Rejection of nine haloacetic acids and coupled reverse draw solute permeation in forward osmosis

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HIGHLIGHTS

• Forward osmosis rejects haloacetic acids (HAAs) well.
• The active-layer facing feed water (AL-FW) orientation is preferred.
• The solution-diffusion model predicts HAA rejection better for AL-FW.
• The solution-diffusion model accurately predicts reverse draw solution permeation.

GRAPHICAL ABSTRACT

The behaviors of haloacetic acid (HAA) rejection by forward osmosis are obtained by experiments and predicted by the solution-diffusion model combined with concentration polarization for both the AL-FW (active layer facing the feed water) and the AL-DS (active layer facing the draw solution) orientations.

A B S T R A C T

The rejection of haloacetic acids (HAAs) by forward osmosis (FO) and the coupled reverse draw solute permeation were experimentally determined and mathematically modeled by using the solution-diffusion model for both the AL-FW (active layer facing the feed water) and the AL-DS (active layer facing the draw solution) orientations. The rejection ratio for each HAA increased with the increase of draw solute concentration for the AL-FW orientation. In contrast, the HAA rejection ratio could reach its maximum under a medium osmotic pressure difference for the AL-DS orientation. The rejection ratios for all HAAs were higher than 94.6% for the AL-FW orientation and ranged from 73.8% to 89.1% for the AL-DS orientation under a draw solute concentration of 1 mol/L NaCl. The reverse draw solute flux for the AL-FW orientation was lower than that for the AL-DS orientation. The model-predicted HAA rejection results matched well with the experimental rejection ratios for the AL-FW orientation. However, the model over-estimated the rejection ratios for the AL-DS mode, likely due to the adoption of inaccurate mass transfer coefficient for internal concentration polarization. Regarding the reverse draw solute permeation, a general agreement between the model prediction and experimental data was observed for both orientations.

1. Introduction

Forward osmosis (FO) is a process driven by the difference in chemical potentials across a semi-permeable membrane with little hydraulic pressure applied. In recent years, the potential application of FO to...
wastewater reclamation has been extensively studied [1–3], which was normally fulfilled by combining FO with other technologies as a hybrid process [4]. The hybrid processes may compete favorably with the simple pressure-driven processes such as reverse osmosis (RO) owing to the fact that the former may have a lower demand on electrical energy and its membranes may suffer less membrane fouling [2,5–7]. One of the biggest concerns about wastewater reclamation is the removal efficiencies for the large number of trace organic compounds at concentrations in the magnitudes of ng/L to μg/L. Common trace organic compounds include endocrine disruptors (EDCs), pharmaceutical and personal care products (PPCPs) and disinfection by-products (DBPs) [8–11]. The reclaimed water is better to be free of these trace organic compounds due to their potentially high health risks to humans and aquatic organisms.

Previous studies [2,12–17] showed that the rejection of PPCPs and EDCs by FO process varied among the compounds and the operational conditions. Results by Hancock revealed that rejection efficiencies by FO depended primarily on molecular size and charge. Rejection of positively and negatively charged trace organic compounds was greater than 80%, while rejection of the nonionic trace organic compounds varied, between approximately 40% and 90% [18]. Xie et al. [13] found that the membrane orientation (AL-FW (active layer facing feed water) and AL-DS (active layer facing draw solution)) affected the rejection performance.

Development of mathematical models capable of predicting the rejection of the trace organic compounds by the FO process will improve the economic efficiency of the process and expand its applications. By far, there has been only a few work conducted on the modeling of the rejection performance by FO, among which the model based on the solution-diffusion model developed by Jin et al. [19] was found was able to accurately predict the FO rejection of inorganic solutes. It is also desirable to model the permeate water flux and the reverse draw solute flux through the membrane. The limited water flux and the substantial reverse draw solute flux are among the biggest impediments to the viability of the FO processes [20,21]. In this regard, a few studies investigated the reverse draw solute permeation in the FO process and proposed a relationship with the water flux [22,23]. Better understanding and prediction of feed contaminant and coupled reverse draw solute permeation in FO membrane processes can facilitate to optimize the operational conditions and benefit to fabricate FO membranes that minimize the loss of draw solute into the feed solution, thereby reducing operating costs.

