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Table. Rejection of organic micro-pollutants comparison under different processes

Membrane	Mode	Rejection (%)			
		Nitrobenzene	Phenol	Aniline	
PESU TFC	FO	76.8 ± 0.9	73.7 ± 2.2	91.8 ± 0.1	• Feed solution: 1000 ppm aromatic aqueous solution
	RO	55.0 ± 5.3	43.1 ± 3.0	52.6 ± 0.2	
Matrimid TFC	FO	76.6 ± 0.3	75.9 ± 1.7	88.4 ± 0.9	• RO test Pressure: 10 bar
	RO	54.5 ± 1.0	56.7 ± 4.8	57.3 ± 0.5	
sPPSU TFC	FO	75.2 ± 3.4	72.1 ± 1.2	91.5 ± 1.2	
	RO	58.8 ± 2.4	60.7 ± 1.6	61.9 ± 2.4	
UTC-70UB	RO	30.1 ± 6.0	59.8 ± 6.7	66.6 ± 6.6	
Filmtech BW30-4040	RO	32.4 ± 2.6	45.8 ± 2.4	56.6 ± 3.7	

Removal of organic micro-pollutants (phenol, aniline and nitrobenzene) via forward osmosis (FO) process: Evaluation of FO as an alternative method to reverse osmosis (RO)

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ABSTRACT

In this study, we have explored and compared the effectiveness of using (1) lab-fabricated forward osmosis (FO) membranes under both FO and reverse osmosis (RO) modes and (2) commercially available RO membranes under the RO mode for the removal of organic micro-pollutants. The lab-fabricated FO membranes are thin film composite (TFC) membranes consisting of a polyamide layer and a porous substrate cast from three different materials; namely, Matrimid, polyethersulfone (PESU) and sulfonated polyphenylene sulfone (sPPSU). The results show that the FO mode is superior to the RO mode in the removal of phenol, aniline and nitrobenzene from wastewater. The rejections of all three TFC membranes to all the three organic micro-pollutants under the FO processes are higher than 72% and can be even higher than 90% for aniline when a 1000 ppm aromatic aqueous solution and 1 M NaCl are employed as feeds. These performances outperform the results obtained from themselves and commercially available RO membranes under the RO mode. In addition, the rejection can be maintained even when treating a more concentrated feed solution (2000 ppm). The removal performance can be further enhanced by using a more concentrated draw solution (2 M). The water flux is almost doubled, and the rejection increment can reach up to 17%. Moreover, it was observed that annealing as a post-treatment would help compact the membrane selective layer and further enhance the separating efficiency. The obtained organic micro-pollutant rejections and water fluxes under various feasible operating conditions indicate that the FO process has potential to be a viable treatment for wastewater containing organic micro-pollutants.

Key words: removal of organic micro-pollutants, forward osmosis, wastewater treatment

INTRODUCTION

Water scarcity is a major problem faced by numerous countries. The situation is further aggravated by population explosion, overexploitation of fossil fuel and contamination of fresh water resources (Chung et al. 2012b, Valladares Linares et al. 2014). Wastewater reclamation has been considered as strategically important in water management. Hence, there is an increasing effort worldwide to develop new technologies for water reuse with higher efficiency and effectiveness (Escobar and Van der Bruggen 2011, Shannon et al. 2008, Xie et al. 2012). However, the presence of organic micro-pollutants such as phenol, aniline and nitrobenzene, is one of the major obstacles preventing the reuse of certain types of wastewater (Basile et al. 2011). These substances widely exist in waste effluents of chemical, pharmaceutical and petrochemical industries (Yang et al. 2015). They have strong adverse effects on organisms even at low concentrations. These organic micro-pollutants also have the ability to penetrate through the existing barriers in wastewater treatment plants and rendering the current treatment methods ineffective (Zietzschmann et al. 2014). Due to the presence of benzoic groups, these organic micro-pollutants may react with free chlorine during the sterilization process to produce chlorinated by-products. Since these by-products are stable and probably more poisonous, they become greater threats to both human health and environments (Gallard and Von Gunten 2002, Gonsior et al. 2014, Maguire-Boyle and Barron 2014). Hence, numerous studies have been conducted to either improve the removal efficiency of the current treatments or develop totally new technologies to eradicate these organic micro-pollutants (Al-Khalid and El-Naas 2012, Fu et al. 2014, Yang and Zheng 2014). Current methods to remove organic micro-pollutants from wastewater can be divided into three categories: physical (such as adsorption, steam stripping, ion exchange, and solvent extraction), chemical (such as oxidation and phase transfer catalysis) and biological treatments (Hao et al. 2000, Pal and Kumar 2014). In the past few decades, membrane

separation has been demonstrated to be a feasible method for wastewater treatment because of its high rejections to a wide variety of contaminants such as dye molecules with acceptable costs (Escobar and Van der Bruggen 2011). Among various membranes, the reverse osmosis (RO) membrane is the preferred treatment method for wastewater containing organic micro-pollutants. However, there is still room for improvement in terms of rejections (as seen in the subsequent sections). In addition, the high operating pressure of RO often leads to a high operating and maintenance cost as well as a severe fouling problem (Escobar and Van der Bruggen 2011, Pal and Kumar 2014, Zaviska et al. 2015).

Forward osmosis (FO) is an emerging membrane technology for water reuse and seawater desalination. During this process, water transports from the feed solution to the draw solution across a semi-permeable membrane. The unwanted components will be effectively rejected by the membrane. The driving force for FO is the osmotic pressure gradient across the semi-permeable membrane and no external pressure is required (Chung et al. 2012a, McGovern and Lienhard 2014, Zhao et al. 2012). The FO potential is currently limited by the lack of (1) suitable FO membranes (Chung et al. 2012a, Chung et al. 2012b, Cui et al. 2013) and (2) effective draw solutes with easy regeneration characteristics (Chung et al. 2012a, Chung et al. 2012b, Ge et al. 2013). Besides, the process design and module configuration also limit the FO applications in practice. Hybridizing systems may be a viable strategy to expand FO applications in wastewater treatment (Van der Bruggen and Luis 2014, Xie et al. 2013). Nevertheless, FO possesses the advantages of having negligible operation pressure and low fouling tendency compared with pressure driven processes. Reversible fouling has often been observed on membrane surface but it can be easily removed by physical cleaning (Chun et al. 2015, Flanagan and Escobar 2013, Li et al. 2014, Li et al. 2012b, Liu and Mi 2012, Zhang et al. 2014b, Zou et al. 2013). In addition, since most FO membranes are designed to reject

small monovalent ions, it is theoretically able to reject the organic micro-pollutants (Xie et al. 2012). Thus, the FO process may provide an effective means to remove the organic micro-pollutants.

In this study, we aim to explore the removal efficiency of the FO process for organic micro-pollutants under different operating conditions as well as to investigate possible methods to further improve the efficiency. The thin film composite (TFC) membranes consisting of a cross-linked polyamide selective layer and a porous substrate made from different materials were employed in this study. The cross-linked polyamide selective layer synthesized by interfacial polymerization often possesses a high flux and a relatively low salt permeability (Cui et al. 2014b, Huang et al. 2013, Park et al. 2015, Zhang et al. 2014a, Zhong et al. 2013). Sodium chloride was utilized as the draw solute for easy comparison of separation performance. In addition, the FO membranes were compared with the state of the art RO membranes to investigate their viability for FO processes. This study may provide useful insights to utilize FO process for the removal of organic micropollutants from wastewater.

