). However, $log\ K_{ow}$ cannot accurately represent the solute hydrophobicity, especially when the solutes are ionized. For ionized solutes, the pH-dependent logarithmic octanol-water distribution coefficient (i.e. $log\ D_{pH}$) can be calculated by using the method suggested by Tetko and Bruneau [22]. For acids,

$$\log D_{pH} = \log K_{ow} - \log\left(1 + 10^{(pH-pKa)}\right) \quad (1)$$

and for bases,

$$\log D_{pH} = \log K_{ow} - \log\left(1 + 10^{(pKa-pH)}\right) \quad (2)$$

Major factors that contribute to the transport of TrOCs were summarized in Table 2.

### 2.3. Lab-scale PAFO tests

Fig. 1 illustrates the experimental set-up for lab-scale PAFO operations. The feed and draw solutions were circulated by gear pumps (Micropump, Cole-Parmer, USA). Additional hydraulic pressure was applied onto the feed side by adjusting the bypass and the pressurization valves. The concentrated feed stream and diluted draw solution passed through temperature regulators to maintain aconstant temperature. TDS and electric scale data were collected with an automated data acquisition system.

The channels of the FO cell have identical dimensions of 7.5 cm (length) × 2.5 cm (width) × 0.3 cm (depth). In order to secure a constant flow in the draw solution channel, 11 layers of reverse osmosis permeate carriers (Hydranautics, USA) were cut and fit into the channel for accommodating the applied hydraulic pressure on the feed side.

The membrane was tested in FO mode with the active layer facing the feed solution (AL-FS). The feed solution containing TrOCs was created by spiking 1mL of stock solution containing 200 mg/L of each TrOC stored at –15ºCto achieve a target concentration of 100 µg/L. Total volume of

Table 1
General physicochemical properties of target TrOCs

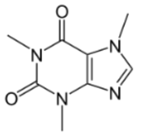
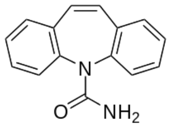
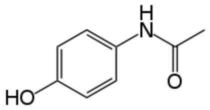
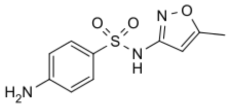
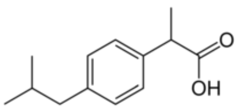
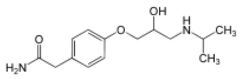
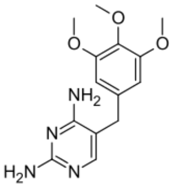
| Name | Chemical structure | Chemical formula | MW (g/mol) | Category |
|---|---|---|---|---|
| Caffeine<br>(CFN) |  | $C_8H_{10}N_4O_2$ | 194.14 | Stimulant |
| Carbamazepine<br>(CMZ) |  | $C_{15}H_{12}N_2O$ | 236.27 | Anticonvulsant |
| Acetaminophen<br>(AAP) |  | $C_8H_9NO_2$ | 151.16 | Analgesic |
| Sulfamethoxazole<br>(SMZ) |  | $C_{10}H_{11}N_3O_3S$ | 253.28 | Antibiotic |
| Ibuprofen<br>(IBP) |  | $C_{13}H_{18}O_2$ | 206.28 | Anti-inflammatory |
| Atenolol<br>(ATN) |  | $C_{14}H_{22}N_2O_3$ | 266.34 | β-Blocker |
| Trimethoprim<br>(TMP) |  | $C_{14}H_{18}N_4O_3$ | 290.32 | Antibiotic |

