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Preliminary studies of water treatment using forward osmosis

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ABSTRACT

Forward osmosis (FO) is an emerging water treatment technology with potential applications in desalination and wastewater reclamation. The FO uses a concentrated draw solution to generate high osmotic pressure, which pulls water across a semipermeable membrane from the feed solution. In this study, we have investigated the effect of draw solution on FO water flux. The 0.1 M NaCl draw solution provides 2 L/m^{2}h water permeation flux, while the 3 M NaCl draw solution provides 10 L/m^{2}h water permeation flux as a result of the greater osmotic driving force across the membrane. About 150% increase in transmembrane water flux was observed with an increase in temperature from 11 to 36°C. The reverse draw solute permeation to feed solution was also explored. The NaCl presents the highest reverse solute movement compared with $MgSO_4$ and $CaCl_2$. In addition, the rejection of quinine surrogated as micropollutans and humic acid by FO process was satisfactory in terms of the removal efficiency by FO membrane.

Keywords: Water treatment; Forward osmosis; Draw solution; Water flux; Organic matter removal

1. Introduction

In the period of 2010–2020, the global cumulative contracted capacity of the desalination market will grow at a cumulative average growth rate of 10.5%, reaching 195.8 million m^3/day in 2020 [1]. A variety of desalination technologies, both thermally driven and membrane-based, have been increasingly employed to enhance the limited freshwater supply. Among them, reverse osmosis (RO) is regarded as the most economical and popular desalination way for water production mainly due to the advancement of membrane technology. These most widely used RO processes use hydraulic pressure as the driving force for water flux in water purification. However, the productivity of these pressure-driven membrane processes is severely hampered by the longstanding problem of fouling. In addition, RO membranes can reject most constituents present in impaired water, but they can achieve only moderate water recovery [2].

In recent years, there has been a growing interest in forward osmosis (FO). FO uses a concentrated draw solution to generate high osmotic pressure, which pulls water across a semipermeable membrane from the feed solution [3]. The water permeation flux is determined by the osmotic pressure difference across the membrane. During this process, the feed solution is concentrated and the draw solution is diluted. The draw solute is then separated from the diluted draw solution in order to be recycled,

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thereby producing clean water product. Unlike typical pressure-driven membrane processes, where a hydraulic pressure is applied onto the feed water to push water through a membrane, FO occurs spontaneously without the need of externally applied pressure [4]. The existing literature shows that FO tends to have lower fouling propensity compared to RO, although the mechanisms involved in FO fouling tends to be more complicated compared to RO fouling [5]. FO advantage includes high solute rejection, low-pressure operation, and low fouling propensity [3,6] that can assist RO in achieving higher water recoveries by a hybrid FO/RO process. FO has been explored for use in seawater desalination, wastewater reclamation, industrial wastewater treatment, and liquid food processing.

The growing interest in FO from various disciplines calls for more fundamental research that can lead to a better understanding of the FO process and further advances in the technology. One notable research area that has been undertaken so far in this emerging technology is internal concentration polarization (ICP). Unlike pressure-driven membrane processes, the FO water flux is highly nonlinear with respect to membrane properties (such as water permeability and solute rejection) and the osmotic driving force due to the presence of ICP. ICP significantly reduces the available osmotic pressure difference across the active rejection layer, and thus it poses a severe limit on the available FO water flux. Furthermore, the salt leakage would result in the loss of the draw solute into the feed solution and the increase of the chemical potential of the feed solution, which further lowers down the osmotic pressure difference across the membrane and increases the operating cost of the system. Moreover, a variety of pollutants removal by FO membranes is intensively studied. Cartinella et al. [7] investigated the removal of three hormones that were spiked into batches of synthetic wastewater. Results revealed that membrane fouling and the presence of surfactants in the feed solution substantially improved rejection of these micropollutans at higher water recoveries. More recent studies on the hybrid FO-RO process by Hancock et al. [8] showed that the dual barrier treatment of impaired water could lead to more than 99% rejection of almost all trace organic compounds that were identified in reclaimed water.

The main objective of this study was to investigate mass transport of solutes in FO under various operating conditions, as well as the effects of draw solution chemistry and temperature on membrane water flux and solute diffusion from the draw solution into the feed. Specifically, the quinine and purified humic acid (HA) were used as model solutes and their rejection by the commercial Hydration Technologies Inc. (HTI) FO membranes were studied.