MATERIALS AND METHODS

Materials. The commercially available polyimide polymer, Matrimid® 5218 (Vantico Inc.), Radel A polyethersulfone (PESU, Solvay Advanced Polymer, L.L.C., GA), and the direct sulfonated 1.5 mol % polyphenylene sulfone (sPPSU) (supplied by BASF SE, Germany) were utilized to fabricate the membrane substrates. The solvent *N*-methyl-2-pyrrolidone (NMP, >99.5%) and the non-solvent polyethylene glycol 400 (PEG 400, $M_w = 400$ g/mol) (Merck) were used to prepare polymeric dope solutions. *m*-phenylenediamine (MPD, >99%), trimesoylchloride (TMC, >98%), sodium dodecyl sulfate (SDS, >99%) were ordered from Sigma-Aldrich and used for the interfacial polymerization (IP) reaction. Sodium chloride

(Merck, Germany), phenol (>99.5%), aniline (>99.5%) and nitrobenzene (>99%) (Sigma-Aldrich, USA) were acquired to determine membrane FO performance and characterize transport properties. Commercial TFC RO membranes, Filmtech BW30-4040 and UTC-70UB obtained from The Dow Chemical Co. and Toray Industries, Inc., respectively, were used for performance comparison with the lab-fabricated TFC FO membranes. Deionized (DI) water was produced by a Milli-Q ultrapure water system (Millipore, USA). All chemicals were used as received.

Fabrication of Membrane Substrates. The flat sheet membranes were fabricated by a casting process, followed by the non-solvent induced phase inversion (Cui et al. 2014b, Li et al. 2012a, Zhang et al. 2010). The dope formulations of the 3 different substrates are PESU/PEG 400/NMP/H₂O with a weight ratio of 20.4/37.7/37.7/4.2, Matrimid/PEG 400/NMP with a weight ratio of 18/16/66, and sPPSU/ PEG 400/NMP with a weight ratio of 15/27/58. Polymers were dried overnight at 80 °C in a vacuum oven to remove moisture prior to preparing dope solutions. The dried polymers and PEG 400 were dissolved in NMP first, followed by adding water inside (if any). Subsequently, the polymer solution was allowed to degas overnight before usage. The membrane was prepared by casting the polymer solution on a glass plate using a casting knife, followed by immersing the membrane into tap water to form an asymmetric structure. The as-cast membranes were removed from the glass plate and preserved in tap water to remove the residual NMP and PEG.

Interfacial Polymerization of Thin-Film-Composite (TFC) Membranes. The formation of a selective polyamide layer on top of the substrates was achieved by an interfacial polymerization reaction between the MPD aqueous and TMC hexane solutions. The as-cast

substrates were firstly immersed in a 2% MPD aqueous solution containing either 1% SDS for PESU and Matrimid substrates or 0.1% SDS for the sPPSU substrate for 120s. Subsequently, the membrane was thoroughly dried with the filter paper to remove excess MPD. A 0.1% TMC hexane solution was then deposited on top of the MPD-saturated substrate for 60s and the resultant membrane was dried in air for 5 min to allow a complete reaction. Then, the as-prepared TFC membrane was preserved into DI water for further usage. The TFC membranes fabricated on different substrates are referred to as Matrimid-TFC, PESU-TFC, and sPPSU-TFC, respectively.

Post-treatment of the TFC membranes. Annealing was adopted as the post-treatment method for these TFC membranes to improve their separation performance (Ghosh et al. 2008, Su et al. 2010b, Sun et al. 2014). The fabricated TFC membranes were simply immersed in a water bath with different temperatures for 10 min. After the treatment, membranes were preserved in DI water at room temperature for further usage.

Water Reclamation through Forward Osmosis. FO experiments were conducted on a lab-scale FO unit (Cui et al. 2014a). The volumetric flows of both draw solution (100 mL NaCl aqueous solution) and feed solution (500 mL DI water or aromatic aqueous solution) were 0.3 L/min. They flowed co-currently through the FO cell and were constantly circulated in the setup. The water flux (J_w , $L \cdot m^{-2} \cdot h^{-1}$, LMH) was calculated based on Eq.1:

$$J_w = \frac{\Delta m}{\Delta t} \frac{1}{A_m} \quad (1)$$

where A_m is the effective area of the FO cell, which is 4 cm²; Δm (g) is the absolute weight loss in the feed solution side, and Δt (h) is the test duration, which is 0.25 h. For each test, a newly-prepared NaCl solution was used.

The reverse salt flux (J_s , $g \cdot m^{-2} \cdot h^{-1}$, gMH) of the draw solution was calculated from the conductivity increment in the feed solution based on Eq.2:

$$J_s = \frac{\Delta C_t V}{\Delta t} \frac{1}{A_m} \quad (2)$$

where ΔC_t (g/L) and $V(L)$ are the changes of salt concentration and feed solution volume, respectively. The reverse salt flux was only measured when pure water was used as the feed solution.

Three types of aromatic aqueous solutions were prepared by dissolving the aromatic compounds, i.e., phenol, aniline and nitrobenzene in ultrapure water, respectively, and used as model wastewaters. The concentrations of model wastewater solutions were 500, 1000, and 2000 ppm. 1500 ppm was chosen for nitrobenzene due to its solubility limitation. The test duration for each solution was 2 h.

The solute rejection R (%) was defined as the percentage of feed solutes that were retained by the membrane. It was calculated as

$$R = 1 - \frac{C_d \times V_d / V_p}{C_f} \quad (3)$$

where C_d (ppm) is the aromatic compound concentration in the draw solution at the end of each FO test, V_d (L) is the final volume of the draw solution, V_p (L) is the volume of the permeate water, and C_f (ppm) is the aromatic compound concentration in the feed solution. C_d (ppm) and C_f (ppm) were determined using UV-Vis spectroscopy and a total organic carbon (TOC) analyzer (ASI-5000A, Shimadze, Japan), respectively. In the UV-Vis spectroscopy, UV light of wavelength ranging from 200 -800nm was used to scan each sample (compound) to determine the maximum absorbance wavelength of them. The peak value was used to determine the concentration. The maximum absorbance wavelengths of phenol, nitrobenzene, and aniline were determined to be 270nm, 268nm and 230nm respectively.

All experimental tests were conducted under the FO mode (i.e., the selective layer faces to the feed solution).

Separation performance of commercial and lab-fabricated TFC membranes under the RO mode. Water permeability, A ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), and solute rejection, R (%), of the commercial and lab-fabricated TFC membranes were determined by testing the membranes under a trans-membrane pressure, ΔP , of 10.0 bar in dead-end cells at room temperature, as described in our previous studies (Li et al. 2012a, Su et al. 2010a). The feed solutions were the three different aromatic aqueous solutions of 1000 ppm. The pure water permeability was calculated as Eq.4:

$$J_w = \frac{\Delta m}{\Delta t} \frac{1}{A_m \Delta P} \quad (4)$$

where Δm (g) is the absolute weight loss in the feed solution side, and Δt (h) is the test duration, A_m is the effective area of the testing cell, ΔP (bar) is the applied trans-membrane pressure. The salt rejection R was calculated based on the given Eq. 5:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (5)$$

The concentrations of aromatic compounds in the feed (C_f) and permeate (C_p) were determined by a TOC analyzer.

Characterizations of TFC Membranes.

Membrane morphology. The membrane morphology was examined by field emission scanning electron microscopy (FESEM). First, the membrane was dried with a freeze-dryer and fractured in liquid nitrogen. After coated with platinum by a Jeol JFC-1100E Ion Sputtering device, membrane morphology was observed using a FESEM (JEOL JSM-6700).

The membrane thickness was measured roughly using the reference bar in the FESEM images.