Table 2
Electric charge, solute hydrophobicity at pH 6.5 ($log\ D_{pH6.5}$) and Stokes radii of TrOCs

| Name | pKa | Electric charge | log $K_{ow}$ | log $D_{pH6.5}$ | Stokes radius (nm)[a] |
|---|---|---|---|---|---|
| Caffeine (CFN) | 10.4 | Neutral | –0.07 | –0.07 | 0.33 |
| Carbamazepine (CMZ) | 13.9 | Neutral | 2.45 | 2.45 | 0.37 |
| Acetaminophen (AAP) | 9.38 | Neutral | 0.46 | 0.46 | 0.29 |
| Sulfamethoxazole (SMZ) | pKa1 = 5.7<br>pKa2 = 1.8 | Negative | 0.89 | 0.03 | 0.38 |
| Ibuprofen (IBP) | 4.91 | Negative | 3.97 | 2.37 | 0.34 |
| Atenolol (ATN) | 9.6 | Positive | 0.16 | -2.94 | 0.39 |
| Trimethoprim (TMP) | 7.12 | Positive | 0.91 | 0.20 | 0.41 |

[a] Ref. [23]

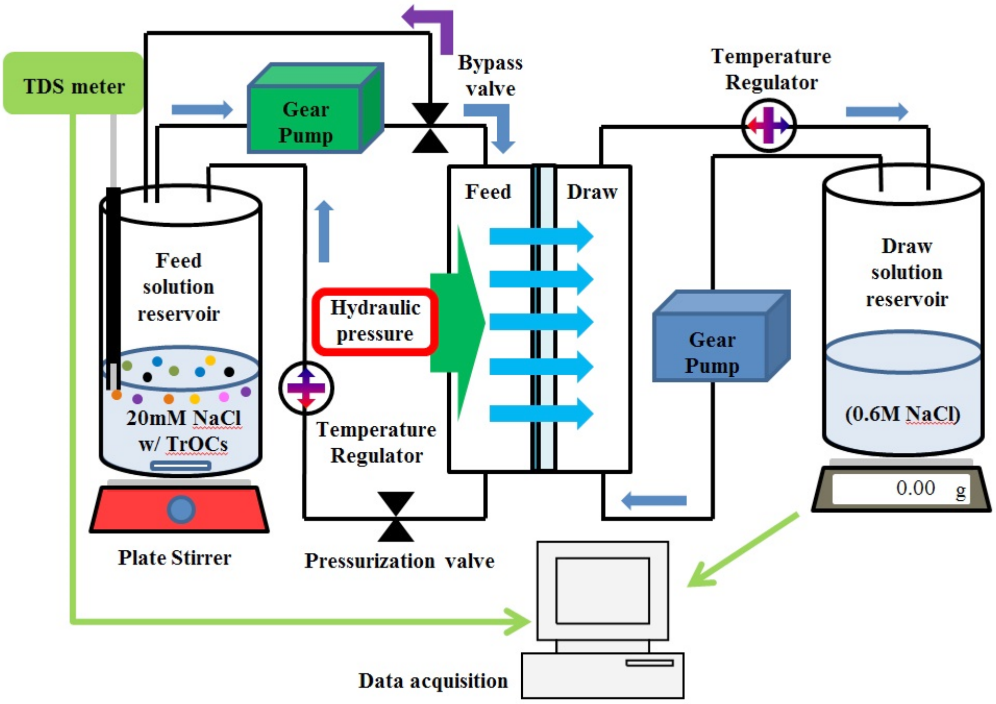


Fig. 1. Experimental set-up for lab-scale PAFO operations.

the initial feed solution was set at 2 L. Prior to each experiment, the membrane was compacted using DI water until the permeate water flux reaches and maintains a constant value for 2.5 h to achieve stable PAFO performance. The feed solution was then circulated under desired pressure for 24 h to ensure that the active layer was fully saturated. The cell assembly was detached from the system and all remaining solutions were removed and the cell assembly was then reassembled bask to the system to conduct the main experiment. New feed solution was created and employed for the actual rejection tests. Hydraulic pressure on the feed side was set as the major independent variable to verify the effects on the transport of TrOCs. Extra-pure NaCl (OCI Company Ltd., Korea) was used to prepare both feed and draw solutions. The flow rates were fixed at 300 mL/min with a cross-flow velocity of 6.67 cm/s. Table 3 summarizes the experimental conditions for PAFO tests.

