Impact of organic and colloidal fouling on trace organic contaminant rejection by forward osmosis: role of initial permeate flux

Ming Xie  
*University of Wollongong, mx504@uowmail.edu.au*

Long D. Nghiem  
*University of Wollongong, longn@uow.edu.au*

William E. Price  
*University of Wollongong, wprice@uow.edu.au*

Menachem Elimelech  
*Yale University*

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Keywords
organic, rejection, colloidal, forward, osmosis, role, initial, permeate, flux, impact, fouling, trace, contaminant

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Impact of organic and colloidal fouling on trace organic contaminant rejection by forward osmosis: Role of initial permeate flux

Desalination

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Ming Xie¹, Long D. Nghiem ¹*, William E. Price ², and Menachem Elimelech ³

¹ Strategic Water Infrastructure Laboratory, School of Civil, Mining and Environmental Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

² Strategic Water Infrastructure Laboratory, School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia

³ Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06520-8286, USA

* Corresponding author: Long Duc Nghiem, Email: longn@uow.edu.au; Ph +61 2 4221 4590
Abstract

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Keywords: Fouling layer structure; forward osmosis; trace organic contaminants (TrOCs); humic acid; colloidal particles.
1. Introduction

The advancement of water treatment processes with low energy consumption that can ensure a reliable, safe, and adequate supply of water is essential in the context of continuing urbanisation, population growth, and climate change [1]. Extracting clean water from unconventional sources, such as seawater and secondary treated effluent, has been recognised as an important avenue to secure a reliable freshwater supply that is independent of the hydrological cycle. Reverse osmosis (RO) membranes have been widely used for both seawater desalination and water reclamation. However, the RO process can be energy intensive, particularly for seawater desalination.

A notable approach to reduce energy consumption by seawater desalination is to use osmotic dilution by operating forward osmosis (FO) and RO processes in tandem [2, 3]. In this concept, FO can safely and efficiently facilitate the use of wastewater or any other impaired water sources to dilute the seawater entering an RO desalination plant. The FO membrane acts as a selective barrier that rejects contaminants and foulants but allows pure water to permeate through to dilute the seawater. Because membrane fouling is generally less problematic in FO than RO, the FO process can also act as a pre-treatment step prior to RO filtration [4]. Although this approach offers a double barrier for contaminant removal, there remain several challenges associated with the reclamation of impaired water for potable use, especially concern over the occurrence of trace organic contaminants (TrOCs) in municipal wastewater [5].

FO processes have recently received increasing attention as a potential new technology for the treatment of highly contaminated water. One example is the use of FO membranes in commercially available personal hydration packs, which use a mixture of sugar and nutrient as the draw solute to provide energy drinks from any water source in emergency situations. In this example, and in the osmotic dilution process described above, it is essential to ensure the removal of TrOCs from the source water. Indeed, several recent studies have shown that the rejection of TrOCs by FO membranes could be significantly influenced by membrane properties [6], physicochemical properties of the solutes [7-9] and solution chemistry [10]. However, since the FO process can be applied to water sources with high fouling propensity, a major research gap is to understand the impact of membrane fouling on the rejection of TrOCs.
The fouling layer may change the membrane surface characteristics, leading to changes in the rejection of TrOCs. Hancock et al. [8] observed that rejection of TrOCs by the FO membrane substantially increased when the membrane was fouled by wastewater effluent. Valladares Linares et al. [9] also reported an increase in rejection of ionic and neutral TrOCs by an FO membrane that was fouled by secondary treated effluent. However, it is noteworthy that these studies were conducted using cellulose-based FO membranes, which were able to generate relatively low permeate water flux (less than 10 L/m²h). To date, however, little is known about the impact of fouling on TrOC rejection by the new generation thin-film composite (TFC) FO membranes which can offer much higher permeate water fluxes due to their superior intrinsic transport properties compared to the asymmetric cellulose-based FO membranes.