Pore size and pore size distribution.

The pore size and pore size distribution of all three TFC membranes were characterized by solute transport experiments (Gao et al. 2014, Shao et al. 2013, Singh et al. 1998, Van der Bruggen and Vandecasteele 2002). Basically, small neutral organic compounds with different molecular weights were employed and the solute rejections were tested under a hydraulic pressure of 10.0 bar. Pore size distribution was calculated based on the assumption of no steric and hydrodynamic interactions between the organic solutes and the membrane material. The molecular weight cut off (MWCO) is defined as the MW of the solute at the $R = 90\%$. The mean effective pore size μ_p (diameter), which is approached as the geometric mean diameter of the solute (μ_s), is given when $R = 50\%$. The geometric standard deviation (σ_p) of the membrane, which approximates the geometric standard deviation of μ_s (σ_g), is the ratio of d_s at $R = 84.13\%$ to $R = 50\%$. The probability density function of a membrane pore diameter can be calculated with the following equation:

$$\frac{dR(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp\left[-\frac{(\ln d_p - \ln \mu_p)^2}{2 (\ln \sigma_p)^2}\right] \quad (6)$$

where d_p is the pore size (diameter). The MWs and diameters of the neutral solutes used during pore size distribution tests are listed in Table 1 (Gao et al. 2014, Sun et al. 2011).

Membrane micro-structure.

Position annihilation spectroscopy (PAS) was utilized as an advanced tool to describe the membrane micro-structure as a function of depth from the top surface. The doppler broadening energy spectroscopy (DBES), which was determined using a PAS coupled with a variable monoenergy slow positron beam, was employed to investigate the TFC membranes

microstructure (Chen et al. 2007, Jean et al. 2008, Jean 2003). For each sample, 29 DBES spectra were obtained at different incident energies in the range of 0.1 to 27 keV measured. An HP Ge detector (EG&G Ortec) with a counting rate of around 1800 counts per second was used to record the spectrum and each spectrum carried 1.0 million counts in total. The incident energy of the PAS beam was correlated to the depth in a membrane by Eq. 7:

$$Z(E_+) = \frac{40}{\rho} E_+^{1.6} \quad (7)$$

where Z (nm) is the depth, ρ (g/cm^3) refers to the density of the polymer, and E_+ (keV) is the incident positron energy.

The DBES spectra are usually interpreted by two parameters, i.e. the R parameter and the S parameter. The R parameter is defined as the ratio of the total counts from the valley region with an energy width between 364.2 and 496.2 keV (from 3γ annihilation) to those from the 511 keV peak region with a width between 504.35 and 517.65 (from 2γ annihilation). The R parameter presents the states of voids in the range of nanometer to micrometer. Therefore, it indicates the changes in pore size and pore size distribution

of a membrane. On the other hand, the S parameter refers to the ratio of integrated counts between 510.3 and 511.7 keV, and it is related to the relative value of low momentum part of positron-electron annihilation radiation. It is sensitive to the changes in membrane chemistry and free volume (Jean et al. 2011, Jean 2003, Shintani et al. 2009).

RESULTS AND DISCUSSION

Membrane characterizations

1. Morphologies of TFC membranes

The typical surface morphologies of Matrimid, PESU and sPPSU substrates and their respective resultant TFC membranes are shown in Fig. 1. These 3 substrates have almost

similar top surface morphologies with relatively dense top skin layers consisting of relatively smooth and tiny pores with sizes less than 10 nm, while their bottom surfaces comprise relatively large pores. However, their cross-section morphologies are quite different. The Matrimid substrate has a fully porous and macrovoid-free cross-section with a total membrane thickness of around 65 μm . In contrast, the PESU substrate possesses a fully porous cross-section with finger-like macrovoids. The thickness of the PESU substrate is around 70 μm . On the other hand, the sPPSU substrate has a similar cross-sectional morphology to the Matrimid substrate but with smaller pores. However, the total thickness of the sPPSU substrate is only one third of the Matrimid substrate. Nevertheless, these three substrates all have a fully porous cross-section structure with interconnected open-cells, which is critical to minimize the transport resistance for water permeation (Cui et al. 2014b, Ramon et al. 2012). The small thickness of the sPPSU substrate and the finger-like macrovoids of the PESU substrate may further reduce water transport resistance. The relationship between membrane morphologies and separation performance will be discussed in greater details in subsequent sections.

2. Mean effective pore size and pore size distribution

Since the size exclusion mechanism is one of the dominant separation mechanisms, it is often necessary to determine the pore size distribution of the membranes in order to effectively remove organic micro-pollutants. Fig. 2 shows the pore size distributions of these three lab-fabricated and two commercial TFC membranes while Table 2 tabulates their mean effective pore sizes and MWCOs. The three lab-fabricated TFC membranes have fairly similar pore size distributions and their effective mean pore sizes range from 0.39 nm to 0.41 nm, which are relatively close to one another. The MWCO values of Matrimid-TFC, PESU-TFC, and sPPSU-TFC are 125 g/mol, 150 g/mol and 120 g/mol, respectively, which correspond well to

the aforementioned mean pore sizes. These results indicate that the use of different substrates may have negligible effects on the pore size of the resultant TFC membranes. On the other hand, the commercial RO TFC membranes have a similar pore size distribution with an effective mean pore size around 0.61~0.62 nm. These two RO membranes also have MWCO values of 160 g/mol and 170 g/mol. In contrast, the lab-fabricated FO TFC membranes have slightly smaller mean effective mean pore sizes and MWCO than the commercial RO TFC ones.

Comparison between RO and FO membranes

Since RO is the currently preferred treatment method for wastewater containing organic micro-pollutants, a direct comparison of membrane performance under RO and FO modes for organic micro-pollutant removal is essential to judge FO suitability as an alternative treatment method to RO. Two commercial TFC RO membranes were first tested under the RO mode using synthetic wastewater as the feed. Then the lab-fabricated TFC membranes were tested under both FO and RO modes for performance comparison. It is important to note that the transport mechanisms under RO and FO modes are different. In the RO mode, both pore-flow and solution-diffusion mechanisms take place. In contrast, in the FO mode, the solution-diffusion model plays a much more dominant role than the pore flow model because no hydraulic pressure is involved. In addition, the reverse salt flux in the FO process may retard the transports of organic micro-pollutants (Heo et al. 2013, Xie et al. 2012).

1. Membrane performance under the RO mode (i.e., at 10 bar)

Tables 3 tabulates the PWP values of commercially available RO and lab-fabricated FO membranes under the RO mode. The PWP values of UTC-70UB and Filmtech BW30-4040 RO membranes are 3.05 and 3.94 LMH/bar, respectively, which are much higher than those

of lab-fabricated TFC membranes. Among these three lab-fabricated TFC membranes, their PWP values follow the order of PESU-TFC > sPPSU-TFC > Matrimid-TFC. The PESU-TFC membrane has the highest PWP due to the presence of large macro-voids in the substrate that reduces the transport resistance and its hydrophobicity nature that lowers water affinity to the membrane (Bargeman et al. 2015).

Table 4 shows their rejections of the three organic micro-pollutants. The rejections vary with the producers of RO membranes as well as micro-pollutants' chemistry and molecular structures. Both commercial RO membranes show the highest rejections of aniline (up to 66.6%), lower rejections of phenol (up to 59.8%), but lowest rejections of nitrobenzene (up to 32.4%). In contrast, the lab-fabricated FO membranes show better rejections of nitrobenzene than commercial RO membranes (i.e., 54.5-58.8 vs. 30.1-32.4%), but they have comparable rejections of phenol and aniline (i.e., 43.1-60.7 vs. 45.8-59.8% for phenol rejection; 52.6-61.9 vs. 56.6-66.6% for aniline rejection). The better rejection of the lab-fabricated TFC membranes to nitrobenzene than the commercial RO membranes may be due to the fact that the lab-fabricated TFC membranes have smaller pore sizes than the commercial RO membranes.

