



UNIVERSITY  
OF WOLLONGONG  
AUSTRALIA

University of Wollongong  
Research Online

---

Faculty of Engineering and Information Sciences -  
Papers: Part A

Faculty of Engineering and Information Sciences

---

2014

# Relating rejection of trace organic contaminants to membrane properties in forward osmosis: measurements, modelling and implications

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*

---

## Publication Details

Xie, M., Nghiem, L. D., Price, W. E. & Elimelech, M. (2014). Relating rejection of trace organic contaminants to membrane properties in forward osmosis: measurements, modelling and implications. *Water Research*, 49 (February), 265-274.

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library:  
[research-pubs@uow.edu.au](mailto:research-pubs@uow.edu.au)

---

# Relating rejection of trace organic contaminants to membrane properties in forward osmosis: measurements, modelling and implications

## Abstract

This study elucidates the relationship between membrane properties and the rejection of trace organic contaminants (TrOCs) in forward osmosis (FO). An asymmetric cellulose triacetate (CTA) and a thin-film composite (TFC) polyamide FO membrane were used for this investigation. The effective average pore radius ( $r_p$ ), selective barrier thickness over porosity parameter ( $l/\epsilon$ ), surface charge, support layer structural parameter ( $S$ ), pure water permeability coefficient ( $A$ ) and salt (NaCl) permeability coefficient ( $B$ ) of the two membranes were systematically characterised. Results show that measured rejection of TrOCs as a function of permeate water flux can be well described by the pore hindrance transport model. This observation represents the first successful application of this model, which was developed for pressure-driven nanofiltration, to an osmotically-driven membrane process. The rejection of charged TrOCs by the CTA and TFC membranes was high and was governed by both electrostatic repulsion and steric hindrance. The TFC membrane exhibited higher rejection of neutral TrOCs with low molecular weight than the CTA membrane, although the estimated pore size of the TFC membrane (0.42 nm) was slightly larger than that of the CTA membrane (0.37 nm). This higher rejection of neutral TrOCs by the TFC membrane is likely attributed to its active layer properties, namely a more effective active layer structure, as indicated by a larger  $l/\epsilon$  parameter, and pore hydration induced by the negative surface charge.

## Keywords

trace, organic, contaminants, membrane, osmosis, measurements, properties, forward, relating, modelling, implications, rejection

## Disciplines

Engineering | Science and Technology Studies

## Publication Details

Xie, M., Nghiem, L. D., Price, W. E. & Elimelech, M. (2014). Relating rejection of trace organic contaminants to membrane properties in forward osmosis: measurements, modelling and implications. *Water Research*, 49 (February), 265-274.



17 **Abstract**

18 This study elucidates the relationship between membrane properties and the rejection  
19 of trace organic contaminants (TrOCs) in forward osmosis (FO). An asymmetric cellulose  
20 triacetate (CTA) and a thin-film composite (TFC) polyamide FO membrane were used for  
21 this investigation. The effective average pore radius ( $r_p$ ), selective barrier thickness over  
22 porosity parameter ( $l/\varepsilon$ ), surface charge, support layer structural parameter ( $S$ ), pure water  
23 permeability coefficient ( $A$ ) and salt (NaCl) permeability coefficient ( $B$ ) of the two  
24 membranes were systematically characterised. Results show that measured rejection of  
25 TrOCs as a function of permeate water flux can be well described by the pore hindrance  
26 transport model. This observation represents the first successful application of this model,  
27 which was developed for pressure-driven nanofiltration, to an osmotically-driven membrane  
28 process. The rejection of charged TrOCs by the CTA and TFC membranes was high and was  
29 governed by both electrostatic repulsion and steric hindrance. The TFC membrane exhibited  
30 higher rejection of neutral TrOCs with low molecular weight than the CTA membrane,  
31 although the estimated pore size of the TFC membrane (0.42 nm) was slightly larger than that  
32 of the CTA membrane (0.37 nm). This higher rejection of neutral TrOCs by the TFC  
33 membrane is likely attributed to its active layer properties, namely a more effective active  
34 layer structure, as indicated by a larger  $l/\varepsilon$  parameter, and pore hydration induced by the  
35 negative surface charge.