Initial permeate water flux could alter the structure of the fouling layer and thus result in notably different fouling behaviour in the FO process. Mi and Elimelech [11] observed a severe water flux decline at the early stage of filtration when the feed water contained model organic foulants (i.e., alginate, humic acid and bovine serum albumin) at a high initial permeate flux. Similar observations were also reported by Tang et al. [12] and Zou et al. [13] who examined the fouling behaviour of humic acid and alginate as a function of initial permeate flux. In addition, direct microscopic observation of membrane fouling in FO also highlighted the effect of initial permeate flux on fouling behaviour. Wang et al. [14] observed a dramatic increase in the amount of latex particles deposited onto the membrane surface when the initial permeate flux was greater than 28 L/m²h. Zou et al. [15] investigated the fouling behaviour of micro-algae as a function of initial permeate flux and observed significant deposition of algae when the initial permeate flux was above 10 L/m²h. However, to date, no attempt has been made to elucidate the impact of fouling layer structures that are formed at both low and high initial permeate fluxes on the rejection of TrOCs.

The aim of this study was to elucidate the fouling behaviour of humic acid and colloidal particles at different initial water fluxes and the associated impact on the rejection of TrOCs by FO. Membrane fouling behaviours were characterised in terms of water flux decline and water flux recovery after membrane flushing to gain insights on fouling layer structure. Mechanisms governing the rejection of TrOCs at different initial permeate fluxes were proposed by relating TrOC rejection behaviour to the different characteristics of fouling layer structures.
2. Materials and methods

2.1. FO membrane and characterisations

A commercially available high-performance TFC FO membrane (Oasys Water, Boston, MA) was used. The membrane is composed of a thin selective polyamide active layer on top of a porous polysulfone support layer. The membrane pure water permeability coefficient \((A)\), salt (NaCl) permeability coefficient \((B)\), and structural parameter \((S)\) were measured using the method previously described by Cath et al [16]. A streaming current electrokinetic analyser (SurPASS, Anton Paar GmbH, Austria) was used to measure the streaming potential from which the zeta potential of the membrane surface was calculated using the Fairbrother-Mastin method [17]. Streaming potential measurement was conducted in a background electrolyte solution containing 10 mM KCl. The same electrolyte solution was used to flush the cell thoroughly prior to automatic pH titration using either hydrochloric acid (1 M) or potassium hydroxide (1 M).

2.2. Model TrOCs and foulants

Twelve organic compounds were selected to represent TrOCs with a range of charge, hydrophobicity and molecular weight (Table 1). These compounds have been frequently detected in wastewater and sewage-impacted water bodies at concentrations from a few ng/L to several µg/L. A combined stock solution containing 1 g/L of each TrOC was prepared in methanol. The stock solution was kept at \(-18 °C\) in the dark and was used within one month.

Aldrich humic acid and Ludox HS-30 silica colloids from Sigma-Aldrich were used to represent organic and colloidal foulants, respectively. The average hydrodynamic radii of Aldrich humic acid and Ludox colloidal silica are approximate 6 nm [18] and 12 nm [19], respectively. A humic acid stock solution of 10 g/L was prepared by dissolving the humic acid powder in Milli-Q water and stored in a sterilized amber glass bottle at 4 °C. The humic acid solution was used within one month. The Ludox HS-30 colloidal silica suspension (35 wt%) was sonicated for 15 min to ensure complete dispersion before adding to the feed solution. Membrane fouling and its subsequent impact on TrOC rejection were examined using either humic acid or silica colloids.
2.3. *FO apparatus and experimental protocol*

Membrane fouling and subsequent TrOC rejection experiments were conducted using a cross-flow FO membrane system [20] (Figures S1 and S2, Supplementary Data). The feed and draw solution temperatures were maintained at 25.0 ± 0.1 °C using a temperature control unit (Neslab RTE 7). The cross-flow rates of both feed and draw solutions were maintained at 1 L/min (corresponding to cross-flow velocity of 9 cm/s). Both feed and draw solutions were recirculated during the experiments. The draw solution concentration was kept constant during the experiments using a conductivity controller, which regulated a peristaltic pump to add a small volume of a concentrated draw solution (6 M of NaCl) to the draw solution reservoir when the draw solution conductivity was below the set point (the control accuracy was ± 0.1 mS/cm). The draw solution and concentrated draw solution makeup reservoirs were placed on the same digital balance. Hence, the transfer of liquid between the two reservoirs did not interfere with the measurement of permeate water flux.