Similar to commercial RO membranes, the lab-fabricated FO membranes have higher rejections of aniline than of phenol. The difference in rejection may be caused by different hydrated sizes and dipole moments of these organic compounds (Sun et al. 2011). In general, the smaller hydrated size and the higher dipole moment result in the greater solute transport and the lower the rejection, respectively. The Stokes diameters of these 3 organic compounds follow the order of nitrobenzene (0.97 nm) > aniline (0.83 nm) > phenol (0.75 nm) and their dipole moments obey the sequence of nitrobenzene (3.8 Debye) > phenol (1.7 Debye) >

aniline (1.5 Debye) (Van der Bruggen et al. 1999). The Stokes diameter is likely to be the controlling factor for phenol and aniline transports because they have relatively low and comparable polarity. Therefore, all 5 membranes show higher rejections of aniline than of phenol because aniline has a larger molecular size than phenol (i.e., 0.83 vs. 0.75 nm).

However, in the case of nitrobenzene, although it has the largest size among these three aromatic compounds, the highest dipole moment may facilitate its transport through the membrane. Given that the TFC surface is negatively charged under a wide range of pH (Kwon et al. 2012, Yangali-Quintanilla et al. 2008, Zhang et al. 2013, Zhu et al. 2015) the electrostatic attraction between the TFC layer and nitrobenzene may promote the charge redistribution in nitrobenzene. Consequently, the positively charged portion of nitrobenzene will be oriented towards the membrane surface so that nitrobenzene can easily pass through the membrane, thus a lower rejection is observed (Van der Bruggen et al. 1999, Van der Bruggen and Vandecasteele 2001). As a result, the overall rejections of these RO and lab-fabricated FO membranes towards these three aromatic compounds follows the order of aniline > phenol > nitrobenzene. Although the rejection of nitrobenzene is improved by using the lab-fabricated TFC membranes, the overall rejections under the RO mode need to be further improved for practical wastewater treatment.

2. Membrane performance under the FO mode (i.e., using 1 M NaCl as the draw solution)

Table 3 also summarizes the FO performance of lab-fabricated TFC membranes using DI water and 1 M NaCl as feed and draw solutions, respectively. As can be observed from the Table, the RO membranes have relatively low water fluxes and selectivity under the FO mode using 1M NaCl and DI water as feeds. This suggests that the RO membranes are not suitable for FO processes. On the other hand, the lab-fabricated TFC membranes achieve

much better FO performance. Different from the results under the RO mode where PESU-TFC has the highest PWP, the sPPSU-TFC membrane achieves the highest water flux among these TFC membranes in FO tests due to its high hydrophilicity and small thickness ($\approx 22 \mu\text{m}$) (Li et al. 2014, Widjojo et al. 2011, Zhong et al. 2013). In comparison, the PESU-TFC membrane has a slightly lower water flux but almost the same selectivity of water over salt as the sPPSU one. This is due to the fact that the PESU substrate is fully porous with large macrovoids, despite having a slightly larger thickness ($\approx 70 \mu\text{m}$) and higher hydrophobicity, as shown in Fig. 2. Meanwhile, the Matrimid-TFC membrane has a slightly lower water flux and selectivity, which may be contributed by its relatively dense and thick ($\approx 65 \mu\text{m}$) substrate.

As revealed in Table 4, the three lab-fabricated TFC membranes show statistically comparable rejections of the same organic micro-pollutants under FO tests. Interestingly, their rejections of these three organic micro-pollutants are all consistently higher than 72%. The rejection of aniline can even reach above 90%. These FO membranes outperform themselves and the commercial RO membranes under the RO mode. It is worth noting that the rejection of nitrobenzene, which is usually low under the RO mode due to the high polarity (Van der Bruggen et al. 1999), has been remarkably improved in the FO process. In addition, the rejection sequence under the FO mode is different from what under the RO mode. The TFC membranes exhibit a rejection order of aniline > nitrobenzene > phenol under the FO mode, and a sequence of aniline > phenol > nitrobenzene under the RO mode. The major difference is the order of nitrobenzene.

The improved rejections of organic micro-pollutants under the FO process could be attributed to the different transport mechanisms between RO and FO modes. Since the dominant

mechanism for organic micro-pollutants across the TFC membrane under the FO mode is the solution diffusion mechanism (Chung et al. 2012a, Cui et al. 2014a, McGovern and Lienhard 2014, Zhao et al. 2012), the transport of these micro-pollutants across the membrane is affected by their solute diffusivity and interactions (i.e., solubility) with the membrane. As aforementioned, phenol and aniline have relatively low and comparable polarity, their transport rates are mainly determined by their diffusivity in the membrane. Since diffusivity decreases with increasing hydrated radius (Ghiu et al. 2003), the lab-fabricated TFC membranes show much higher rejections of aniline than of phenol under the FO mode. In the case of nitrobenzene, even though it has the largest size, it has the strongest interactions with the TFC membranes due to its highest dipole moment. This enables nitrobenzene to diffuse through the membrane faster than aniline. On the other hand, the water flux of nitrobenzene is the lowest among the three, which leads to a less pronounced dilution effect. As a result, the rejection of nitrobenzene is lower than aniline and slightly higher than phenol.

Since both pore-flow and solution-diffusion mechanisms take place under the RO mode, the high pressure applied under the RO mode may facilitate the transport of these micro-pollutants across the membrane. In addition, the reverse salt flux in the FO process could retard the diffusion of organic micro-pollutant to the draw side, which may also contribute to the higher rejection under the FO mode (Heo et al. 2013, Xie et al. 2012). As a result, all 5 membranes show inferior rejections under the RO mode to those under the FO mode. In addition, the FO flux may vary significantly with TFC membranes made from different substrates but show quite similar rejections against these organic micro-pollutants. Using sPPSU-TFC as an example, its water flux under the FO mode can reach 22 LMH (Table 3), which is higher than its permeance of 8.4 LMH if being operated under the RO mode at 10 bar. This FO water flux is also higher than the RO permeances of 21.1 LMH and 6.8 LMH of

the other two lab-fabricated TFC membranes under 10 bar. Meanwhile, all lab-fabricated TFC membranes have comparable rejections of organic micro-pollutants under the FO mode. Thus, by choosing a proper substrate, the removal efficiency of the resultant TFC FO membranes can be further improved. In summary, the experimental results evidently indicate that FO membranes have a niche application over RO membranes for the removal of organic micro-pollutants.

Effects of feed solutions

Given that various industries usually prefer to dispose highly concentrated wastewater, it is worthwhile investigating the extent to which the feed solution can be concentrated while maintaining a satisfactory rejection. Thus, the effects of organic micro-pollutant concentration on water flux and solute rejection of the three organic micro-pollutants using 1M NaCl as the draw solution were explored, and the results were presented in Fig. 3. Let's take the PESU-TFC membrane as an example, the water flux follows the sequence of aniline > (or $\approx$) phenol > nitrobenzene. In addition, the water flux exhibits an overall decreasing trend with an increase in feed concentration. The water fluxes of phenol and aniline decrease from 17.9LMH to 15.2LMH and 18.1LMH to 14.7LMH, respectively, when their concentrations increase from 500ppm to 2000ppm. A similar trend can be observed when the nitrobenzene concentration raises from 500 ppm to 1500 ppm, its water flux also decreases by 13%. This phenomenon is due to the slight reduction in osmotic pressure difference between feed and draw solutions.