Haloacetic acids (HAAs) are among the DBPs with the highest concentrations in chlorinated or chloraminated sewage treatment plant effluent. The trichloroacetic acid (TCAA) concentration can be as high as 471 μg/L in the chlorinated wastewater effluent [24]. This study mainly investigated the rejection of nine HAAs and the reverse draw solute permeation in the FO process for both the AL-FW and the AL-DS orientations. Substantial attention was paid to the mathematical description of the water, HAA and draw solute fluxes. This study also evaluated the feasibility of the solution-diffusion model in predicting the rejection of organic contaminants and coupled draw solute permeation in the FO process.

2. Materials and methods

2.1. The FO system and operations

The schematic diagram of the bench-scale FO system is shown in Fig. 1. The membrane unit was custom built with two flow channels of 2 mm in height both, which were separated by an FO membrane coupon that had an effective area of 40.5 cm². The commercial FO membrane was provided by Hydration Technologies, Inc. (Albany, OR) and, according to the manufacturer, was made of cellulose triacetate supported by embedded polyester screen mesh. The recirculation flows of the feed water (FW) and the draw solution (DS) on the two sides of the membrane were counter-current with a flow velocity of 20.4 cm/s both, each regulated by a variable-speed gear pump (Longer, USA). The relatively high cross-flow velocity can substantially suppress the external concentration polarization (ECP) that will be described in detail later.

Ultrapure water (Milli-Q, Millipore, USA) was used for the FW and the DS preparation. The FW was prepared by dissolving a mixture of the nine haloacetic acids (HAAs) (Sigma-Aldrich, Germany) into a 10 mmol/L NaCl (as background solute) solution with the final concentration for each HAA at 200 μg/L. The FW ionic strength was similar to the typical values for freshwater including sewage treatment plant effluent, although our preliminary study showed that the FW ionic strength (0–20 mmol/L) had negligible influence on the rejection of HAAs. The nine HAAs were monochloroacetic acid (MCAA), monobromoaetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoaetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBBAA) and tribromoaetic acid (TBA). Physicochemical properties for each HAA including molecular weight (MW) and dissociation constant (pKa) were summarized in Table 1. Sodium bicarbonate was added into the FW to adjust the pH to neutral (pH = 7). No natural organic matter (NOM) or soluble microbial products (SMPs) were contained in the FW, though both NOM and SMP could not only adsorb certain trace organic compounds but also lead to membrane fouling, which would greatly affect the rejection performance of the FO process [12]. The DS was a NaCl solution at a concentration varying from 0.1 to 3 mol/L.

The FO experiments were conducted in an air-conditioned room with the temperature set at 25 ± 1 °C. Each FO test lasted for about 4 h. The duration was long enough to obtain accurate water, HAA and reverse draw solute permeation fluxes. On the conclusion of each FO test, the volume variation of the DS (or the FW) was less than 5%, and as such the draw solute (in the DS) and the HAA (in the FW) concentration variation were negligible. The FW tank was placed on a digital scale (Mettler Toledo, Germany) connected to a computer data logging...
system. The weight change as a function of time was utilized to determine the permeate water flux,

$$J_w = \frac{\Delta m}{\Delta A t_{m}}$$  \hspace{1cm} (1)

where $\Delta m/\Delta A t$ is the weight change rate and $A_{m}$ is the effective area of the membrane coupon.

At specified time intervals, samples were taken from either the FW tank or the DS tank for HAA concentration, chloride ion and pH value determination. The variation of the HAA concentrations in the DS was used to determine the HAA flux through the FO membrane, while the variation of the NaCl concentration in the FW was used for the determination of the reverse solute flux through the FO membrane,

$$J_w = \frac{\Delta V_c}{\Delta t_{m}}$$  \hspace{1cm} (2)

where $\Delta V_c/\Delta t_{m}$ is the variation of target compound in the FW or DS tanks during the specified time interval $\Delta t$.

Given the permeate water flux ($J_w$) and the HAA fluxes ($J_{HAA}$), the rejection ratio of each HAA compound ($R_{HAA}$) in the FO process can be obtained by

$$R_{HAA} = 1 - \frac{J_{HAA}}{J_w c_{F,HAA}}$$  \hspace{1cm} (3)

where $c_{F,HAA}$ is the HAA concentrations in the FW, which did not change significantly in each FO test.