The initial volumes of the feed and draw solutions were 5 and 1 L, respectively. For each experiment, a new membrane sample was placed in the membrane cell. The FO system was then stabilised using the background solution (20 mM NaCl, 1 mM NaHCO₃ and 1 mM CaCl₂) for at least one hour. Next, humic acid or silica colloidal stock solutions was introduced to the feed solution to obtain the target feed foulant concentrations of 100 mg/L humic acid or 1 g/L colloidal silica. The initial water flux was set at 9 or 20 L/m²h by using an appropriate concentration of the NaCl draw solution. The high initial water flux of 20 L/m²h was selected to simulate a typical water flux in a wastewater reclamation RO plant [21], while the low initial water flux of 9 L/m²h was selected to represent the water flux obtained by current state-of-the-art commercial cellulose triacetate FO membranes (Hydration Technology Innovations, Albany, OR) using 0.5 M NaCl draw solution (equivalent to seawater). A baseline experiment (i.e., feed without any foulant) was carried out to correct the flux decline due to the continuous concentration of the feed solution and the reverse diffusion of draw solute. Fouling experiments at the conditions described above were carried out for 20 hours.

TrOC rejection experiments by the fouled membrane were conducted immediately after the fouling experiment. The feed solution was replaced with the same background solution which contained 2 µg/L of each TrOC. The draw solution was the same as that used in the fouling experiment. The TrOC rejection experiment was concluded when 1 L water had permeated through the fouled membrane. Feed and draw solution samples (500 mL in
volume) were taken at the beginning and after 1 L water had permeated through the fouled membrane. Samples were analysed using the preparation and protocols given in section 2.5. TrOC rejection by the clean membrane was conducted using the same protocols except that the concentration of the draw solution was adjusted to attain the same water flux as that at the conclusion of the fouling experiment.

TrOC rejection was calculated taking account of the dilution of the draw solution using a mass balance approach. The dilution factor (DF) is defined as:

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

(1)

where $V_{ds,f}$ is the final volume of the draw solution and $V_p$ is the volume of permeate. Hence, the actual TrOC rejection, $R$, is calculated using:

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

(2)

Here, $C_{ds,f}$ is the final concentration of TrOC in the draw solution and $C_{f,0}$ is the initial concentration of TrOC in the feed solution.

The reverse draw solute flux was determined using mass balance as follows:

$$J_{salt} = \frac{(C_0V_t - C_tV_0)}{At}$$

(3)

where $C_0$ and $C_t$ are the concentrations of the draw solute in the feed at time 0 and $t$, respectively; $V_0$ and $V_t$ are the volumes of the feed at time 0 and $t$, respectively; $A$ is the membrane area; and $t$ is the operating time of the experiment. Draw solute concentration of NaCl in the feed solution was determined using electrical conductivity measurements and calibration using standard NaCl solutions.

2.4. Characterization of fouling layer

The morphology of the fouling layer on the membrane surface under two different initial water fluxes was characterised using a scanning electron microscope (SEM) (JEOL JCM-6000, Tokyo, Japan). Prior to SEM analysis, fouled membrane samples were air-dried in a desiccator and subsequently coated with an ultra-thin layer of carbon using a carbon sputter (SPI Module, West Chester, PA).
The reversibility of the fouling layer was determined by physically flushing it at an elevated cross flow velocity (i.e. 18 cm/s or twice the value used in the fouling experiment) for 30 min using a 10 mM NaCl solution [4]. This membrane flushing procedure was conducted immediately at the conclusion of the fouling experiment (section 2.3). During the cleaning step, the draw solution was replaced by a 10 mM NaCl solution (i.e., same osmotic pressure as the feed solution) to avoid any permeation of water through the membrane. The water flux recovery, \( R_{\text{water}} \), is defined as:

\[
R_{\text{water}} = \frac{J_c - J_a}{J_b - J_a} \cdot 100\% \tag{4}
\]

where \( J_a \) is the water flux after fouling, \( J_b \) is the water flux by of clean membrane, and \( J_c \) is the water flux after physical cleaning of the membrane.

2.5. Analytical methods

TrOC concentrations in the feed and draw solution samples were determined using a liquid chromatography – mass spectrometry (LC-MS) method as described elsewhere [22]. Briefly, samples were prepared using solid phase extraction followed by quantitative measurement using an LC-MS system (LC-MS 2020, Shimadzu, Japan) equipped with an electrospray ionization (ESI) interface. The LC-MS analysis was conducted in selective ion monitoring mode: ESI positive ionization \([M+H]^+\) mode was adopted for caffeine, primidone, trimethoprim, sulfamethoxazole, carbamazepine, bezafibrate, atrazine, linuron and amitriptyline, while ESI negative ionization \([M-H]^−\) mode was used for pentachlorophenol, diclofenac and triclosan.