36 *Keywords:* forward osmosis; solute rejection, membrane surface charge; trace organic  
37 contaminants (TrOCs); permeate flux; pore hindrance transport model; pore size.

38

## 39 **1. Introduction**

40 More than four billion people live in areas where drinking water security and  
41 ecosystem biodiversity are being threatened by freshwater shortages. This problem is being  
42 exacerbated by urbanization, population growth and climate change (Grant et al. 2012). As a  
43 result, significant research efforts have been made to facilitate the extraction of clean water  
44 from unconventional resources, such as seawater and wastewater effluent, to augment  
45 drinking water supplies. Membrane filtration processes, such as reverse osmosis (RO) and  
46 nanofiltration (NF), have contributed to a remarkable increase in the utilisation of  
47 unconventional water resources (Elimelech and Phillip 2011, Shannon et al. 2008). However,  
48 numerous trace organic contaminants (TrOCs) are being frequently detected in wastewater  
49 and sewage-impacted water bodies (Basile et al. 2011, Carballa et al. 2004, Schwarzenbach et  
50 al. 2006, Snyder et al. 2003 ). As a result, in addition to existing membrane processes such as  
51 NF and RO, novel treatment technologies, which can potentially provide a more efficient and  
52 cost-effective barrier against TrOCs, have also been explored.

53 Forward osmosis (FO) is one such novel membrane process that has the potential to  
54 advance water and wastewater treatment (Cath et al. 2006, Zhao et al. 2012). In FO, a semi-  
55 permeable membrane is placed between a feed solution and a concentrated draw solution  
56 with high osmotic pressure. The extraction of water is driven by the osmotic pressure  
57 difference and, at the same time, salt and contaminants in the feed solution are being rejected  
58 by the FO membrane. To produce freshwater, FO is usually combined with pressure-driven  
59 membrane processes, such as NF and RO (Hoover et al. 2011, Shaffer et al. 2012, Yangali-  
60 Quintanilla et al. 2011), or thermal processes, such as conventional column distillation  
61 (McCutcheon et al. 2005, McGinnis and Elimelech 2007) and membrane distillation (Cath et  
62 al. 2005, Martinetti et al. 2009). In these hybrid treatment systems, TrOCs in the feed are first  
63 subjected to rejection by the FO membrane and then by the subsequent process that is used to  
64 both concentrate the draw solution and produce freshwater, thereby providing a dual barrier  
65 for TrOCs. Hence, it is of paramount importance to better elucidate the removal of TrOCs in  
66 the FO process.

67 High removal efficiency of TrOCs by the FO process has been demonstrated in  
68 several previous studies. Cartinella et al. (2006) found a near complete rejection of three  
69 hormones in FO. Cath et al. (2010) reported the rejection of six TrOCs, ranging from 72%  
70 (salicylic acid) to more than 99% (diclofenac). A comprehensive study on the removal of 23  
71 TrOCs revealed that the rejection of charged TrOCs was consistently above 80%, whereas the

72 rejection of neutral TrOCs varied from 40 to 90% (Hancock et al. 2011b). A similar  
73 observation was also reported by Valladares Linares et al (2011) when examining the  
74 removal of 13 TrOCs. Alturki et al. (2013) elucidated the mechanisms governing the  
75 rejection of 40 TrOCs compounds by FO, indicating that the rejection of charged TrOCs is  
76 governed by both electrostatic interaction and size exclusion, while rejection of neutral  
77 compounds is dominated by size exclusion.

78 It is noteworthy that to date most studies investigating the removal of TrOCs by the  
79 FO process employed an asymmetric cellulose triacetate (CTA) membrane. Given the recent  
80 progress in the development of new membrane materials for FO applications, polyamide thin-  
81 film composite (TFC) membranes have been recently introduced. These TFC membranes  
82 have been reported to have higher water permeability and solute rejection compared to their  
83 CTA counterparts (Wang et al. 2010, Wei et al. 2011, Yip et al. 2010). Because there are  
84 considerable differences between asymmetric CTA and polyamide TFC membranes, it is  
85 worthwhile to systematically examine their rejection performance and provide insights into  
86 the relationship between membrane properties and TrOCs rejection.