### 2.2. Mathematical expressions for the water, HAA and draw solute fluxes

The mathematical expressions for the water, HAA and draw solute fluxes can be referred to the model developed by Elimelech, Tang and their colleagues [25–29]. Most of the previous models made use of the solution-diffusion model coupled with concentration polarization. For the AL-FW orientation, the draw solute experiences dilutive internal concentration polarization (ICP) on the DS side and concentrative ECP on the FW side. The permeate water flux $J_w$ is expressed by

$$J_w = A \left( \pi_{D,NaCl} \exp \left( -J_w/K_{m,NaCl} \right) - \pi_{F,NaCl} \exp \left( J_w/K_{m,NaCl} \right) \right).$$  \hspace{1cm} (4)

The reverse draw solute flux $J_{NaCl}$ can be expressed as

$$J_{NaCl} = B_{NaCl} \left( c_{D,NaCl} \exp \left( -J_{w}/K_{m,NaCl} \right) - c_{F,NaCl} \exp \left( J_{w}/K_{m,NaCl} \right) \right).$$  \hspace{1cm} (5)

The HAA flux through the FO membrane can be expressed as

$$J_{HAA} = \frac{B_{HAA} \exp \left( J_{w}/K_{m,NaCl} \right)}{1 + B_{HAA}/J_w} c_{F,HAA}$$  \hspace{1cm} (6)

where $A$ and $B$ are the water permeability coefficient and the solute (draw solute or HAA) permeability coefficient, respectively, and $K_{m}$ and $c_{m}$ are the mass transfer coefficients for ICP and ECP, respectively. $K_{m}$ is also called the solute resistivity for diffusion within the porous layer, and is related with the $S$ value by $K_{m} = D/S$. The $S$ parameter is the intrinsic length scale of ICP in the FO membrane support layer, which is analogous to the boundary layer thickness for ECP. Mathematically, $S$ is related to the thickness ($t$), tortuosity ($\tau$) and porosity ($\varepsilon$) of the support layer by $S = \tau t / \varepsilon$. The $S$ value is usually obtained by fitting the water flux vs. draw solute osmotic pressure data under known hydraulic conditions (Eq. (4) or Eq. (7) below). (Care however must be taken in that it is not a direct method and the inaccuracy of a number of parameters would lead to the inaccurate determination of the $S$ value.) Given the $S$ value, the $K_{m}$ value for any solute can be easily obtained only if the diffusivity ($D$) is known. $K_{m}$ is hardly affected by the hydrodynamic conditions. In contrast, the $K_{m}$ value is controlled by the hydrodynamics and can be calculated by $k_{m} = Sh d_{w}$, where $Sh$ and $d_{w}$ are the Sherwood number and the hydraulic diameter of the FO cell channel, respectively.

For the AL-DS orientation, the draw solute experiences dilutive ECP on the DS side and concentrative ICP on the FW side. The permeate water flux can be expressed as

$$J_w = A \left( \pi_{D,NaCl} \exp \left( -J_{w}/K_{m,NaCl} \right) - \pi_{F,NaCl} \exp \left( J_{w}/K_{m,NaCl} \right) \right).$$  \hspace{1cm} (7)

The reverse draw solute flux can be expressed as

$$J_{NaCl} = B_{NaCl} \left( c_{D,NaCl} \exp \left( -J_{w}/K_{m,NaCl} \right) - c_{F,NaCl} \exp \left( J_{w}/K_{m,NaCl} \right) \right).$$  \hspace{1cm} (8)

### Table 1

<table>
<thead>
<tr>
<th>Haloacetic acids (HAAs)</th>
<th>Structure</th>
<th>MW [g/mol]</th>
<th>pKa</th>
<th>$D_w^b$ (m²/s)</th>
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</thead>
<tbody>
<tr>
<td>Chloroacetic acid (MCAA)</td>
<td><img src="image1" alt="Structure" /></td>
<td>93.98</td>
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<td>138.95</td>
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<td>1.16E-09</td>
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<td><img src="image3" alt="Structure" /></td>
<td>128.94</td>
<td>1.37</td>
<td>1.07E-09</td>
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<td>Bromochloroacetic acid (BCAA)</td>
<td><img src="image4" alt="Structure" /></td>
<td>173.39</td>
<td>1.39</td>
<td>1.04E-10</td>
</tr>
<tr>
<td>Dibromoacetic acid (DBAA)</td>
<td><img src="image5" alt="Structure" /></td>
<td>217.84</td>
<td>1.47</td>
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<tr>
<td>Trichloroacetic acid (TCAA)</td>
<td><img src="image6" alt="Structure" /></td>
<td>163.39</td>
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<td>0.051</td>
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<td>Chlorodibromoacetic acid (CDBAA)</td>
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<td>0.13</td>
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<td>Tribromoacetic acid (TBA)</td>
<td><img src="image9" alt="Structure" /></td>
<td>296.74</td>
<td>0.22</td>
<td>8.96E-10</td>
</tr>
</tbody>
</table>

*a* Obtained by using the ACD Lab software.