3. Results and discussion

3.1. Membrane properties

The characterised membrane pure water permeability \( A \), salt (NaCl) permeability \( B \) and structural parameter \( S \) are tabulated in Table 2. The TFC FO membrane has a much higher water permeability coefficient and a slightly higher salt permeability coefficient compared to asymmetric cellulose triacetate FO membranes that were used extensively in previous FO studies [23]. Thus, using 0.25 and 1 M NaCl as draw solutions and deionized water as feed, the TFC FO membrane yielded markedly higher water fluxes in FO mode (9
and 20 L/m²h, respectively) than those obtained with commercially available asymmetric cellulose triacetate FO membranes [23].

[Table 2]

3.2. Membrane fouling behaviour

3.2.1 Water flux decline

Different initial permeate flux values resulted in notably different water flux decline for humic acid (Figure 1a) and colloidal particles (Figure 1b). The water flux decline was relatively small at the low initial permeate flux (9 L/m²h) for both humic acid and colloidal particles, with normalized water fluxes (\(J_w/J_{w,0}\)) for humic acid and colloidal particles at the conclusion of the fouling experiments attaining values of 0.89 and 0.81, respectively. By contrast, substantial water flux decline was observed at the high initial permeate flux (20 L/m²h) for humic acid and colloidal particles. For fouling runs at the high initial water flux, two distinct stages of water flux decline could be seen for both humic acid and colloidal fouling. Water flux decreased significantly during the first ten hours of filtration for humic acid (Figure 1a). This severe water flux was initiated by adsorption of humic acid to the membrane surface, followed by a continuous build-up of a cohesive and compact humic acid fouling layer [24, 25]. Similarly, water flux decreased dramatically to 12 L/m²h within three hours for colloidal fouling (Figure 1b). Similar water flux behaviour has been reported by Boo et al. [26] who examined silica fouling in FO and ascribed it to formation of a cohesive silica fouling layer on the membrane surface. We hypothesize that foulants accumulated on the membrane surface transitioned from a fluid-like, sparse, loose fouling layer at low initial permeate flux to a more compact and cohesive fouling layer at high initial permeate flux [27].

[Figure 1]

3.2.2 Fouling layer structure

To examine the transition between a fluid-like cake at low initial permeate flux and a cohesive compact cake at high initial permeate flux, fouling layer structures were characterised by SEM images and through recovery of water flux after physical cleaning of the fouled membranes. Differences in fouling layer morphology under these two initial permeate flux values observed by SEM analysis were small (Figure 1). However, water flux recovery was notably higher when the membrane was fouled at the initial permeate flux of 9 L/m²h compared to that at the higher value of 20 L/m²h (Figure 2). This observation is consistent with our hypothesis that the fouling layer at low initial permeate flux was much
less cohesive compact than that at the higher flux of 20 L/m²h. Previous studies with pressure-driven NF and RO membranes filtration reported that the initial permeate flux induced a transition in fouling layer structure. Kim and Hoek [28] concluded that the structure of any colloidal fouling layer (i.e., porosity and density) was highly dependent on the initial permeate flux. In a later study, Chen et al. [29] simulated the transition of a colloidal fouling layer from fluid-like to solid-like structure when the initial permeate flux increased.

3.3. Impact of membrane fouling on TrOC rejection

3.3.1. General behaviour

Impacts of membrane fouling on TrOC rejection were markedly different by fouling layer at different initial permeate fluxes (Figures 3 and 4). Generally, TrOC rejection increased by fouling layer at low initial permeate flux of 9 L/m²h; whereas that decreased by fouling layer at high initial permeate flux of 20 L/m²h. TrOC rejection could be related to varying fouling layer structure at different initial permeate flux.