The rejections of these organic micro-pollutants also show a similar decreasing trend as the feed concentration increases. Using the PESU-TFC membrane as an example, the rejections of phenol and aniline drop by around 4% when their concentrations increase from 500 ppm to

2000 ppm. Similarly, the rejection of nitrobenzene declines from 77.8 % to 75.1% when its concentration increases from 500 ppm to 1500 ppm. Although a higher feed concentration may induce a high solute permeate across the membrane, the permeate amount of the solute should be proportional to the concentration gradient. Thus, the reduction in water flux across the membrane results in a lower solute rejection. However, the overall rejections of these three organic micro-pollutants remain relatively high and satisfactory. This suggests that FO is applicable to treat wastewater containing organic micro-pollutants with concentrations equivalent to or higher than 2000 ppm.

Effects of draw solutions

Generally, a larger throughput is preferred as it improves the efficiency of the treatment plant. The increment in throughput may be achieved by using a more concentrated draw solution. Fig. 4 illustrates the effects of draw solution concentration on water flux and solute rejection. The water flux almost doubles when the draw solution concentration increases from 0.5 M to 2 M. Using the PESU-TFC as an example, the water flux increases from around 10 LMH to 20 LMH. Meanwhile, the rejections of organic micro-pollutants also significantly improve. This is due to the fact that the degree of enhancement in water flux by increasing the draw solution concentration is higher than that in solute flux. Meanwhile, the reverse salt flux increases with the increment of draw solution concentration. This leads to a more significant retarded diffusion of the organic compounds to the draw solution side. As a result, the rejection of phenol increases pronouncedly from 66% to 80% when the draw solution concentration is raised from 0.5M to 2 M. The rejection of nitrobenzene also boosts from 73% to 81%. However, the rejection of aniline increases slightly from 88% to 92%. The other 2 membranes exhibit an alike trend.

In order to explain why the rejection of aniline does not increase as significantly as the rest two organic compounds, Fig. 5 displays the permeate amount of each organic micro-pollutant as a function of draw solution concentration. Generally, organic micro-pollutants permeate more with a higher water flux because water permeation facilitates solute permeation (Geise et al. 2014, Zhang et al. 2014b). However, the effect of pore flow on the solute transport cannot be fully neglected even though the increment is not significant. Since its increment amount is not proportional to the water flux increment, the solution diffusion is still the dominant transport mechanism. Hence, the improved rejections of the organic micro-pollutants are mainly attributed to the dilution effect by the increment water flux, despite having a greater amount of organic micro-pollutants permeating through the membrane. Since the dilution effect is less crucial in improving rejection when the rejection is relatively high, the rejection of aniline increases less significantly than the rest two organic compounds. In summary, employing a more concentrated draw solution is a potential option to enhance the FO performance for the treatment of organic micro-pollutant wastewater.

Effects of annealing

To further improve the rejections of these TFC membranes to organic micro-pollutants, the post-treatment method of annealing is adopted because it is an effective means to narrow down pore sizes and compact membranes (Ghosh et al. 2008, Su et al. 2010b, Sun et al. 2014). Fig. 6 (a), (b) and (c) display its effect on membrane rejection and water flux. As shown, all rejections of the three organic micro-pollutants increase after annealing. Greater enhancements of the rejections are achieved with further elevating annealing temperature. In general, a statistical increase of 10% or even higher in rejection of phenol and nitrobenzene can be observed when annealing takes place at 70°C. For example, comparing with the pristine PESU-TFC membrane, the 70°C annealed PESU-TFC one has a 12% increment in

phenol rejection of 85.6%. The rejection of nitrobenzene also increases by 9.3% to 82.6%. However, the rejection of aniline increases slightly of about 2-3%.

To gain a better understanding of the reasons behind variations in membrane performance after annealing, PAS was employed to examine the micro-structure of the TFC membranes. The evolution of R and S parameters were utilized to examine the states of micro-voids and free-volume related to the transports of organic micro-pollutants and water, respectively. The state of the voids can be analysed by the depth profile of R parameter as illustrated in Fig. 7(a), (b) and (c). The PESU-TFC membrane is used as an example. All depth profile curves show a drastic decrease at first, and then increase sharply after reaching the lowest point. Since R parameter represents the state of voids, it will decrease as the voids reduce in size or quantity. From the macroscopic aspect, the concave region (i.e. 0 keV to around 2 keV) represents the dense part of the membrane, i.e., the polyamide layer. As shown in this figure, the thickness of the polyamide layer decreases with an increase in annealing temperature. The other two membranes also follow a similar trend. This suggests that the polymer nodules in the polyamide layer coalesce and the layer becomes more compact during annealing (Su et al. 2010b). Hence, the membrane becomes thinner after annealing and it has higher rejections of organic micro-pollutants.

Interestingly, the water flux is not remarkably affected by the annealing, as shown in Fig. 6 (d) (e) and (f). The water flux fluctuates within a narrow range as the annealing temperature increases. This is also reflected in the depth profile of S parameter, as displayed in Fig. 7 (d) (e) and (f) where the free volume intensity of membranes treated with different annealing temperatures varies negligibly. The reason behind this phenomenon is that the free volume intensity are intimately related to molecular movements of polymer chain segments (Su et al.

2010b, Szocs et al. 1995). Since annealing at 70°C is not high enough to significantly alter the status of segmental chain movement (Su et al. 2010b, Szocs et al. 1995), the free volume size and quantity for water transport remain almost intact during the low-temperature annealing. Hence, a harsher annealing condition may be applicable to achieve a further improvement. Therefore, employing annealing is a potential choice to enhance membrane separation capability to remove organic micro-pollutants.

CONCLUSION

In this study, we have successfully demonstrated that FO is capable to remove organic micro-pollutants such as phenol, aniline and nitrobenzene from wastewater and revealed the basic science behind it. Three TFC membranes were fabricated from three different substrates; namely, Matrimid, PESU, sPPSU and then studied under both RO and FO modes. Their separation performances were also compared with two commercial RO membranes for the removal of organic micro-pollutants. The following conclusions can be drawn from this study:

1. In the FO process, the rejections of the three different organic micro-pollutants are all consistently above 72%, and the rejection of aniline can even reach above 90% when using 1000 ppm aromatic aqueous solutions and 1 M NaCl as feeds. These rejections are significantly higher than that can be achieved under the RO mode using either commercial RO membranes or lab-fabricated membranes.
2. The FO process is able to maintain reasonable rejections when treating a more concentrated organic micro-pollutant wastewater. Only a slight decrease in rejection when the feed concentration increases from 500 ppm to 2000 ppm for phenol and aniline, and to 1500 ppm for nitrobenzene.

- 545 3. The use of a more concentrated draw solution is a promising option to enhance the
546 membrane performance for the removal of organic micro-pollutants. When the draw
547 solution concentration increases from 0.5 M to 2 M, the water flux is almost doubled,
548 and the rejection increment can reach up to 17%.
- 549 4. Annealing as a post-treatment will compact the membrane selective layer, and
550 improve the rejection of organic micro-pollutants.