*b* Calculated using the Wilke-Chang equation.
The HAA flux from the FW to the DS can be expressed as

\[
J_{\text{HAA}} = \frac{B_{\text{HAA}} \exp\left(\frac{J_w}{K_{m,\text{HAA}}}\right)}{1 + B_{\text{HAA}} \exp\left(\frac{J_w}{K_{m,\text{HAA}}}\right) \exp\left(-\frac{-J_w}{K_{m,\text{HAA}}}\right) c_L^{m,\text{HAA}}.}
\]  

A rough calculation revealed that the Sherwood number and the \( k_m \) value were approximately 150 and 4 \times 10^{-5} \text{ m/s}, the latter of which was much larger than the water permeation flux (\( J_w \)) (see below). Therefore, ECP was sufficiently suppressed so that it did not affect the flux of water, NaCl or HAA in this study (i.e. \( J_w / k_m \approx 1 \)).

### 2.3. Determination of the permeability coefficients

A pressurized cross-flow filtration test unit was used for the determination of the water, NaCl and HAA permeability coefficients pertinent to the FO membrane [30]. In the filtration unit, the active layer of the FO membrane faced the high pressure side (i.e. under RO testing mode) to eliminate the influence of ICP. The effective membrane area was 42 cm² and the water temperature was maintained at 25 ± 1 °C.

The water permeability coefficient (\( A \)) was derived from the water flux versus the applied pressure (0–12 bar) obtained by filtering high-purity water (Milli-Q, Millipore, USA), i.e. \( J_w = A \cdot \Delta \pi \). The NaCl permeability coefficient (\( B_{\text{NaCl}} \)) was derived from the rejection ratio versus the applied pressure (Eq. (10)) by filtering a 10 mmol/L NaCl solution.

\[
R = \frac{1}{\frac{B_{\text{NaCl}}}{1 + \frac{B_{\text{NaCl}}}{A \cdot \Delta \pi}}}
\]

where \( \Delta \pi \) is the osmotic pressure difference across the membrane. The HAA permeability coefficients (\( B_{\text{HAA}} \)) were also derived from the rejection ratio versus the applied pressure (Eq. (10)) by filtering the mixed solution of the nine HAAs with 10 mmol/L NaCl as background. It was assumed that the rejection of each HAA was independent when the background salt concentration was much higher than that of any HAA.

The HAA permeability coefficients can also be determined by using the diaphragm cell test [31]. The cylindrical diffusion cell (Fig. 1) was made of glass and consisted of two compartments which were separated by an FO membrane with an effective surface area of 20.4 cm². Each compartment had a volume of 1 L. For the diaphragm cell test, one compartment contained a solution of NaCl at 10 mmol/L, and the other contained a solution of both NaCl at 10 mmol/L and the target HAAs at 500 μg/L each. The pH of the HAA solution was adjusted to around 7 by using a minimum volume of the NaHCO₃ solution. The ionic strength of the two compartments was almost the same (approximately 500 μmol/L), thus avoiding water permeation driven by osmotic pressure difference. The solutions in both compartments were continuously magnetically stirred and thermostatically stabilized at a temperature of 25 ± 1 °C. Samples from the two compartments were taken for HAA measurement every day that lasted for 18 days. The permeability coefficient can be calculated by using Eq. (11) [31].

\[
B = \frac{1}{A_{\text{at}}(1/(V_{\text{So}}) + 1/(V_{\text{Re}}))} \ln \left( \frac{c_{\text{So}}^{l} - c_{\text{Re}}^{l}}{c_{\text{So}}^{r} - c_{\text{Re}}^{r}} \right)
\]

where \( c_{\text{So}}^{l} \) and \( c_{\text{So}}^{r} \) are the HAA concentrations in the source and receiver of the diffusion process at \( t = 0 \), \( c_{\text{So}}^{l} \) and \( c_{\text{Re}}^{l} \) are the concentrations of the solute in the source and receiver at time \( t \), \( A_{\text{at}} \) is the membrane area, and \( V_{\text{So}} \) and \( V_{\text{Re}} \) are the volumes of the source and receiver of the diaphragm cell, respectively.

### 2.4. Analytical methods

The HAAs were analyzed by a gas chromatograph equipped with an electron capture detector (Agilent 7890A, Santa Clara, USA) after liquid-extraction according to the U.S. EPA Standard Method 552.3 [U.S. EPA, 2003]. The NaCl concentration was determined by monitoring the chloride ion concentration, which was detected by an ion chromatograph (Metrohm, Switzerland).