87 In this study, we examine and compare the rejection of 12 TrOCs by an asymmetric  
88 CTA and a polyamide TFC membrane as a function of permeate water flux. Key properties of  
89 the CTA and TFC membranes were characterised to facilitate the understanding of their  
90 TrOC rejection behaviour. The membrane pore hindrance transport model was used to predict  
91 the rejection of the TrOCs as a function of permeate water flux and model predictions were  
92 compared with the experimentally measured data. Rejection of TrOCs by the CTA and TFC  
93 membranes was related to the membrane properties and mechanisms responsible for the  
94 rejection of TrOCs were proposed and elucidated.

## 95 **2. Materials and methods**

### 96 *2.1. Trace organic contaminants*

97 Twelve TrOCs, frequently detected in secondary treated effluent and sewage-impacted  
98 water bodies at trace levels, were used for this investigation. The TrOCs were selected to  
99 cover a diverse range of properties including charge, hydrophobicity and molecular weight  
100 (Table 1). A combined stock solution containing 1 g/L of each TrOC was prepared in  
101 methanol. The stock solution was kept at  $-18\text{ }^{\circ}\text{C}$  in the dark and was used within one month.

102

[Table 1]

## 103 *2.2. Forward osmosis and reverse osmosis systems*

104 A bench-scale FO system consisting of a cross-flow membrane cell with a total  
105 effective membrane area of 123.5 cm<sup>2</sup> was employed. The membrane cell had two identical  
106 and symmetrical flow chambers with length, width and channel height of 130, 95, and 2 mm,  
107 respectively. The circulation flow rates of the feed and draw solutions were kept constant at 1  
108 L/min (corresponding to a cross flow velocity of 9 cm/s). The draw solution reservoir was  
109 placed on a digital balance (Mettler Toledo Inc., Hightstown, NJ) and weight changes were  
110 recorded by a computer to calculate the permeate water flux. A conductivity controller (Cole-  
111 Parmer, Vernon Hills, IL) was used to maintain a constant draw solution concentration when  
112 inorganic salt was used as the draw solute. Further details of this conductivity control system  
113 are available elsewhere (Xie et al. 2012a).

114 A bench-scale RO system with a rectangular stainless-steel cross-flow cell was used to  
115 characterise the membrane pore radius and membrane transport parameters. The RO  
116 membrane cell had an effective membrane area of 40 cm<sup>2</sup>, with channel length, width and  
117 depth of 100, 40 and 2 mm, respectively. The unit was equipped with a Hydra-Cell pump  
118 (Wanner Engineering Inc., Minneapolis, MN). The temperature of the feed solution was kept  
119 constant using a chiller/heater (Neslab RTE 7). Permeate flow was measured by a digital flow  
120 meter (FlowCal 5000, Tovatech, South Orange, NJ).

## 121 *2.3. Characterization of forward osmosis membranes*

122 An asymmetric CTA and a polyamide TFC membrane were acquired from Hydration  
123 Technology Innovations (Albany, OR) and Oasys Water (Boston, MA), respectively. The  
124 CTA membrane is composed of a cellulose triacetate layer with an embedded woven support  
125 mesh (Cath et al. 2006, McCutcheon and Elimelech 2008). The TFC membrane is made of a  
126 thin selective polyamide active layer on top of a porous polysulfone support layer (Cath et al.  
127 2013, McGinnis et al. 2013).

### 128 *2.3.1 Membrane transport parameters*

129 Key membrane transport parameters were characterised following the protocol  
130 previously described by Cath et al. (2013), including pure water permeability coefficient of  
131 the active layer,  $A$ , the salt (NaCl) permeability coefficient of the active layer,  $B$ , and the  
132 structural parameter of the support layer,  $S$ . Briefly, the membrane  $A$  and  $B$  values were  
133 determined using the RO cross-flow filtration system (section 2.2). The membrane  $A$  value