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REFERENCE

- Al-Khalid, T. and El-Naas, M.H. (2012) Aerobic biodegradation of phenols: A comprehensive review. *Critical Reviews in Environmental Science and Technology* 42(16), 1631-1690.
- Bargeman, G., Westerink, J.B., Manuhutu, C.F.H. and Kate, A.t. (2015) The effect of membrane characteristics on nanofiltration membrane performance during processing of practically saturated salt solutions. *Journal of Membrane Science* 485, 112-122.
- Basile, T., Petrella, A., Petrella, M., Boghetich, G., Petruzzelli, V., Colasuonno, S. and Petruzzelli, D. (2011) Review of endocrine-disrupting-compound removal technologies in water and wastewater treatment plants: An eu perspective. *Industrial & Engineering Chemistry Research* 50(14), 8389-8401.
- Chen, H.M., Hung, W.S., Lo, C.H., Huang, S.H., Cheng, M.L., Liu, G., Lee, K.R., Lai, J.Y., Sun, Y.M., Hu, C.C., Suzuki, R., Ohdaira, T., Oshima, N. and Jean, Y.C. (2007) Free-volume depth profile of polymeric membranes studied by positron annihilation spectroscopy: Layer structure from interfacial polymerization. *Macromolecules* 40(21), 7542-7557.
- Chun, Y., Zaviska, F., Cornelissen, E. and Zou, L. (2015) A case study of fouling development and flux reversibility of treating actual lake water by forward osmosis process. *Desalination* 357, 55-64.
- Chung, T. S., Li, X., Ong, R.C., Ge, Q., Wang, H. and Han, G. (2012a) Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications. *Current Opinion in Chemical Engineering* 1(3), 246-257.
- Chung, T.S., Zhang, S., Wang, K.Y., Su, J.C. and Ling, M.M. (2012b) Forward osmosis processes: Yesterday, today and tomorrow. *Desalination* 287, 78-81.
- Cui, Y., Ge, Q., Liu, X.Y. and Chung, T.S. (2014a) Novel forward osmosis process to effectively remove heavy metal ions. *Journal of Membrane Science* 467, 188-194.

- 584 Cui, Y., Liu, X. Y. and Chung, T. S. (2014b) Enhanced osmotic energy generation from
585 salinity gradients by modifying thin film composite membranes. *Chemical Engineering*
586 *Journal* 242(0), 195-203.
- 587 Cui, Y., Wang, H.L., Wang, H. and Chung, T.S. (2013) Micro-morphology and formation of
588 layer-by-layer membranes and their performance in osmotically driven processes. *Chemical*
589 *Engineering Science* 101, 13-26.
- 590 Escobar, I.C. and Van der Bruggen, B. (2011) Modern applications in membrane science and
591 technology, American Chemical Society Books.
- 592 Flanagan, M.F. and Escobar, I.C. (2013) Novel charged and hydrophilized
593 polybenzimidazole (PBI) membranes for forward osmosis. *Journal of Membrane Science*
594 434(0), 85-92.
- 595 Fu, F.L., Dionysiou, D.D. and Liu, H. (2014) The use of zero-valent iron for groundwater
596 remediation and wastewater treatment: A review. *Journal of Hazardous Materials* 267, 194-
597 205.
- 598 Gallard, H. and Von Gunten, U. (2002) Chlorination of phenols: Kinetics and formation of
599 chloroform. *Environmental Science & Technology* 36(5), 884-890.
- 600 Gao, J., Sun, S. P., Zhu, W. P. and Chung, T. S. (2014) Polyethyleneimine (PEI) cross-linked
601 P84 nanofiltration (NF) hollow fiber membranes for Pb^{2+} removal. *Journal of Membrane*
602 *Science* 452(0), 300-310.
- 603 Ge, Q., Ling, M. and Chung, T. S. (2013) Draw solutions for forward osmosis processes:
604 Developments, challenges, and prospects for the future. *Journal of Membrane Science* 442(0),
605 225-237.
- 606 Geise, G.M., Paul, D.R. and Freeman, B.D. (2014) Fundamental water and salt transport
607 properties of polymeric materials. *Progress in Polymer Science* 39(1), 1-42.

- 608 Ghiu, S.M.S., Carnahan, R.P. and Barger, M. (2003) Mass transfer in RO TFC membranes -
609 dependence on the salt physical and thermodynamic parameters. *Desalination* 157(1–3), 385-
610 393.
- 611 Ghosh, A.K., Jeong, B. H., Huang, X. and Hoek, E.M.V. (2008) Impacts of reaction and
612 curing conditions on polyamide composite reverse osmosis membrane properties. *Journal of*
613 *Membrane Science* 311(1–2), 34-45.
- 614 Gonsior, M., Schmitt-Kopplin, P., Stavklint, H., Richardson, S.D., Hertkorn, N. and
615 Bastviken, D. (2014) Changes in dissolved organic matter during the treatment processes of a
616 drinking water plant in Sweden and formation of previously unknown disinfection
617 byproducts. *Environmental Science & Technology* 48(21), 12714-12722.
- 618 Hao, O.J., Kim, H. and Chiang, P.C. (2000) Decolorization of wastewater. *Critical Reviews*
619 *in Environmental Science and Technology* 30(4), 449-505.
- 620 Heo, J., Boateng, L.K., Flora, J.R.V., Lee, H., Her, N., Park, Y. G. and Yoon, Y. (2013)
621 Comparison of flux behavior and synthetic organic compound removal by forward osmosis
622 and reverse osmosis membranes. *Journal of Membrane Science* 443, 69-82.
- 623 Huang, L., Bui, N. N., Meyering, M.T., Hamlin, T.J. and McCutcheon, J.R. (2013) Novel
624 hydrophilic nylon 6,6 microfiltration membrane supported thin film composite membranes
625 for engineered osmosis. *Journal of Membrane Science* 437(0), 141-149.
- 626 Jean, Y.C., Chen, H.M., Zhang, S., Chen, H.Z., Lee, L.J., Awad, S., Huang, J., Lau, C.H.,
627 Wang, H., Li, F.Y. and Chung, T.S. (2011) Characterizing free volumes and layer structures
628 in polymeric membranes using slow positron annihilation spectroscopy. 12th International
629 Workshop on Slow Positron Beam Techniques (Slopos12) 262.
- 630 Jean, Y.C., Hung, W.S., Lo, C.H., Chen, H., Liu, G., Chakka, L., Cheng, M.L., Nanda, D.,
631 Tung, K.L., Huang, S.H., Lee, K.R., Lai, J.Y., Sun, Y.M., Hu, C.C. and Yu, C.C. (2008)

- 632 Applications of positron annihilation spectroscopy to polymeric membranes. Desalination
633 234(1-3), 89-98.
- 634 Jean, Y.C., Mallon, P.E., Schrader, D.M. (2003) Principle and applicaiton of positron and
635 positronium chemistry, Word Scientific Press.
- 636 Kwon, Y. N., Shih, K., Tang, C. and Leckie, J.O. (2012) Adsorption of perfluorinated
637 compounds on thin-film composite polyamide membranes. Journal of Applied Polymer
638 Science 124(2), 1042-1049.
- 639 Li, P., Lim, S.S., Neo, J.G., Ong, R.C., Weber, M., Staudt, C., Widjojo, N., Maletzko, C. and
640 Chung, T.S. (2014) Short- and long-term performance of the thin-film composite forward
641 osmosis (TFC-FO) hollow fiber membranes for oily wastewater purification. Industrial &
642 Engineering Chemistry Research 53(36), 14056-14064.
- 643 Li, X., Wang, K.Y., Helmer, B. and Chung, T.S. (2012a) Thin-film composite membranes
644 and formation mechanism of thin-film layers on hydrophilic cellulose acetate propionate
645 substrates for forward osmosis processes. Industrial & Engineering Chemistry Research
646 51(30), 10039-10050.
- 647 Li, Z. Y., Yangali-Quintanilla, V., Valladares-Linares, R., Li, Q., Zhan, T. and Amy, G.
648 (2012b) Flux patterns and membrane fouling propensity during desalination of seawater by
649 forward osmosis. Water Research 46(1), 195-204.
- 650 Liu, Y. and Mi, B. (2012) Combined fouling of forward osmosis membranes: Synergistic
651 foulant interaction and direct observation of fouling layer formation. Journal of Membrane
652 Science 407–408(0), 136-144.
- 653 Maguire-Boyle, S.J. and Barron, A.R. (2014) Organic compounds in produced waters from
654 shale gas wells. Environmental Science-Processes & Impacts 16(10), 2237-2248.