### 3. Results and discussion

#### 3.1. Permeability coefficients of the FO membrane

By conducting the pressurized cross-flow filtration tests, the \( A \) and \( B_{\text{NaCl}} \) values were determined as 2.38 ± 0.04 \times 10^{-7} \text{ m/(s bar)} and 2.90 ± 0.5 \times 10^{-7} \text{ m/s}, respectively, which are very close to that reported by others [19].

The determined permeability coefficients for each HAA by both the pressurized cross-flow filtration test and the diaphragm cell test were shown in Table 2 (the determination of the TBAA permeability coefficient was not attainable using the diaphragm cell test due to the substantial hydrolysis of TBAA [8] during the test). The values obtained from the diaphragm unit were slightly higher than that from the pressurized filtration (Table 2). This might lie in the fact that the permeability coefficient of the solute is a concentration-dependent parameter. Studies showed that both the diffusion coefficient in the dense polymer and the partitioning coefficient at the solution–polymer (both of which determine the permeability coefficient) are weakly dependent on the solution concentration [32,33]. However, the reliance of the permeability coefficient on the solute concentration can usually be ignored [34,35].

#### 3.2. Water permeation, HAA and reverse NaCl fluxes

An increase in water permeation flux was observed with an increase in the DS NaCl concentration (i.e. apparent osmotic pressure difference between the DS and FW) for both the AL-FW and AL-DS orientations (Fig. 2). Under the same osmotic pressure difference, the water permeation flux for the AL-FW orientation was always lower than that for the AL-DS orientation. For example, when the DS NaCl concentration was 1 mol/L, the water permeation fluxes for the AL-FW and AL-DS orientations were 12.8 and 20.6 L/(m²h), respectively. When the FO membrane was operated in the AL-FW orientation, severe dilutitive ICP of the draw solution occurred which greatly reduced the effective osmotic pressure difference across the FO membrane. In contrast, mild concentrative ICP was mainly responsible for the decrease of the effective osmotic pressure for the AL-DS orientation. Given the permeability coefficients of water (\( A \)) and NaCl (\( B_{\text{NaCl}} \)), the mass transfer coefficient of NaCl (\( K_{\text{m,NaCl}} \)) can be obtained by fitting the water flux and the osmotic pressure data using either Eq. (4) (for the AL-FW orientation) or Eq. (7) (for the AL-DS orientation). The \( K_{\text{m,NaCl}} \) values obtained from the AL-FW orientation data and the AL-DS orientation data were almost

<table>
<thead>
<tr>
<th>HAAs</th>
<th>Diaphragm cell test (m/s)</th>
<th>Pressurized filtration test (m/s)</th>
<th>Average values (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCAA</td>
<td>3.00E-07</td>
<td>2.05E-07</td>
<td>2.53E-07</td>
</tr>
<tr>
<td>MBAA</td>
<td>2.18E-07</td>
<td>1.59E-07</td>
<td>1.89E-07</td>
</tr>
<tr>
<td>DCAA</td>
<td>8.62E-08</td>
<td>6.13E-08</td>
<td>7.37E-08</td>
</tr>
<tr>
<td>TCAA</td>
<td>4.34E-08</td>
<td>3.26E-08</td>
<td>3.80E-08</td>
</tr>
<tr>
<td>BCAA</td>
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<td>3.30E-08</td>
<td>3.84E-08</td>
</tr>
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</tr>
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<td>CBAA</td>
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<td>1.46E-08</td>
</tr>
<tr>
<td>TBAA</td>
<td>NA^4</td>
<td>1.49E-08</td>
<td>1.49E-08</td>
</tr>
</tbody>
</table>

^4 Not available due to substantial hydrolysis [8].
identical, which were $2.78 \times 10^{-6}$ and $2.73 \times 10^{-6}$ m/s respectively. These values matched well with those reported by Jin et al. [19] ($2.73 \times 10^{-6}$ m/s), but somewhat lower than those reported by Tang et al. [27] ($4.2 \times 10^{-6}$ and $3.3 \times 10^{-6}$ m/s for the AL-FW and AL-DS orientations, respectively). With both $K_{m,NaCl}$ ($2.76 \times 10^{-6}$ m/s) and the diffusion coefficient of NaCl ($D_{NaCl}$, $1.5 \times 10^{-9}$ m$^2$/s [36]) known, the $S$ value (i.e. the intrinsic parameter of the FO membrane which determines the ICP within the supporting layer by membrane thickness, tortuosity and porosity) was calculated to be $5.43 \times 10^{-4}$ m. Note however that the osmotic pressure for the draw solution might be under-estimated due to use of the Morse equation (i.e. linear relationship of the osmotic pressure with the concentration) for the calculation. It indicates that the $K_{m,NaCl}$ value might be somewhat over-estimated and in turn the $S$ value was somewhat under-estimated. However, the under-estimation was estimated within 10%.