3.3.2. Relationship between TrOC rejection and fouling layer structure

The difference in TrOC rejection could be correlated to the difference in the fouling layer structures at low and high initial permeate fluxes. TrOC rejections increased by the loose fouling layer at low initial permeate flux of 9 L/m²h (Figures 3a and 4a). The loose fouling layer enhanced steric hindrance by pore blockage, which was consistent with previous studies [30, 31]. This mechanism was evident by the fact that the increase in rejection of neutral TrOCs with low molecular weight (e.g., caffeine) was more significant than that of neutral TrOCs with high molecular weight (e.g., carbamazepine). Similarly, the enhanced steric hindrance also played an important role in rejection of charged TrOCs, the increment of which became less significant with the increase of molecular weight for charged TrOCs. By contrast, TrOC rejection was reduced by the stagnant compact fouling layer structures at the high initial permeate flux of 20 L/m²h (Figures 3b and 4b). This decrease in rejection by the stagnant compact fouling layer could be mainly driven by cake-enhanced concentration polarisation as previously reported by Ng and Elimelech [32]. The stagnant
fouling layer hindered the diffusion of feed TrOC solute back to the bulk solution, resulting in an elevated concentration of feed TrOC solute within the stagnant compact fouling layer [33]. Consequently, the cake-enhanced concentration polarization led to an elevated concentration gradient of feed TrOC across the membrane, and hence, a lower rejection. In fact, a similar decrease in TrOC rejection was also observed in NF and RO filtration. Nghiem et al [25] attributed the decrease in rejection of bisphenol A by a humic acid fouled membrane to cake-enhanced concentration polarization. Vogel et al. [34] proposed cake-enhanced concentration polarization to be responsible for the dramatic decrease in rejection of sulfamethoxazole, ibuprofen and carbamazepine by a colloidal particle fouled membrane.

The impact of initial permeate flux on fouling behaviour and TrOC rejection reported here has important implications for the operation and management of an FO process for the treatment of source waters with high fouling propensity, such as wastewater. A trade-off between obtaining high water flux and minimizing the negative impact of membrane fouling should be considered in system design and operation. Much attention should, therefore, be paid to determine an appropriate initial permeate flux for an FO process in order to prevent deleterious fouling and to secure the quality of the product water. In addition, these findings are also relevant to seawater desalination where membrane fouling and associated impact on boron rejection are critical to the process.

4. Conclusion

Results reported here indicate that the initial permeate water flux has a significant impact on the fouling behaviour and TrOC rejection in an FO process. Fouling behaviours of humic acid and colloidal particles were markedly different at initial permeate fluxes of 9 and 20 L/m²h. Water flux decline was relatively insignificant for fouling at the low initial permeate flux of 9 L/m²h, whereas substantial decrease in water flux was observed for fouling at high initial permeate flux (20 L/m²h). More importantly, the water flux recovery after physical cleaning of the fouled membrane was consistently higher for fouling runs at the lower initial permeate flux value (9 L/m²h) than that at 20 L/m²h. Thus, it is hypothesized that the fouling layer structure transitioned from a fluid-like loose layer at an initial water flux of 9 L/m²h to a stagnant compact layer at an initial permeate flux of 20 L/m²h. As a result, a fluid-like loose layer that was formed at initial permeate flux of 9 L/m²h caused pore blockage and thus enhanced steric hindrance, thereby leading to an increase in TrOC rejection. By contrast, the cohesive and compact fouling layer that was formed at an initial
permeate flux of 20 L/m²h exacerbated cake-enhanced concentration polarization and resulted in a decrease in TrOC rejection.

5. Acknowledgments

The authors would like to thank the Oasys Water for providing membrane samples. University of Wollongong is acknowledged for the provision of a doctoral scholarship to Ming Xie. A top-up scholarship to Ming Xie from the Global Challenge program (University of Wollongong) is also gratefully acknowledged.

6. References


### Table 1: Key physicochemical properties of selected trace organic contaminants (TrOCs).

<table>
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<tr>
<th>Compound</th>
<th>Category</th>
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<th>Log $D^{a,b}$ (pH 7)</th>
<th>$pK_a^{a}$</th>
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*Values for $pK_a$ and log $D$ were obtained from the SciFinder Scholar (ACS) database

*Log $D$ refers to the logarithm of the octanol-water distribution coefficient at specific pH value