134 was measured at a pressure of 10 bar using deionised water. NaCl was then added to the feed  
 135 solution to determine the  $B$  value. The RO system was stabilised for two hours before  
 136 recording permeate water flux with 2000 mg/L NaCl solution,  $J_w^{NaCl}$ , and taking feed and  
 137 permeate samples to determine the observed NaCl rejection,  $R_o$ . Membrane The membrane  $A$   
 138 value was calculated by dividing the pure water permeate flux ( $J_w^{RO}$ ) by the applied hydraulic  
 139 pressure,  $\Delta P$ :

$$140 \quad A = J_w^{RO} / \Delta P \quad (1)$$

141 The observed salt (NaCl) rejection,  $R_o$ , was calculated from the difference between the  
 142 bulk feed ( $c_b$ ) and permeate ( $c_p$ ) salt concentrations,  $R_o = 1 - c_p/c_b$ , and then the membrane  $B$   
 143 value was determined from:

$$144 \quad B = J_w^{NaCl} \left( \frac{1 - R_o}{R_o} \right) \exp \left( - \frac{J_w^{NaCl}}{k_f} \right) \quad (2)$$

145 where  $k_f$  is the mass transfer coefficient for the cross-flow of RO membrane cell.

146 The mass transfer coefficient ( $k_f$ ) was experimentally determined using the Sutzkover  
 147 et al. method (Sutzkover et al. 2000). Using the permeate and feed salt concentrations (and  
 148 thus, the corresponding osmotic pressures based on van't Hoff equation,  $\pi_p$  and  $\pi_b$ ,  
 149 respectively), the applied pressure ( $\Delta P$ ), the pure water flux ( $J_w^{RO}$ ), and the permeate flux  
 150 with the 2000 mg/L NaCl solution ( $J_w^{NaCl}$ ) enabled the evaluation of the salt concentration at  
 151 the membrane surface. This membrane surface concentration was used with thin-film theory  
 152 for concentration polarization to determine  $k_f$ :

$$153 \quad k_f = \frac{J_w^{NaCl}}{\ln \left[ \frac{\Delta P}{\pi_b - \pi_p} \left( 1 - \frac{J_w^{NaCl}}{J_w^{RO}} \right) \right]} \quad (3)$$

154 The membrane structural parameter,  $S$ , was evaluated in the cross-flow FO setup  
 155 (section 2.2). The water flux,  $J_w^{FO}$ , using a 0.5 M NaCl draw solution and deionised water  
 156 feed solution was measured with the membrane in FO mode (i.e., active layer facing the feed  
 157 solution). The membrane  $S$  value was determined using:

$$158 \quad S = \frac{D_s}{J_w^{FO}} \ln \left( \frac{B + A\pi_{D,b}}{B + J_w + A\pi_{F,m}} \right) \quad (4)$$



159 where  $D_s$  is the bulk solution diffusivity of the draw solute,  $\pi_{D,b}$  is the bulk osmotic pressure  
 160 of the draw solution, and  $\pi_{F,m}$  is the osmotic pressure at the membrane surface on the feed  
 161 side (zero for deionised water feed). The values of  $A$  and  $B$  in Eq. 4 were calculated using  
 162 Eqs. 1 and 2.

### 163 2.3.2 Membrane average pore radius

164 Erythritol, xylose, and glucose (Sigma-Aldrich, Saint Louis, MO) were used as the  
 165 reference organic solutes to estimate the membrane active layer effective pore size. The  
 166 solutes were individually dissolved in Milli-Q water to obtain a concentration of 40 mg/L (as  
 167 total organic carbon (TOC)). Prior to the RO filtration experiments with these reference  
 168 organic solutes, the membrane was pre-compacted at 18 bar for one hour and subsequent  
 169 experiments were conducted at 8, 10, 12, 14, and 16 bar with a cross-flow velocity of 25 cm/s.  
 170 At each pressure value, the RO filtration system was operated for one hour before taking  
 171 permeate and feed samples for analysis.

172 The membrane average pore radius was determined based on the pore hindrance  
 173 transport model previously described by Nghiem et al (2004) for nanofiltration. In this model,  
 174 the FO membrane was considered as a bundle of cylindrical capillary tubes with the same  
 175 radius. In addition, we assumed that the spherical solute particles enter the membrane pores  
 176 in random fashion. It is noteworthy that the pore hindrance model was developed for neutral  
 177 and non-adsorptive solutes. Thus, it may underestimate the rejection of charged organic  
 178 compounds and overestimate the rejection of hydrophobic organic compounds.