2. Materials and methods

2.1. Chemicals

Unless otherwise specified, all reagents and chemicals were of analytical grade. Deionized water was used throughout the experiments. Ultrapure water with a resistivity of $18.2\,\mathrm{M\Omega\,cm}$ (Millipore and purification system) was used to prepare all working solutions. Quinine and HAs were purchased from Sinopharm Chemical Reagent Co., Ltd. In this study, HA was used as a substitute of dissolved organic matter (DOM). The stock solution was purified following the procedure described by Hong and Elimelech [9] with HA solution adjusted to 1 g/L and stored in a sterilized bottle at 4°C. The powdered quinine was dissolved in Mill-Q water (1 g/L) and diluted prior to use.

2.2. FO membrane

The FO membrane used in this study was kindly provided by Hydration Technologies, Inc. (Albany, OR). The membrane properties have been reported by several previous studies [4,5]. Briefly, it has an asymmetric structure and is made of cellulose acetate cast onto a nonwoven backing consisting of polyester fibers individually coated with polyethylene. This membrane is shipped "dry" where vegetable-based glycerin has been used to replace the water. We have soaked the membranes for 30 min in deionized water to remove the glycerin.

2.3. Bench-scale FO experiments

The FO experiments were performed with a flat-sheet bench-scale membrane system as depicted in Fig. 1. The cross-flow membrane cell was built with equally structured channels on both sides of the membrane. For each test, a clean FO membrane coupon ($70 \times 26\,\mathrm{mm}^2$ active membrane area) was used in the cross-flow test cell. In all cases, the draw solution was in direct contact with the porous support layer, while the feed water reached the active sides of the membranes. The co-current cross-flow was used to minimize strain on the suspended membrane without mesh spacers in the channels. Variable speed peristaltic pumps (WT600-2J, Longerpump, Baoding) were used to generate cross-flows, forming separate closed loops for the feed and draw solutions on the opposite sides of the membrane of 10 mL/s. The cross-flow

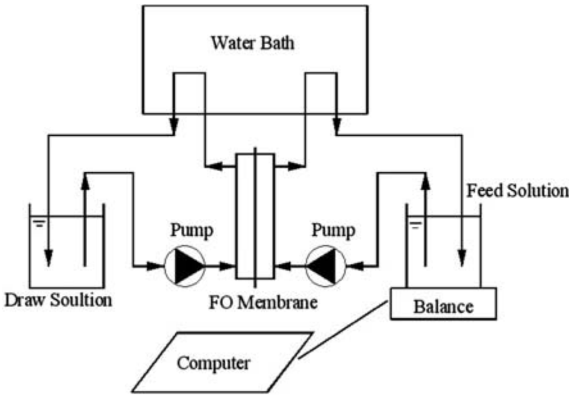


Fig. 1. Schematic diagram of a laboratory-scale FO set-up.

velocity for the draw and feed solutions was maintained at 11.5 cm/s. The FO performances were evaluated by determining the water flux and reverse solute diffusion. The feed solution tank was placed on a digital scale (SE602F, Ohaus Instruments) and weight changes were monitored by a computer to record the permeate flux. The water permeation flux is determined from the slope of the weight change of the feed solution divided by the effective membrane surface area. The conductivity in the feed water was measured by a digital conductivity meter (Multi 3430, WTW, Germany) at the predetermined time interval to monitor the solute transport through the FO membrane. The temperature of the feed and draw solution was controlled to within ±1℃ by a water bath (DKB-1915, Jinghong, Shanghai). Each experiment was carried out for three hours to obtain the stable flux phenomenon and simultaneously minimize the variation of concentration of the draw solution. Each experiment was conducted twice. First the deionized water was used in both the draw and feed solutions to rinse the FO membrane at the cross-flow velocity of 11.5 cm/s. Then, the membrane coupon was stabilized for 20 min for each experiment.

2.4. Analytical methods

The temperature and the concentration of NaCl, $CaCl_2$, and $MgSO_4$ solutions were measured by using an electric conductivity meter (Multi 3430, TetraCon 925, WTW, German). The concentration of the reverse solute flux of solutes to the feed water was determined online from the measurement of electric conductivity meter connected to a computer for data logging using a calibration curve derived from a series of single solutions.