- 655 McGovern, R.K. and Lienhard, J.H. (2014) On the potential of forward osmosis to
656 energetically outperform reverse osmosis desalination. *Journal of Membrane Science* 469,
657 245-250.
- 658 Pal, P. and Kumar, R. (2014) Treatment of coke wastewater: A critical review for developing
659 sustainable management strategies. *Separation and Purification Reviews* 43(2), 89-123.
- 660 Park, M.J., Phuntsho, S., He, T., Nisola, G.M., Tijting, L.D., Li, X. M., Chen, G., Chung, W. J.
661 and Shon, H.K. (2015) Graphene oxide incorporated polysulfone substrate for the fabrication
662 of flat-sheet thin-film composite forward osmosis membranes. *Journal of Membrane Science*
663 493, 496-507.
- 664 Ramon, G.Z., Wong, M.C.Y. and Hoek, E.M.V. (2012) Transport through composite
665 membrane, part 1: Is there an optimal support membrane? *Journal of Membrane Science*
666 415–416, 298-305.
- 667 Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Marinas, B.J. and Mayes, A.M.
668 (2008) Science and technology for water purification in the coming decades. *Nature*
669 452(7185), 301-310.
- 670 Shao, L., Cheng, X.Q., Liu, Y., Quan, S., Ma, J., Zhao, S.Z. and Wang, K.Y. (2013) Newly
671 developed nanofiltration (NF) composite membranes by interfacial polymerization for
672 Safranin O and Aniline blue removal. *Journal of Membrane Science* 430, 96-105.
- 673 Shintani, T., Shimazu, A., Yahagi, S. and Matsuyama, H. (2009) Characterization of methyl-
674 substituted polyamides used for reverse osmosis membranes by positron annihilation lifetime
675 spectroscopy and MD simulation. *Journal of Applied Polymer Science* 113(3), 1757-1762.
- 676 Singh, S., Khulbe, K.C., Matsuura, T. and Ramamurthy, P. (1998) Membrane
677 characterization by solute transport and atomic force microscopy. *Journal of Membrane*
678 *Science* 142(1), 111-127.

- 679 Su, J., Yang, Q., Teo, J.F. and Chung, T.S. (2010a) Cellulose acetate nanofiltration hollow
680 fiber membranes for forward osmosis processes. *Journal of Membrane Science* 355(1–2), 36-
681 44.
- 682 Su, J., Zhang, S., Chen, H., Chen, H., Jean, Y.C. and Chung, T. S. (2010b) Effects of
683 annealing on the microstructure and performance of cellulose acetate membranes for
684 pressure-retarded osmosis processes. *Journal of Membrane Science* 364(1–2), 344-353.
- 685 Sun, S.P., Chung, T.S., Lu, K.J. and Chan, S.Y. (2014) Enhancement of flux and solvent
686 stability of matrimid (R) thin-film composite membranes for organic solvent nanofiltration.
687 *Aiche Journal* 60(10), 3623-3633.
- 688 Sun, S.P., Hatton, T.A. and Chung, T.S. (2011) Hyperbranched polyethyleneimine induced
689 cross-linking of polyamide-imide nanofiltration hollow fiber membranes for effective
690 removal of ciprofloxacin. *Environmental Science & Technology* 45(9), 4003-4009.
- 691 Szocs, F., Sausa, O., Kristiakova, K., Kristiak, J. and Klimova, M. (1995) Influence of high-
692 pressure annealing on free-volume in polycarbonate studied by positron-annihilation.
693 *European Polymer Journal* 31(10), 1019-1020.
- 694 Valladares Linares, R., Li, Z., Sarp, S., Bucs, S.S., Amy, G. and Vrouwenvelder, J.S. (2014)
695 Forward osmosis niches in seawater desalination and wastewater reuse. *Water Research* 66,
696 122-139.
- 697 Van der Bruggen, B. and Luis, P. (2015) Forward osmosis: understanding the hype. *Reviews*
698 *in Chemical Engineering* 31(1), 1-12.
- 699 Van der Bruggen, B., Schaep, J., Wilms, D. and Vandecasteele, C. (1999) Influence of
700 molecular size, polarity and charge on the retention of organic molecules by nanofiltration.
701 *Journal of Membrane Science* 156(1), 29-41.

- 702 Van der Bruggen, B. and Vandecasteele, C. (2001) Flux decline during nanofiltration of
703 organic components in aqueous solution. *Environmental Science & Technology* 35(17),
704 3535-3540.
- 705 Van der Bruggen, B. and Vandecasteele, C. (2002) Modelling of the retention of uncharged
706 molecules with nanofiltration. *Water Research* 36(5), 1360-1368.
- 707 Widjojo, N., Chung, T.S., Weber, M., Maletzko, C. and Warzelhan, V. (2011) The role of
708 sulphonated polymer and macrovoid-free structure in the support layer for thin-film
709 composite (TFC) forward osmosis (FO) membranes. *Journal of Membrane Science* 383(1-2),
710 214-223.
- 711 Xie, M., Nghiem, L.D., Price, W.E. and Elimelech, M. (2012) Comparison of the removal of
712 hydrophobic trace organic contaminants by forward osmosis and reverse osmosis. *Water*
713 *Research* 46(8), 2683-2692.
- 714 Xie, M., Nghiem, L.D., Price, W.E. and Elimelech, M. (2013) A Forward Osmosis–
715 Membrane Distillation Hybrid Process for Direct Sewer Mining: System Performance and
716 Limitations. *Environmental Science & Technology* 47(23), 13486-13493.
- 717 Yang, M. and Zheng, S.K. (2014) Pollutant removal-oriented yeast biomass production from
718 high-organic-strength industrial wastewater: A review. *Biomass & Bioenergy* 64, 356-362.
- 719 Yang, S.X., Sun, Y., Yang, H.W. and Wan, J.F. (2015) Catalytic wet air oxidation of phenol,
720 nitrobenzene and aniline over the multi-walled carbon nanotubes (MWCNTs) as catalysts.
721 *Frontiers of Environmental Science & Engineering* 9(3), 436-443.
- 722 Yangali-Quintanilla, V., Kim, T.U., Kennedy, M. and Amy, G. (2008) Modeling of RO/NF
723 membrane rejections of PhACs and organic compounds: A statistical analysis. *Drinking*
724 *Water Engineering and Science* 1(1), 7-15.