179 In the pore hindrance transport model, the ratio of solute radius ( $r_s$ ) to the membrane  
 180 pore radius ( $r_p$ ),  $\lambda = r_s/r_p$ , is related by the distribution coefficient  $\phi$  when only steric  
 181 interactions are considered:

$$182 \quad \phi = (1 - \lambda)^2 \quad (5)$$

183 The real rejection of the reference organic solutes ( $R_r$ ) was determined from:

$$184 \quad R_r = 1 - \frac{c_L}{c_o} = 1 - \frac{\phi K_c}{1 - \exp(-P_e)(1 - \phi K_c)} \quad (6)$$

185 where  $c_o$  and  $c_L$  are the solute concentration just outside the pore entrance and pore exit,  
 186 respectively;  $\phi$  is the distribution coefficient for hard-sphere particles when only steric  
 187 interactions are considered;  $K_c$  is the hydrodynamic hindrance coefficient for convection; and  
 188  $P_e$  is the membrane Peclet number defined as:

189 
$$Pe = \frac{K_c J_v l}{K_d D \varepsilon} \quad (7)$$

190 Here,  $K_d$  is the hydrodynamic hindrance coefficient for diffusion,  $J_v$  is the membrane  
 191 volumetric permeate flux,  $D$  is the Stokes-Einstein diffusion coefficient,  $l$  is the theoretical  
 192 pore length (i.e., active layer thickness), and  $\varepsilon$  is the effective porosity of the membrane  
 193 active later. Details on the calculations of  $Pe$ ,  $K_c$  and  $K_d$  are given elsewhere (Bungay and  
 194 Brenner 1973, Nghiem et al. 2004). The  $\phi K_c$  and  $\phi K_d$  are two hindrance factors accounting  
 195 for solute convection and diffusion, respectively. These factors are significantly dependent on  
 196  $\lambda$ , the ratio of solute radius ( $r_s$ ) to the membrane pore radius ( $r_p$ ).

197 The real rejection in Eq. 6 is linked to the observed rejection  $R_o$  using the film theory  
 198 which accounts for concentration polarization:

199 
$$\ln \frac{(1-R_r)}{R_r} = \ln \left( \frac{1-R_o}{R_o} \right) - \frac{J_v}{k_f} \quad (8)$$

200 where  $k_f$  is the mass transfer coefficient and  $J_v$  is the water permeate flux.

### 201 2.3.3 Membrane surface charge

202 The zeta potential of the membrane surface was determined using a SurPASS  
 203 electrokinetic analyser (Anton Paar GmbH, Graz, Austria). The value for each surface was  
 204 calculated from the measured streaming potential using the Fairbrother-Mastin approach  
 205 (Elimelech et al. 1994). All streaming potential measurements were conducted in a  
 206 background electrolyte solution containing 10 mM KCl. The same electrolyte solution was  
 207 used to flush the cell thoroughly prior to pH titration using either hydrochloric acid (1 M) or  
 208 potassium hydroxide (1 M). All measurements were performed at room temperature  
 209 (approximately 22 °C).

### 210 2.4. Trace organic contaminant rejection experiment

211 The TrOC stock solution was added to a background electrolyte solution (20 mM NaCl  
 212 and 1 mM NaHCO<sub>3</sub>) to obtain a feed solution concentration of 2 µg/L. Either HCl (1 M) or  
 213 NaOH (1 M) was used to adjust the initial pH value of the feed solution.

214 In FO experiments, the initial volumes of the feed and draw solutions were 4 and 1 L,  
 215 respectively. The feed and draw solutions were kept at 25 ± 0.1 °C using a temperature  
 216 controller (Neslab RTE 7). A new FO membrane sample was used for each experiment,

217 which was concluded when 1 L water had permeated through the FO membrane (i.e., 25%  
218 water recovery). The reverse solute flux of NaCl was determined using electric conductivity  
219 measurements and an NaCl calibration curve. A 500 mL aliquot of sample from the feed and  
220 draw solutions were taken at the beginning and after 1 L water had permeated through the FO  
221 membrane for solid phase extraction (SPE) using Oasis HBL SPE cartridge and subsequent  
222 liquid chromatography-mass spectrometry (LC-MS) analysis.

### 223 *2.5. Analysis of trace organic contaminants*

224 The TrOC concentrations in the feed and draw solution samples were determined by  
225 liquid chromatography – mass spectrometry (LC-MS) using an electrospray ionization  
226 interface. The analysis was conducted in selective ion monitoring mode using a Shimadzu  
227 LC-MS 2020. Further details on the TrOC analytical method can be found in a previous  
228 publication (Xie et al. 2013).