### 2.4. Quantification of TrOCs and rejection

Solid phase extraction (SPE) method has been widely employed in quantification of compounds in aqueous

Table 3
Experimental conditions

| Operational factors | Description | Note |
|---|---|---|
| Membrane | CTA-ES (HTI) | FO mode (AL-FS) |
| Effective membrane area (cm$^2$) | 18.75 | |
| Feed solution | 20 mM NaCl, 2L | Containing 100 µg/L of TrOCs |
| Draw solution | 0.6 M NaCl, 2L | – |
| Flow rate (mL/min) | 300 | Equivalent to cross-flow velocity of 6.67 cm/s |
| Temperature (°C) | 20 | ± 0.3 |
| Hydraulic pressure (bar) | 0, 2 and 4 | Applied to feed side |
| Feed solution pH | 6.5 | ± 0.2 |

phase at trace level. Anautomated SPE system (Autotrace 280, DIONEX, USA) and Oasis HLB 6cc (500 mg) cartridges (Waters, Ireland) were used for extraction of TrOCs. The cartridges were preconditioned twice with methanol (HPLC grade, Fisher Scientific, USA) and DI water with a volume of 10 mL. 400 mL of aqueous samples of the feed and draw solutions were obtained operation and were then transported through the cartridges. For eluent, 10 mL of the HPLC grade methanol was used for final extraction of TrOCs. To quantify TrOCs, an LC-MS/MS system (Waters, Ireland) with a UV-Vis detection equipment was employed. The detection limit of the system was 0.5 µg/L.

With increasing hydraulic pressure, the permeate water flux also increases, and the dilution factor (*DF*) for the draw solution must be taken into account to accurately measure TrOC rejection [24,25]. *DF* is the ratio between the final volume of draw solution, $V_{ds,f}$, and the permeate volume, $V_p$.

$$DF = \frac{V_{ds,f}}{V_p} \tag{3}$$

Hence, the actual rejection can be computed as:

$$R(\%) = \left(1 - \frac{DF \times C_{ds,f}}{C_{f,0}}\right) \times 100 \tag{4}$$

where $C_{ds,f}$ is the final TrOC concentration in the draw solution and $C_{f,0}$ is the initial TrOC concentration in the feed solution. After each experiment, samples were collected from both feed and draw solution tanks. The TrOC concentrations in the feed were converted back considering the amount of water permeated through the membrane and the mass balances of the target TrOCs were validated. This justifies the use of $C_{f,0}$ in Eq. (4) regardless of the TrOC concentration changes during operation.

Pearson correlation analysis was conducted to see the direction and strength of a linear relationship between transport behaviors and rejection of respective TrOC as the significance level, α, was set as 0.1 (2-tailed).