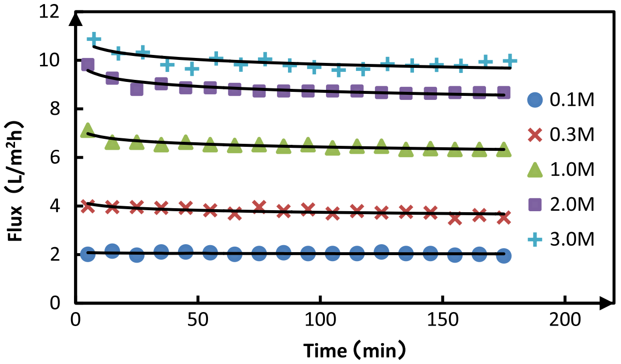
The concentration of DOM was measured by UVA254 nm with an UV-vis scanning spectrophotometer (Lengguang, UV765, Shanghai) at a wavelength of 254 nm using cells of 1 cm length. The DOM in feed water and draw solution was also characterized with Fluorescence spectroscopy. The excitation–emission matrices (EEMs) were obtained using a Cary Eclipse (Australia) fluorescence spectrometer with a xenon flash lamp, slit widths of 5 nm, and a scan rate of 1,200 scans per second. The excitation wavelength was scanned from 200 to 450 nm in 10-nm increments and the emission wavelength from 260 to 560 nm in 2-nm increments. Samples were analyzed on the fluorometer without dilution or pH adjustment.

3. Results and discussion

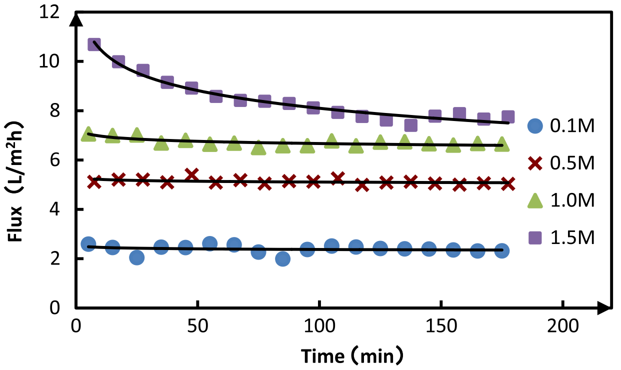
3.1. Effect of draw solution on FO water flux

To study the effect of draw solution concentration on FO water flux, experiments were carried out with deionized water as feed water and varied concentrations of NaCl, $CaCl_2$, and $MgSO_4$ as draw solutions. Fig. 2 shows the experimental FO water flux as a function of filtration time for different draw solution concentrations. For all solutes, it is obvious that the FO water flux increased with increasing draw solution concentrations. For example, the 0.1 M NaCl draw solution provides 2 L/m^2h water permeation flux after 180 min operation, while the 3 M NaCl draw solution provides 10 L/m^2h water permeation flux showed in Fig. 2(a) as a result of the greater apparent driving force across the membrane. In addition, the water fluxes increase roughness linearly at low draw solution concentrations, while it seems to be leveled off at higher concentrations, although the classical solution-diffusion model predicts a linear water flux vs. draw solution concentrations relationship. This phenomenon is most likely attributed by the dilutive ICP within the support layer which considerably reduce the efficiency of osmotic driving force due to higher water flux at higher draw solution concentration. The solute concentration inside the porous support layer (C_{support}) can be drastically diluted by the FO permeate water, causing C_{support} to be much smaller than draw solution concentration.

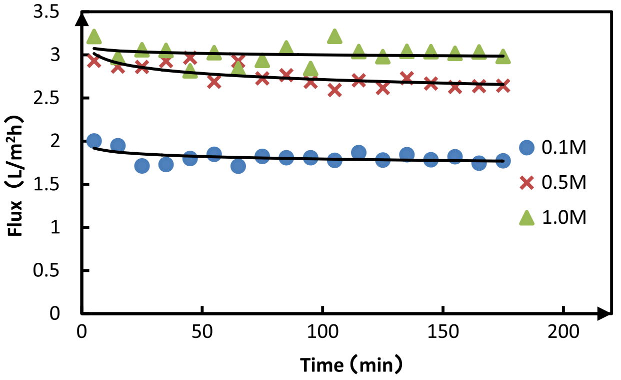
Water flux is one of the most important performance criteria for all membrane processes. To investigate the effect of temperature on the water permeate flux, experiments were carried out by varying the operation temperature over the range of 11–36℃ at constant flow rate of 600 ml/min. Fig. 3 shows the permeate water flux as a function of time under various temperatures with deionized water as feed water and 1 M NaCl as draw solutions. Increasing the temperature of the system had an obvious effect on the water permeate flux. About 150% increase in