### Table 2: Key membrane properties of the TFC membrane (average ± standard deviation from duplicate measurements)

- Water permeability coefficient, $A$ (L/m²hbar) = 4.7 ± 0.2
- Salt (NaCl) permeability coefficient, $B$ (L/m²h) = 0.164 ± 0.030
- Membrane structure parameter, $S$ (µm) = 524 ± 110
- Zeta potential at pH 6.5 (mV) = -17.8
**Figure 1:** Comparison of (a) humic acid and (b) colloidal particle fouling under two initial water fluxes. SEM images were taken after humic acid (Figures a1 and a2) and colloidal particle (Figures b1 and b2) fouling at an initial water flux of 9 and 20 L/m²h, respectively. Experimental conditions were: feed solution contained 100 mg/L humic acid or 1 g/L colloidal silica in a background electrolyte solution (20 mM NaCl, 1 mM NaHCO₃ and 1 mM CaCl₂); draw solutions to generate initial water flux of 9 and 20 L/m²h were 0.25 and 1 M NaCl, respectively. Temperatures of feed and draw solutions were 25 ± 1°C; cross-flow rates of feed and draw solutions were 1 L/min (corresponding to cross-flow velocity of 9 cm/s).
Figure 2: Comparison of water flux recoveries after physical cleaning of (a) humic acid and (b) colloidal particle fouled membrane under two initial water fluxes. Physical cleaning of the colloidal particle fouled membrane was carried out with: 10 mM NaCl foulant-free cleaning solution, no permeate water flux and cross-flow rate of 2 L/min (corresponding to cross-flow velocity of 18 cm/s), for a total cleaning time of 30 min. The water flux recovery was calculated using Eq. 4. Error bars represent standard deviation from duplicate experiments.
Figure 3: Comparison of rejection of trace organic contaminants (TrOCs) by clean and humic acid fouled membranes at initial permeate fluxes of (a) 9 L/m²h and (b) 20 L/m²h. Feed solution contained 2 µg/L of each TrOC in a background electrolyte (1 mM NaHCO₃ and 20 mM NaCl). TrOC rejections by clean and humic acid fouled membranes were measured at the same permeate water flux by varying the concentration of the NaCl draw solution. Temperatures of feed and draw solutions were maintained at 25.0 ± 0.1°C. Cross-flow rates of feed and draw solutions were 1 L/min (corresponding to cross-flow velocity of 9 cm/s). Error bars represent standard deviation from duplicate experiments. Symbols of +, -,
nh and n denote negatively charged, positively charged, neutral hydrophobic, and neutral hydrophilic compounds.
Figure 4: Comparison of rejection of trace organic contaminants by clean and colloidal particle fouled membranes at initial permeate fluxes of (a) 9 L/m$^2$h and (b) 20 L/m$^2$h. Error bars represent standard deviation from duplicate experiments. Experimental conditions and symbols were described in Figure 3.
Supplementary Data

Impact of organic and colloidal fouling on trace organic contaminant rejection by forward osmosis: Role of initial permeate flux

Desalination

Ming Xie 1, Long D. Nghiem 1*, William E. Price 2, and Menachem Elimelech 3

1 Strategic Water Infrastructure Laboratory, School of Civil, Mining and Environmental Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

2 Strategic Water Infrastructure Laboratory, School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia

3 Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06520-8286, USA
Supplementary materials and methods

FO experiments were conducted using a closed-loop bench-scale FO membrane system (Supplementary Data, Figures S1 and S2). The membrane cell was made of acrylic plastic and had channel dimensions of 13 cm long, 9.5 cm wide, and 0.2 cm deep. The total effective membrane area is 123.5 cm².

Two variable speed gear pumps (Micropump, Vancouver, WA) were used to circulate the feed and draw solutions. Flow rates of the feed and draw solutions were monitored using rotameters and kept constant at 1 L/min (corresponding to a cross flow velocity of 9 cm/s). The draw solution reservoir was placed on a digital balance (Mettler Toledo Inc., Hightstown, NJ) and weight changes were recorded by a computer to calculate the permeate water flux. The conductivity of the draw solution was continuously measured using a conductivity probe with a cell constant of 1 cm⁻¹ (Cole-Parmer, Vernon Hills, Illinois). To maintain a constant draw solution concentration, a peristaltic pump was used and was regulated by a conductivity controller to intermittently dose a small volume of a concentrated draw solution (6 M of NaCl) into the draw solution reservoir (control accuracy was ± 0.1 mS/cm). The concentrated draw solution makeup reservoir was also placed on the same digital balance. This setup ensured that the transfer of liquid between the two reservoirs did not interfere with the measurement of permeate water flux and that the system could be operated at a constant osmotic pressure driving force during the experiment.

Figure S1: Schematic diagram of the laboratory-scale FO system.
Figure S2: A photo of the laboratory-scale FO system.