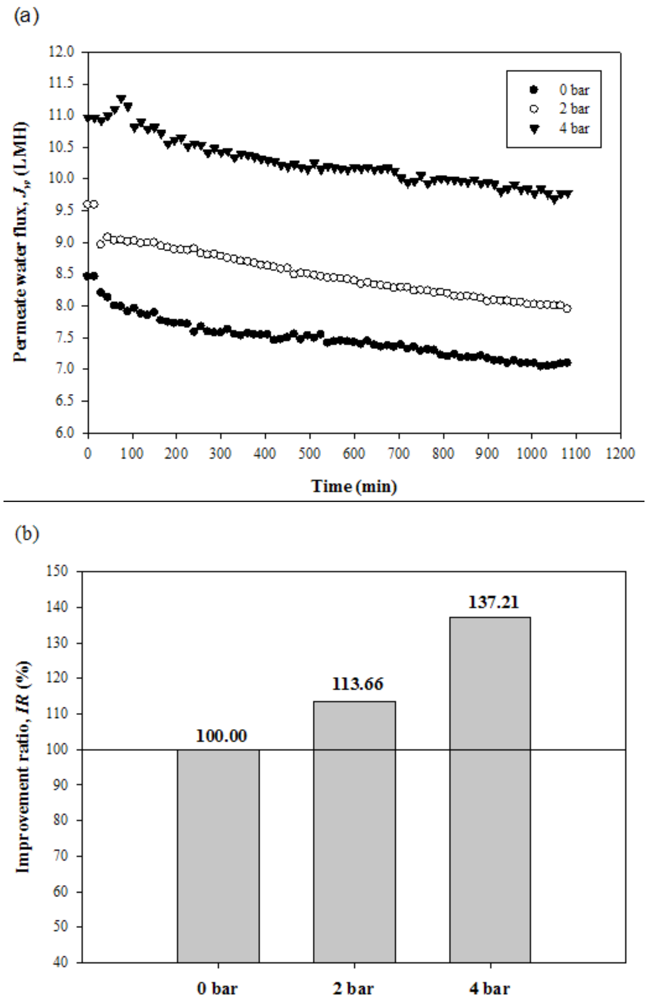


Fig. 2. (a) Permeate water flux behaviors and (b) improvement ratio (*IR*) with increasing pressure.

## 3. Results and discussion

### 3.1. Permeate water flux ($J_w$) and reverse solute flux ($J_s$)

The average permeate water fluxes at 0, 2 and 4 bar during the operation time were 7.48, 8.51 and 10.27 LMH, respectively. Clear differences in $J_w$ were observed depending on varying hydraulic pressure (Fig. 2a). For quantitative comparison, improvement ratio, *IR* (the ratio of the permeate water flux in PAFO, $J_{w,PAFO}$ to the permeate water flux in FO, $J_{w,FO}$) was calculated at each pressure condition. In was found that *IR* increased by 13.66% at 2 bar and 37.21% at 4 bar (Fig. 2(b)).The results showed a similar pattern in the previous study [26].

Reverse solute fluxes ($J_s$) were found to exhibit a clear decreasing pattern with increasing pressure as opposed to the pattern of $J_w$ change. For accurate quantification of the effect on $J_s$, solute flux ratio, *SFR* (ratio of the reverse solute flux in PAFO, $J_{s,PAFO}$ (mole/m$^2$h) to the reverse solute flux in FO, $J_{s,FO}$ (mole/m$^2$h)) was utilized and depicted in Fig. 3.

The number of NaCl solutes transported to the feed side is significantly decreased with escalating pressure. Reduction in reverse solute fluxes showed 60.43% and 70.78% at 2 and 4 bar, respectively. The primary cause of this phenomenon is the faster water transport induced by hydraulic pressure when the solute diffusivity is fixed, resulting in a severer ICP. The severer ICP represents the reduction of effective osmotic driving force which consequently leads to the decrease of reverse solute flux based on the solution-diffusion theory [26]. The results show a clear pattern of which $J_s$ asymptotically approaches to null as pressure increases.