(a) FO permeate flux of NaCl draw solutes



(b) FO permeate flux of $CaCl_2$ draw solutes



(c) FO permeate flux of $MgSO_4$ draw solutes

Fig. 2. Effect of draw solution concentrations on FO permeate flux.

transmembrane water flux was observed with an increase in temperature from 11 to 36℃. The increase of the water fluxes with the rise of temperature can be explained by several possible factors, such as fluid viscosity, concentration polarization, water permeability, and mass transfer coefficient, which are all closely related to temperature [10,11]. The rise in temperature reduces the viscosity of solution and increases the diffusion coefficients, which results in an increase in transmembrane flux [12].

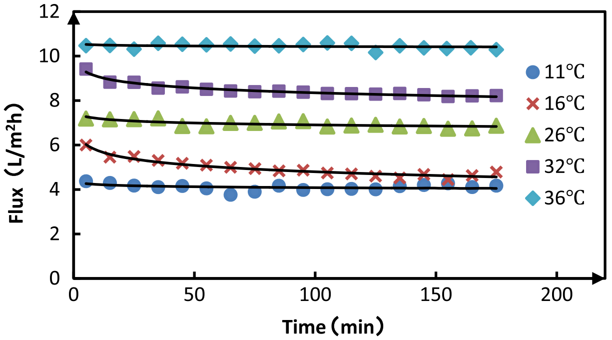


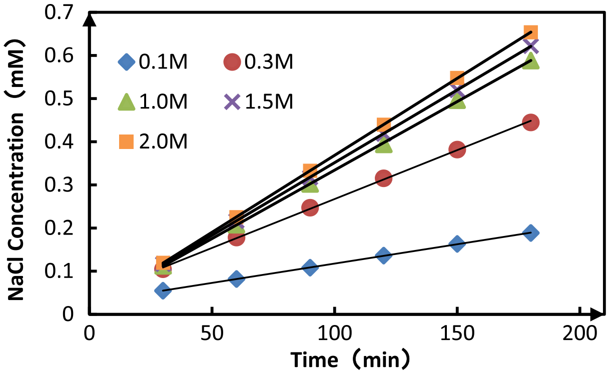
Fig. 3. Effect of temperature on FO permeate flux.

3.2. *Reverse draw solute flux*

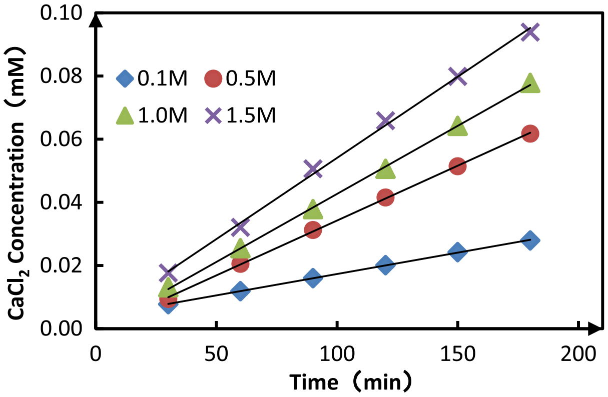
Reverse solute movement can be a significant disadvantage for FO because it can complicate the feed solution concentrate management and also is likely to decrease the net osmotic potential or driving force and fouling potential of the feed solution [13]. Phillip et al. [14] indicated that a thorough understanding of the phenomenon of reverse solute permeation is critical to the effective development of osmotic driven membrane technologies. The fundamentals and models to describe reverse draw solute permeation through the semipermeable membrane are described elsewhere [4,14,15]. As the concentration of the draw solution increases, the measured reverse draw solute flux should both increase. In this work, we examined the reverse salt solute flux of NaCl, $CaCl_2$, and $MgSO_4$ with deionized water as feed water. The performance of draw solutions in terms of reverse solute flux varied widely depending on the type of solute used as shown in Fig. 4. As anticipated, the reverse salt flux increases with increasing NaCl concentrations. This is consistent with prior experiment [16–18]. Data shown in Fig. 4 also indicate that $CaCl_2$ exhibited much slower reverse salt flux than NaCl. This may be explained by the sodium that diffused through the membrane more rapidly than the other constituents, likely because of its relatively small hydration radius and lower valence charge. Hancock et al. [15] attributed the reduction in reverse salt flux of divalent salts to Donnan equilibrium effects, whereby the relatively large divalent cation diffused slowly through the membrane and subsequently limited the diffusion of the counter ion (chloride).