- 725 Zaviska, F., Chun, Y., Heran, M. and Zou, L. (2015) Using FO as pre-treatment of RO for
726 high scaling potential brackish water: Energy and performance optimisation. *Journal of*
727 *Membrane Science* 492(0), 430-438.
- 728 Zhang, S., Qiu, G.L., Ting, Y.P. and Chung, T.S. (2013) Silver-PEGylated dendrimer
729 nanocomposite coating for anti-fouling thin film composite membranes for water treatment.
730 *Colloids and Surfaces A-Physicochemical and Engineering Aspects* 436, 207-214.
- 731 Zhang, S., Sukitpaneemit, P. and Chung, T.S. (2014a) Design of robust hollow fiber
732 membranes with high power density for osmotic energy production. *Chemical Engineering*
733 *Journal* 241, 457-465.
- 734 Zhang, S., Wang, K.Y., Chung, T.S., Chen, H.M., Jean, Y.C. and Amy, G. (2010) Well-
735 constructed cellulose acetate membranes for forward osmosis: Minimized internal
736 concentration polarization with an ultra-thin selective layer. *Journal of Membrane Science*
737 360(1-2), 522-535.
- 738 Zhang, S., Wang, P., Fu, X.Z. and Chung, T.S. (2014b) Sustainable water recovery from oily
739 wastewater via forward osmosis-membrane distillation (FO-MD). *Water Research* 52, 112-
740 121.
- 741 Zhao, S., Zou, L., Tang, C.Y. and Mulcahy, D. (2012) Recent developments in forward
742 osmosis: Opportunities and challenges. *Journal of Membrane Science* 396(0), 1-21.
- 743 Zhong, P.S., Fu, X.Z., Chung, T.S., Weber, M. and Maletzko, C. (2013) Development of
744 thin-film composite forward osmosis hollow fiber membranes using direct sulfonated
745 polyphenylenesulfone (sPPSU) as membrane substrates. *Environmental Science &*
746 *Technology* 47(13), 7430-7436.
- 747 Zhu, W.P., Gao, J., Sun, S.P., Zhang, S. and Chung, T.S. (2015) Poly(amidoamine)
748 dendrimer (PAMAM) grafted on thin film composite (TFC) nanofiltration (NF) hollow fiber
749 membranes for heavy metal removal. *Journal of Membrane Science* 487, 117-126.

750 Zietzschmann, F., Altmann, J., Ruhl, A.S., Dunnbier, U., Dommisch, I., Sperlich, A., Meinel,
751 F. and Jekel, M. (2014) Estimating organic micro-pollutant removal potential of activated
752 carbons using UV absorption and carbon characteristics. *Water Research* 56, 48-55.

753 Zou, S., Wang, Y.-N., Wicaksana, F., Aung, T., Wong, P.C.Y., Fane, A.G. and Tang, C.Y.
754 (2013) Direct microscopic observation of forward osmosis membrane fouling by microalgae:
755 Critical flux and the role of operational conditions. *Journal of Membrane Science* 436, 174-
756 185.

TABLES

Table 1. Molecular weight and Stoke diameter of neutral solutes

Table 2. Mean effective pore size and molecular weight cut off

Table 3. Pure water permeability under the RO mode and FO performance of the TFC membranes

Table 4. Rejection of organic micro-pollutants comparison under different processes

FIGURES

Fig. 1. Typical membrane morphologies of Matrimid, PESU, sPPSU substrates and the respective resultant TFC membranes

Fig. 2. Pore size and pore size distribution of TFC membranes

Fig. 3 (a)-(c) Water flux and (d)-(f) solute rejection as a function of feed solution concentration; Draw solution: 1M NaCl

Fig. 4 (a)-(c) Water flux and (d)-(f) solute rejection as a function of draw solution concentration; Feed solution concentration: 1000 ppm

Fig. 5. Permeate amount of different organic micro-pollutants as a function of draw solution concentration

Fig. 6. (a)-(c) Solute rejection and (d)-(f) water flux as a function of annealing temperature

Treatment duration: 10 min; Feeds: 1000 ppm aromatic aqueous solution, 1M NaCl as draw solution

Fig. 7. Depth profiles of (a)-(c) R parameter and (d)-(f) S parameter of TFC membranes annealed at different temperature

Table1. Molecular weight and Stoke diameter of neutral solutes

Solute	Mw (g/mol)	ds (nm)
Ethyleneglycol	62	0.47
Diethyleneglycol	106	0.582
Triethyleneglycol	150	0.668
Glucose	180	0.73
Sucrose	342	0.94

Table 2. Mean effective pore size and molecular weight cut off

Membrane	d_p (nm)	σ_p	MWCO (g/mol)
PESU-TFC	0.41	1.40	150
Matrimid-TFC	0.39	1.43	125
sPPSU-TFC	0.41	1.35	120
Filmtech BW30-4040	0.61	1.34	160
UTC-70UB	0.62	1.39	170

Draw solution: 1M NaCl; Feed solution: DI water

Table 3. Pure water permeability under the RO mode and FO performance of the TFC membranes

Membrane	PWP (LMH/bar) (RO mode)	water flux (LMH) (FO mode)	Reverse salt flux (gMH) (FO mode)	J_s/J_w
PESU-TFC	2.11	20.6 ± 1.7	3.54 ± 1.1	0.17
Matrimid-TFC	0.68	14.0 ± 1.5	4.27 ± 0.6	0.30
sPPSU-TFC	0.84	22.0 ± 1.5	4.05 ± 0.8	0.18
UTC-70UB	3.05	3.39 ± 1.91	7.91 ± 0.93	2.34
Filmtech BW30-4040	3.94	6.15 ± 1.17	6.29 ± 0.42	1.02

Feed solution: DI water

Draw solution for FO test: 1 M NaCl

Table 4. Rejection of organic micro-pollutants comparison under different processes

Membrane	Process	Rejection (%)		
		Nitrobenzene	Phenol	Aniline
PESU TFC	FO	76.8 ± 0.9	73.7 ± 2.2	91.8 ± 0.1
	RO	55.0 ± 5.3	43.1 ± 3.0	52.6 ± 0.2
Matrimid TFC	FO	76.6 ± 0.3	75.9 ± 1.7	88.4 ± 0.9
	RO	54.5 ± 1.0	56.7 ± 4.8	57.3 ± 0.5
sPPSU TFC	FO	75.2 ± 3.4	72.1 ± 1.2	91.5 ± 1.2
	RO	58.8 ± 2.4	60.7 ± 1.6	61.9 ± 2.4
UTC-70UB	RO	30.1 ± 6.0	59.8 ± 6.7	66.6 ± 6.6
Filmtech BW30-4040	RO	32.4 ± 2.6	45.8 ± 2.4	56.6 ± 3.7

- Feed solution: 1000 ppm aromatic aqueous solution
- Low pressure RO test Pressure: 10 bar

Fig. 1. Typical membrane morphologies of Matrimid, PESU, sPPSU substrates and the resultant TFC membranes

Fig. 2. Pore size and pore size distribution of TFC membranes

PESU-TFC membrane **Matrimid-TFC membrane** **sPPSU-TFC membrane**

Fig.3 (a)-(c) Water flux and (d)-(f) solute rejection as a function of feed solution concentration; Draw solution: 1M NaCl

Fig.4 (a)-(c) Water flux and (d)-(f) solute rejection as a function of draw solution concentration; Feed solution concentration: 1000 ppm

Fig. 5. Permeate amounts of different organic micro-pollutants as a function of draw solution concentration

PESU-TFC membrane **Matrimid-TFC membrane** **sPPSU-TFC membrane**

Fig. 6. (a)-(c) Solute rejection and (d)-(f) water flux as a function of annealing temperature

Treatment duration: 10 min; Feeds: 1000 ppm aromatic aqueous solution, 1M NaCl as the draw solution

Fig. 7. Depth profiles of (a)-(c) R parameter and (d)-(f) S parameter of TFC membranes annealed at different temperature

- Removal of phenol, aniline and nitrobenzene by FO processes was explored for the first time.
- FO is able to treat more concentrated wastewater without sacrificing rejection.
- A more concentrated draw solution helps to enhance membrane performance.
- Annealing is a suitable post-treatment method to improve membrane performance.