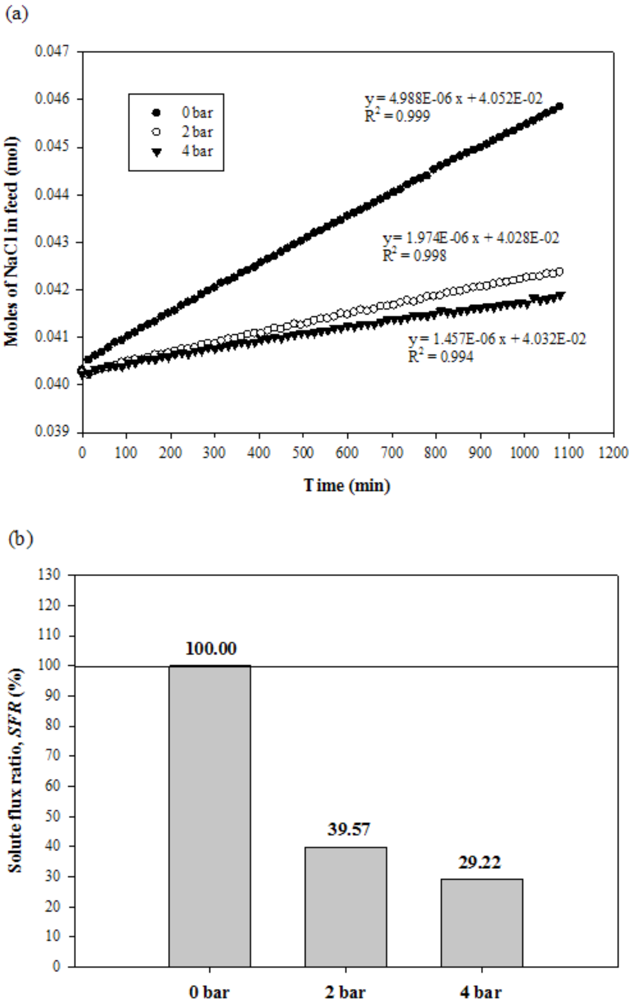


Fig. 3. (a) Moles of NaCl in the feed solution and (b) solute flux ratio (*SFR*) with increasing pressure.

## 3.2. Reverse solute diffusion, $J_{sw}$

Reverse solute diffusion is defined as $J_s/J_w$ and this particularly important because it can represent the overall effect of both $J_s$ and $J_w$on the transport of TrOCs. $J_{sw}$ was calculated for each pressure and employed for generating solute diffusion ratio, *SDR* (the ratio of the reverse solute diffusion in PAFO, $J_{sw,PAFO}$ (mole/L) to the reverse solutediffusion in FO, $J_{sw,FO}$ (mole/L)). It is important to note that SDR can be defined as the ration of *SFR* to *IR* (i.e. *SDR* = *SFR*/*IR*). The *SDR*s for each pressure condition are depicted in Fig. 4. As noticed, under pressurized conditions (i.e. 2 and 4 bar), *SDR* (i.e. 34.82 at 2 bar and 21.29 at 4 bar) is lower than *SFR* (i.e. 39.57 at 2 bar and 29.22 at 4 bar) which leads to the repression of reverse solute diffusion with increasing pressure. *IR* and *SDR* will be incorporated in Pearson correlation analysis for TrOC rejection in the later section.

## 3.3. Rejection of TrOCs

### 3.3.1 Rejection of neutral TrOCs

Rejection of TrOCs is affected by various physicochemical factors such as permeate water flux [25], ionic strength [27], electrostatic interactions [28,29], solute hydrophobicity [30,31]. The results of TrOC rejection are shown in Fig. 5. For neutral compounds, steric hindrance has been known as the governing transport mechanism for neutral TrOCs [28,32]. As depicted in Fig. 5, the larger the molecular weight and the Stokes radius, the higher the rejection. Regardless of the presence of hydraulic pressure, molecular weight (CMZ (236.27) > CFN (194.14) > AAP (151.16)) and the Stokes radii in nanometers (CMZ (0.37) > CFN (0.33) > AAP (0.29)) are in the same order with the rejection (CMZ > CFN > AAP). It is intriguing to note that the rejection of CFN and CMZ increased and this is due to the enhanced steric hindrance effect with increasing pressure.

This can further be supported by the negligible change in rejection of AAP. In the current study, a significant difference in rejection between AAP and CFN tells the existence of average pore radius possibly below 0.30 nm. The

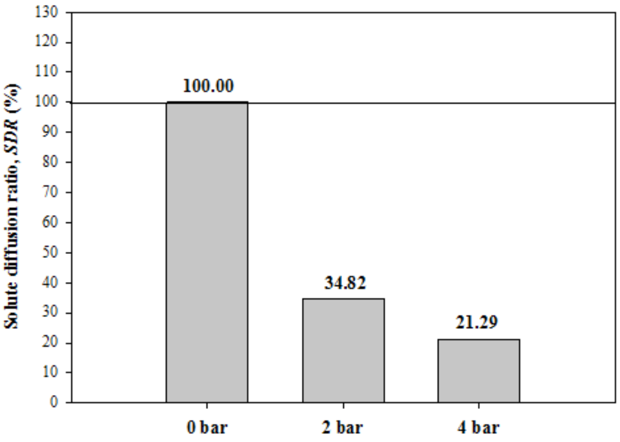


Fig. 4. Solute diffusion ratio (*SDR*) with increasing pressure.