3.3. *Rejection of quinine and HA by FO*

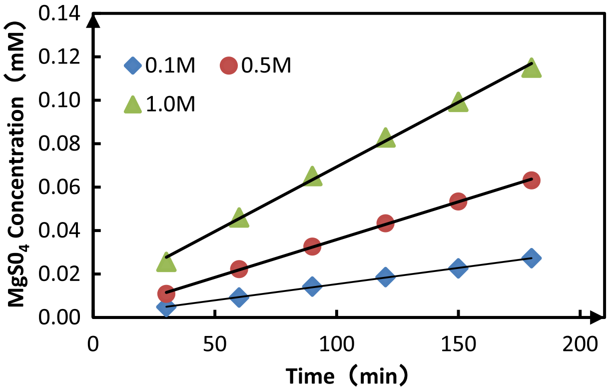
Organic micropollutants are raising concern among researchers and regulatory agencies, because most of them are not yet regulated and their impacts on human life are not quite known [19]. Quinine is a



(a) Reverse solute diffusion of NaCl draw solutes



(b) Reverse solute diffusion of NaCl draw solutes



(c) Reverse solute diffusion of $MgSO_4$ draw solutiones

Fig. 4. Differences of reverse solute diffusion of various draw solutes.

natural white crystalline alkaloid. Being pharmaceutical, it is an old antimalarial drug. The side effects of quinine commonly seen at therapeutic concentrations are referred to as cinchonism, with mild forms including tinnitus, slight impairment of hearing, headache, and nausea [20]. To investigate the rejection performance of PPCPs by FO, quinine is spiked in deionized water as feed solution using 0.5 M NaCl as draw solution. The permeation of quinine to draw solution after three hours of FO with different concentrations of feed solution is shown in Fig. 5. The quinine concentration of draw solution increased from 1.66 to 3.29 μg/L when the feed quinine concentration increased from 0.1 to 1.0 mg/L. The FO membrane provides effective barrier against the selected micropollutants.

HA, which represent the major fraction of dissolved natural organic matter (NOM) in aquatic environments, has been the focus of much research. It is responsible for natural water color and for initiating photochemical transformations of both organic compounds and trace metals [21]. In this paper, HA removal is also studied to evaluate the rejection efficiency on combined pollutants by FO process. Experiments were carried out with 0.5 M NaCl as draw solution and HA spiked into deionized water as feed solute. The feed total organic carbon (TOC) concentrations were set at 3 and 6 mg/L, respectively. After the equilibrium, the corresponding concentrations of TOC in the draw solution come to 0.2 and 0.4 mg/L. The organic matter comparison of feed solution and draw solution according to EEM based on 6 mg/L initial TOC spiked to deionized water as feed solution and 0.5 M NaCl as draw solution is illustrated in Fig. 6. When exited by ultraviolet and visible light, NOM fluoresces and the characteristics and intensity of the fluorescence varies depending on the fluorophores present [22]. The composition of NOM can be visualized as a pattern of fluorescence peaks within an EEM. Fluorescence peaks can be attributed to both humic-like fluorescence, defined as peaks C located in the region of 300–360 nm excitation and 400–480 nm emission wavelength, and protein-like fluorescence, defined as peaks T located in the region around 280 nm excitation and 350 nm emission [23]. In this test, the feed was HA, which was located in the region of peaks C (Fig. 6(a)). However, in the Fig. 6 (b), there is little intensity of flurescence in the region of peaks C, which indicates that most HAs were well rejected by the FO membrane.