For both orientations, the HAA fluxes also increased with the increase of the DS NaCl concentration (Fig. 3). A general trend could be found that the smaller the molecular weight of the HAA species, the higher the HAA flux through the FO membrane. In other words, the HAA flux mainly followed the declining order of MCAA, MBAA, DCAA, TCAA/BCAA, DBAA/BDCAA, CDBAA and TBAA. It was assumed that FO follows the solution-diffusion model, and an HAA of smaller weight might have a higher "diffusion" rate within the active layer of the FO membrane. In addition, the stability (i.e. hydrolysis) and the water bonding potential of HAAs would probably also influence the permeation of HAAs through the FO membrane [37,38].

The main difference between the two orientations is that under the same osmotic difference, the HAA flux for the AL-FW orientation was much lower than that for the AL-DS orientation (Fig. 3). Severe concentrative ICP of the HAA species occurred for the AL-DS orientation, which greatly increased the HAA concentration at the active layer–supporting layer interface. In contrast, no ICP of the HAA species would occur for the AL-FW orientation. Another difference between the two orientations is that the HAA fluxes increased acceleratedly for the AL-DS orientation while it increased decelerately for the AL-FW orientation when the DS NaCl concentration was increased. The higher water flux for the AL-DS orientation than that for the AL-FW orientation and the critical role of ICP of HAA are responsible for the difference. The extent of HAA concentration polarization is exponentially dependent on the water permeation flux which results from the severe concentrative ICP caused by high water flux for the AL-DS orientation [39].

For reverse draw solute permeation, as the DS NaCl concentration increased, the measured reverse draw solute flux increased for both orientations (Fig. 4). However, the reverse draw solute flux for the AL-FW
orientation is much lower than that for the AL-DS orientation. For instance, when the DS NaCl concentration was 1 mol/L, the reverse draw solute fluxes were 0.21 and 0.55 mol/(m²h) for the AL-FW and AL-DS orientations, respectively (Fig. 4).

3.3. HAA rejection ratios

With both the water permeation flux and the HAA fluxes obtained, the rejection ratios of the various HAAs by FO could be calculated using Eq. (3). The results demonstrated that the rejection ratio for each HAA showed a monotonous increase with the increase of DS NaCl concentration for the AL-FW orientation (Fig. 5). This is due to the more enhancement of the water permeation flux than the HAA flux with the increase of the DS NaCl concentration (Eq. (3)). In contrast, the HAA rejection ratios could reach their maximum under a medium osmotic pressure difference for the AL-DS orientation. The increase in water permeation flux was faster than the HAA flux when the DS NaCl concentration was relatively low, while the increase in water permeation flux was slower when the DS NaCl concentration was relatively high. Therefore, HAA rejection increased initially with the increase of water flux due to the enhanced dilution effect and a further increase in water flux resulted in a reduced rejection due to very severe ICP of HAAs. This convex profile was also observed in other studies for boric acid removal by FO [19].

The rejection ratios for MCAA and MBAA were 94.6% and 95.1%, respectively, and that for the rest of HAAs were higher than 97.0% for the AL-FW orientation, with a DS NaCl concentration at 1 mol/L. This performance is comparable to that of nanofiltration (NF) and reverse osmosis (RO). Agus and Sedlak reported that the HAA rejection ratios were between 56% and 100% by NF, and between 86% and 94% by RO depending on the applied pressures [38]. If all FO, NF and RO reject solute by the same mechanism, the FO membrane should have a surface “pore” size that is comparable to that of an NF or RO membrane. In addition, similar to the NF/RO membranes, another mechanism contributing to the HAA removal in FO might be charge repulsion [19]. HAAs were highly rejected by FO, NF or RO because HAAs dissociate and are negatively charged unless the pH is very low (≤3). HAAs were highly rejected by FO, NF or RO because HAAs dissociate and are negatively charged unless the pH is very low (≤3) (Table 1). Most FO, NF and RO membrane surfaces are also negatively charged at circum-neutral pH ranges. Under the DS NaCl concentration of 1 mol/L, the rejection ratios for all the respective HAAs ranged from 73.8% to 89.1% for the AL-FW orientation, which were high but lower than those for the AL-FW orientation. It is because of the much higher HAA flux, albeit relatively higher water permeation flux for the AL-FW orientation. Based on current FO membrane technology, the AL-FW orientation may not be preferred due to its lower removal efficiency of pollutants and higher membrane fouling potential [14,19].