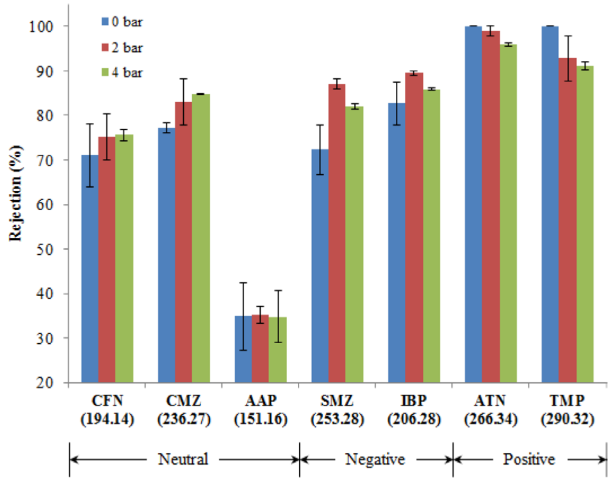


Fig. 5. Summary of TrOC rejection results.

estimated pore radius of the CTA-ES membrane is 0.37 ± 0.04 nm in the previous study by Xie et al. [19] and this supports the rejection behavior of AAP. The Stokes radius of AAP is not within the range but CFN and CMZ fall into the reported pore radius. This implies that the applied hydraulic pressure enhanced the steric hindrance effect for the compounds which possess comparable or bigger size to the active layer's average pore size. The results once again support that size exclusion is the governing mechanism for the neutral compounds regardless of the presence of additional hydraulic pressure in FO.

### *3.3.2 Rejection of charged TrOCs*

For negatively charged compounds (i.e. SMZ and IBP), it is known that the electrostatic repulsion is the governing rejection mechanisms for negatively charged compounds [20] since electrostatic interaction primarily affects the transport of charged TrOCs prior to the transport mechanisms such as steric hindrance and hydrophilic/hydrophobic interaction that are valid only when compounds are in the vicinity of the membrane surface. In general, the rejections of negatively charged compounds are higher than those of neutral compounds due to combined effect of electrostatic repulsion and steric hindrance. However, it can be noticed that the rejection of SMZ (i.e. negatively charged) is slightly lower than that of CMZ (i.e. neutral) even though the molecular weight and Stoke's radius of SMZ are larger than those of CMZ. It is because the solute hydrophobicity of SMZ (i.e. 0.03) is significantly lower than that of CMZ (i.e. 2.54) which facilitated the diffusive transport of SMZ with water molecules through the membrane.

It is important to note that the rejection of negatively charged TrOCs (i.e. SMZ and IBP) increased at 2 bar but diminished at 4 bar. The effect of electrostatic repulsion might have been enhanced at 2 bar since the membrane's active layer is negatively charged (i.e. –5.79 ± 1.17 mV of surface zeta-potential) but diminished at 4 bar possibly due to the enhanced convective transport of the negatively charged compounds toward the membrane surface along with enhanced water flux. Primary difference between PAFO and RO is the amount of hydraulic pressure applied on the feed side. Hydraulic pressure in RO is generally higher than that of PAFO and such intriguing trend on the rejection of negatively charged TrOCs has not been reported in the previous study [16] possibly due to the higher pressure (i.e. from 6 to 7.8 bar) than the pressure applied in this study. Such phenomenon could also be observed if operated at low hydraulic pressure ranges.