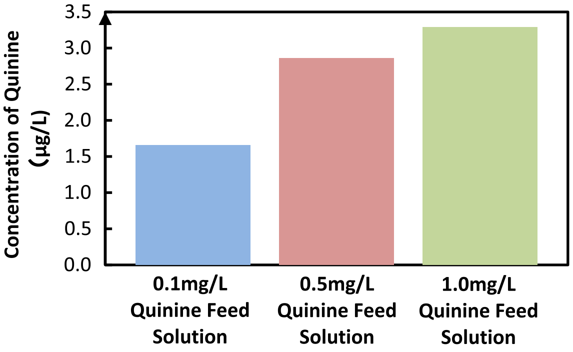


Fig. 5. Quinine concentrations in draw solutions after each experiment.

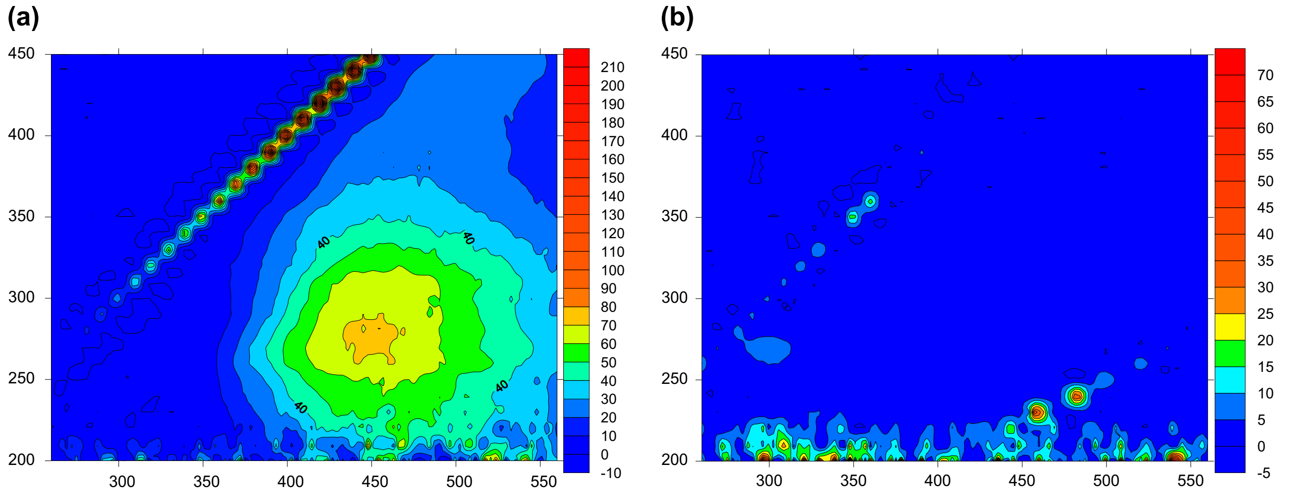


Fig. 6. Scanning of fluorescence of 6 mg/L HA feed solution; (a) At the beginning of the experiment in feed solution, (b) After text in draw solution.

4. Conclusion

A flat-sheet bench-scale FO system was built in this paper to investigate the effects of draw solution chemistry and temperature on membrane water flux and the reverse solute diffusion from the draw solution into the feed was examined. Specifically, quinine and purified HA was used as model solutes and their rejection by the commercial HTI FO membranes were also studied. Results showed that the FO water flux increased with increasing draw solution concentrations. The 0.1 M NaCl draw solution provides 2 L/m^{2}h water permeation flux after 180 min operation, while the 3 M NaCl draw solution provides 10 L/m^{2}h water permeation flux. Increasing the temperature of the system had an obvious effect on the water permeate flux. About 150% increase in transmembrane water flux was observed with an increase in temperature from 11 to 36℃. As the concentration of the draw solution increases, the measured reverse draw solute flux increases and $CaCl_2$ exhibited the slowest reverse salt flux in this study. In addition, the rejection of quinine surrogated as micropollutans and HA by FO process was satisfactory in terms of the removal efficiency. The quinine concentration of draw solution increased from 1.66 to 3.29 μg/L when the feed quinine concentration increased from 0.1 to 1.0 mg/L. According to the EEM contour plots, most HAs were well rejected by the FO membrane.

Acknowledgments

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