3.4. HAA rejection and reverse draw solute flux prediction

With the S value obtained, the mass transfer coefficient for each HAA (Km,HAA) can be calculated by the ratio of respective diffusion coefficient listed in Table 1 to the S value (Km = D/S). In this study, the average of the two values of the HAA permeability coefficient (BHAA) was used for the prediction of the rejection ratios of the HAAs (Table 2).

Given the water permeability coefficient (A), the HAA permeability coefficient (BHAA) and the HAA mass transfer coefficient (Km,HAA), the rejection ratio for each HAA can be predicted by using Eq. (3) in combination with Eq. (6) for the AL-FW orientation or Eq. (9) for the AL-DS orientation. The modeling results matched well with the experimentally-obtained rejection ratios when the FO was operated in the AL-FW orientation mode (Fig. 5). However the modeling results over-estimated the rejection ratios when the FO was operated in the AL-DS mode (for which Km,HAA took an important role). There are some possible reasons for the over-estimation. As described earlier, the under-estimation of the S value would be partly responsible for the over-estimation of the Km,HAA value and in turn the HAA rejection ratios. If it were the case, the rejection ratio over-estimation would be more significant for MCAA and MBAA, because both of them have smaller molecular weight and thus larger diffusion coefficient than others. Recently, studies [40] showed that the permeability coefficient might be better quantified by Km = δD/S, where δ is the so-called constricitivity factor. The constricitivity factors for sodium ion, chloride ion and the HAAs may not be identical, which was also partly responsible for the over-estimation of the HAA rejection ratios. However, because Na+, Cl– and the HAA species are all small molecules, such effect of δ would be very limited. Another probable reason for the over-estimation of the rejection ratio was that the actual diffusivity for each HAA was lower than that shown in Table 1. In this study, the molecular size of each HAA was calculated by using the Wilke–Chang equation, which was then utilized for the calculation of the diffusivity by using the Einstein–Stokes equation. More accurate determination of the diffusivity for each HAA in the FO membrane support layer may to some extent reduce the difference between the predicted and the experimental results for the HAA rejection ratios. Moreover, FO membranes were recently found containing pores of sub-nm sizes in the active layer [41–43]. As such, somewhat in contradictory to the assumption of the solution-diffusion model that the solute (both NaCl and HAA) was

![Fig. 5. The HAA rejection ratios obtained by experiments and predicted by the model as a function of the DS NaCl concentration for the AL-FS orientation (top) and the AL-DS orientation (bottom).](image-url)
transferred through the FO membrane active layer by diffusion only, mass transfer of HAA through the active layer by convection was also possible especially when the water permeation flux was high. The contribution by this mechanism however needs more investigation.

Given the water permeability coefficient \(A\) and the NaCl permeability coefficient \(B_{NaCl}\), the reverse draw solute (NaCl) flux can be predicted by using Eq. (12) [23,27].

\[
\frac{J_{NaCl}}{J_{w}} = \frac{B_{NaCl}}{A n R_g T}
\]

where \(n\) is the number of dissolved species of the draw solute (2 for NaCl), \(R_g\) the universal gas constant, and \(T\) the absolute temperature. An assumption that underlies Eq. (12) is that the calculation of the osmotic pressure follows the van’t Hoff equation [22,23,27]. Eq. (12) shows that the ratio of reverse draw solute flux to the water flux is independent of the DS concentration or the extent of the concentration polarization [22,23,27]. As shown in Fig. 6, the experimental results confirmed that the ratio of reverse draw solute to the water flux was a constant for both the AL-FW and AL-DS orientations. The desire for higher water flux and the concurrent higher reverse draw solute flux are in contradiction for the current FO process. Compared with the AL-FW orientation, both water flux and reverse draw solute flux for the AL-DS orientation are higher because of the absence of dilutive ICP of the draw solute. According to Eq. (12), the best way to reduce the reverse flux of the draw solute is to either decrease the NaCl permeability coefficient \(B_{NaCl}\) or increase the water permeability coefficient \(A\). By far, a number of studies were devoted primarily to the increase of the water permeability coefficient by incorporation into the FO membrane active layer of highly water-permeable aquaporin-based proteoliposomes [44] or nanomaterials (e.g. zeolite particles or nanotube) [45,46].