On the contrary, positively charged TrOCs (i.e. ATN and TMP) are attracted to the negatively charged membrane surface by electrostatic interaction at 0 bar (i.e. 100% rejection). This can be further supported by the previous study that shows almost complete rejection for positively charged compounds in FO [24]. With increasing hydraulic pressure, however, the concentrations of positively charged TrOCs in the permeate water increases. In the previous study [24], the enhanced permeate water flux solely induced by the higher osmotic pressure does not reduce the rejection of ATN and TMP. Thus, the decrease in rejection implies that the ATN and TMP are readily transported through the membrane due to the effect of hydraulic pressure.

Also, as reported in [17], for pressure driven membrane processes using NF membrane, only neutral compounds show clear relationship with molecular weight which represents the size of compounds while charged compounds (i.e. either negatively or positively) do not show clear relationship with molecular weights. For charged solutes, rejection is predominantly governed by electrostatic interactions rather than steric hindrance. In addition, according to [27], Debye length can be found for charged solute species and it is primarily determined by the charge and the electron density of the species. Even though the size of TMP is bigger than ATN, the effective size of TMP can be smaller than ATN due to potentially higher electron density considering the structural atomic compositions. TMP exhibits more round shape compared to ATN and this implies that the electron density of TMP can be higher. Higher electron density reduces the Debye length, thus the effective size of TMP can be smaller than TMP. Thus, the rejection of TMP (i.e. MW = 290.32, Stoke's radius = 0.41 nm) can be lower than that of ATN (i.e. MW = 266.34, Stoke's radius = 0.39), but this should be further elaborated by testing the rejection of multiple positively charged species.

### *3.4. Pearson correlation*

For quantitative comparison, specific rejection ratio, *SRR* (the ratio of the TrOC rejection in PAFO, $R_{PAFO}$, to the TrOC rejection in FO, $R_{FO}$) was computed for each compound. In this section, Pearson correlation was conducted on *SRR* with *IR* and *SDR*, respectively. Note that the flux and rejection data are normalized for fair comparison (i.e. dimensionless).

To see the correlation of rejection with the permeate water flux ($Corr_{IR}$), *IR* and *SRR* were put into the Pearson correlation analysis (Table 4).

*IR* showed positive correlation for CFN and CMZ meaning that the enhanced permeate water flux positively affected the rejection to a moderate degree. However, ATN and TMP, the positively charged compounds, exhibited

Table 4
Pearson correlation result for *IR* ($Corr_{IR}$)

| Pressure (bar) | IR | Specific rejection ratio (SRR) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | CFN | CMZ | AAP | SMZ | IBP | ATN | TMP |
| 0 | 100.00 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 2 | 113.66 | 1.059 | 1.076 | 1.010 | 1.203 | 1.082 | 0.989 | 0.928 |
| 4 | 137.21 | 1.064 | 1.100 | 0.997 | 1.134 | 1.038 | 0.959 | 0.911 |
| Correlation ($Corr_{IR}$) | | 0.822 | 0.902 | –0.352 | 0.526 | 0.323 | –0.993 | –0.878 |
| p value ($\alpha = 0.1$) | | 0.386 | 0.285 | 0.771 | 0.648 | 0.791 | 0.078 | 0.317 |

Table 5
Pearson correlation result for *SDR* ($Corr_{SDR}$)

| Pressure (bar) | SDR | Specific rejection ratio (SRR) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | CFN | CMZ | AAP | SMZ | IBP | ATN | TMP |
| 0 | 100.00 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 2 | 34.82 | 1.059 | 1.076 | 1.010 | 1.203 | 1.082 | 0.989 | 0.928 |
| 4 | 21.29 | 1.064 | 1.100 | 0.997 | 1.134 | 1.038 | 0.959 | 0.911 |
| Correlation ($Corr_{SDR}$) | | –0.996 | –0.998 | –0.155 | –0.876 | –0.747 | 0.804 | 1.000 |
| p value ($\alpha = 0.1$) | | 0.058 | 0.043 | 0.901 | 0.320 | 0.463 | 0.405 | 0.010 |

negative correlation thus negatively affected by the permeate water flux. Only ATN showed a significant correlation with *IR* ($p < 0.1$) and this is due to the strong hydrophilicity of ATN ($logD_{pH6.5} = -2.94$) compared to other compounds. This suggests the positively charged ATN adsorbed on the membrane have been transported through the membrane along with the water molecules more readily as hydraulic pressure was applied on the feed side.