The reverse draw solute flux can be also predicted by the solution-diffusion model (Eq. (5) for the AL-FW orientation and Eq. (8) for the AL-DS orientation) by assuming that the NaCl concentrations in the feed and draw solutions are constant, given the experimentally determined parameters of the membrane \(K_{m,NaCl} = 2.76 \times 10^{-6}\) m/s, \(D_{NaCl} = 1.5 \times 10^{-9}\) m²/s, \(S = 5.43 \times 10^{-4}\) m), and \(k = 1.96 \times 10^{-5}\) m/s. The agreement between the model prediction and the experimental data is evident (Fig. 7), with the slope of the correlation line equal to 1. It demonstrated that the solution-diffusion model combined with concentration polarization can be used for the prediction of the reverse draw solute permeation in a multicomponent system.

4. Conclusions

In this paper, the water flux, solute flux and reverse draw solute flux were systematically investigated:

(1) For both membrane orientations, the HAA fluxes and reverse draw solution permeation flux increased with the increase of the DS concentration. The smaller the molecular weight of an HAA, the higher the HAA flux through the FO membrane. The HAA fluxes increased acceleratedly for the AL-DS orientation while it increased deceleratedly for the AL-FW orientation with the increase of the DS concentration. The reverse draw solute flux for the AL-FW orientation was much lower than that for the AL-DS orientation.

(2) The rejection ratio for each HAA showed a monotonous increase with the increase of DS concentration for the AL-FW orientation. In contrast, the HAA rejection ratios could reach their maximum under a medium osmotic pressure difference for the AL-DS orientation. The rejection ratios for HAAs were more than 94.6% for the AL-FW orientation and ranged from 73.8% to 89.1% for the AL-DS orientation under the DS NaCl concentration of 1 mol/L.

(3) The solution-diffusion model combined with the concentration polarization model was able to predict the bi-directional mass transfer in FO systems. However the modeling results overestimated the rejection ratios for HAAs for the AL-DS orientation.
Nomenclature

- \( A \): water permeability of the membrane (L/(m² h bar))
- \( A_m \): effective area of the membrane coupon (cm²)
- \( B \): solute permeability of the membrane (µg/(m² h bar))
- \( c \): solute concentrations (µg/L)
- \( c_0 \): concentrations of the solute at \( t = 0 \) (µg/L)
- \( c^\prime \): concentrations of the solute at time \( t \) (µg/L)
- \( d_h \): hydraulic diameter of the channel (m)
- \( D \): diffusion coefficient (m²/s)
- \( J_w \): permeate water flux (L/(m² h))
- \( J_{\text{HAA}} \): HAA fluxes (µg/(m² h))
- \( k_m \): mass transfer coefficient accounting for ECP (m/s), \( k_m = \frac{\mu_{\text{g}}}{t} \)
- \( k_m' \): resistivity for diffusion within the porous support layer (m/s), \( k_m' = \frac{1}{t} \)
- \( M_b \): molecular weight of the solvent (water) (g/mol)
- \( n \): number of dissolved species of the draw solute (2 for NaCl)
- \( R \): solute rejection ratio
- \( R_b \): universal gas constant (J/(K mol))
- \( S \): intrinsic parameter related to support layer structure (m), \( S = \frac{t_t}{t} \)
- \( S_h \): Sherwood number of the appropriate flow regime in the rectangular flow channel
- \( T \): absolute temperature (K)
- \( t \): thickness of the support layer (m)
- \( V \): volume of the solution in the diaphragm cell (L)
- \( V_A \): solute molar volume at the boiling point (m³/(kg mol))

Greek symbols

- \( \Delta t \): variation of time interval (h)
- \( \Delta (V_c) \): weight change of target compound content (kg)
- \( \Delta m/\Delta t \): weight change rate (µg/(L h))
- \( \Delta P \): hydraulic pressure difference (bar)
- \( \Delta P_{\text{osm}} \): osmotic pressure difference across the membrane (bar)
- \( \Delta c \): solute concentration difference across the active layer (mol/L)
- \( \mu_s \): solvent viscosity (Pa s)
- \( \varepsilon \): porosity of the support layer
- \( \varphi \): tortuosity of the support layer
- \( \psi \): association parameter of the solvent (2.6 for water)

Subscripts

- \( D \): draw solution
- \( F \): feed water
- \( \text{HAA} \): each of the halaetic acids
- \( \text{NaCl} \): draw solute
- \( R_e \): receiver of the diffusion process
- \( S_o \): source of the diffusion process
- \( w \): water

References