To see the combined effect of both $J_w$ and $J_s$, *SDR*was put into correlation with *SRR* in accordance with TrOC rejection ($Corr_{SDR}$). Table 5 summarizes the correlation results.

*SDR* showed a strong positive correlation for CFN and CMZ compared to $Corr_{IR}$ ($p < 0.1$). This indicates the two neutral compounds were significantly affected by both the enhanced $J_w$ and reduced $J_s$. $Corr_{IR}$ for ATN was significantly higher than TMP, but $Corr_{SDR}$ for ATN is significantly lower than TMP. This impliesthe reduction of $J_s$ due to hydraulic pressure does not affect the transport behavior of ATN for its strong hydrophilicity (i.e. being transported with water molecules) while it actively engages in the transport of TMP.

In the FO-RO hybrid concept, TrOCs are rejected in both FO and RO processes thus the quality of the final product can be more adaptable various uses, even for potable water supply. This comes with the additional capital expenditure (CAPEX) due to installation of FO trains and feed and draw pumps and operating expenditure (OPEX) induced by the use of the pumps for the FO process. Despite such economic disadvantages, the OPEX for the following RO step can be significantly reduced due to the dilution of seawater (i.e. draw stream) thus the FO-RO hybridization can efficiently compensate such additional economic hurdles in regards of the implementation of the hybrid process in the long-term. Replacing FO with PAFO can reduce the CAPEX for the FO step due to enhanced water permeation and further accelerate the energy cost reduction in the RO step.

## 4. Conclusions

In the current work, the mechanistic effect of hydraulic pressure on the TrOC rejection in PAFO is studied and the following conclusions were drawn:

1. Additional hydraulic pressure enhanced permeate water flux ($J_w$) and reduced reverse solute flux ($J_s$), the similar trend observed in previous studies.
2. TrOC rejection in PAFO showed a clear variation depending on the physicochemical properties of the TrOCs. Rejection of neutral compounds is strictly governed by steric hindrance. Rejections of negatively charged compounds increases with additional hydraulic pressure but to a critical level of which the rejection decreases with further hydraulic driving forcedue to potential elimination of electrostatic repulsion induced by hydraulic pressure.Positively charged compounds showed a clear decreasing pattern in rejection with increasing hydraulic pressure due to facilitated diffusion of adsorbed compounds on the membrane surface.
3. Pearson correlation analysis for the rejection of neutral compounds showed the strongest correlation with *SDR* suggesting that the transport of neutral compounds with sizes bigger than the pore size of the membrane were affected by the combined effect

of both permeate water flux and reverse solute fluxin association with steric hindrance. Negatively charged compounds showed no correlation due to its unique rejection pattern. Unlike the rejections of neutral and negatively charged compounds, positively charged compounds followed a clear decreasing rejection pattern in high correlation with *IR* and *SDR* suggesting the facilitated diffusion of positively charged compounds.

PAFO can improve the membrane performance but the rejection of TrOCs can vary depending on their physicochemical properties. Cautious investigation is required in regards of removal of charged compounds in PAFO.

The FO-RO hybrid process for seawater desalination offers dual barrier for the TrOC rejection thus further guarantee the quality of the final product. The additional expenditures for the FO step can be compensated bythe dilution of seawater in the FO step which induces the energy cost reduction in the following RO step. Along with the benefits of dual barrier for TrOC rejection, replacing FO with PAFO can create further benefits of the dilution in the economic aspect.

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