## 229 **3. Results and discussion**

### 230 *3.1. Membrane properties*

#### 231 *3.1.1 Transport parameters*

232 Transport parameters of the CTA and TFC membranes are summarized in Table 2.  
233 The CTA membrane was found to have a lower pure water permeability coefficient ( $A$  value)  
234 and a higher structural parameter ( $S$  value) than the TFC membrane. As a result, using a 0.5  
235 M NaCl draw solution and deionised water feed, the obtained average water fluxes of the  
236 CTA and TFC membranes were 5.4 and 15.1 L/m<sup>2</sup>h, respectively. Furthermore, the salt  
237 (NaCl) permeability coefficient of the CTA membrane was significantly higher than that of  
238 the TFC membrane (Table 2). Consequently, the reverse NaCl flux of the CTA membrane  
239 (82.7 mmol/m<sup>2</sup>h) was one order of magnitude higher than that for the TFC membrane (5.5  
240 mmol/m<sup>2</sup>h) under the same operating conditions.

241 **[Table 2]**

#### 242 *3.1.2 Surface charge*

243 Zeta potential measurements suggested that the surface of the TFC membrane was  
244 significantly more negatively charged than that of the CTA membrane at an experimental pH  
245 of 6.5 (Figure 1). The highly negatively charged surface of the TFC membrane can be  
246 attributed to the dissociation of free or uncross-linked carboxylic functional groups of the

247 polyamide active skin layer (Petersen 1993). On the other hand, the predominant functional  
248 group on the CTA membrane surface is hydroxyl (Mi and Elimelech 2010), which can only  
249 be deprotonated at high pH. Tiraferri and Elimelech (2012) measured the distribution of  
250 negatively charged functional groups of the CTA membrane using the toluidine blue O  
251 method and reported that the number of negatively charged functional groups was negligible.  
252 Indeed, the marginal negative charge of the CTA membrane observed in Figure 1 can be  
253 attributed to preferential adsorption of anions, such as chloride and hydroxide, onto the  
254 membrane surface (Childress and Elimelech 1996, Elimelech and O'Melia 1990).

255 **[Figure 1]**

### 256 *3.1.3 Average pore radius and active layer structure*

257 Real rejection ( $R_r$ ) of each reference organic solute was determined from observed  
258 rejection ( $R_o$ ) by accounting for concentration polarization effects using Eq. 7 and the mass  
259 transfer coefficient calculated from Eq. 3. The real rejections obtained at different permeate  
260 fluxes were used to calculate the membrane average membrane pore size based on the  
261 membrane pore hindrance transport model presented earlier (Eq. 6). The parameters  $\phi K_c$  and  
262  $P_e/J_v$ , are uniquely related to  $R_r$ . Thus, they could be determined by fitting the reference  
263 organic solute rejection data to the model (Eq. 6) using an optimization procedure (Solver,  
264 Microsoft Excel). Because the parameters  $\phi K_c$  and  $P_e/J_v$  can be expressed as a sole function  
265 of the variable  $\lambda$  (which is the ratio of solute radius ( $r_s$ ) to membrane pore radius ( $r_p$ )),  $\lambda$  can  
266 be obtained for each reference organic solute and the membrane. The membrane average pore  
267 radius was then calculated for each reference solute rejection data. The membrane active  
268 layer structure indicated by the  $l/\varepsilon$  value could also be determined from the values of  $\phi K_c$ ,  
269  $P_e/J_v$ , and the diffusion coefficient of the reference organic solute. The obtained average pore  
270 radii and the  $l/\varepsilon$  values of each membrane are shown in Table 3.

271 **[Table 3]**

272 For each membrane, the pore radii obtained from the three reference organic solutes  
273 only slightly deviate from one to another. Results reported in Table 3 show that the average  
274 pore radius of the CTA membrane is smaller than that of the TFC membrane. In general  
275 agreement with their comparative average pore size, the CTA membrane had a smaller water  
276 permeability coefficient (Table 2) and a lower reverse draw solute flux (Table 4) in  
277 comparison to the TFC membrane when  $MgSO_4$  or glucose was used as draw solute. On the  
278 other hand, the active layer structural characteristic value,  $l/\varepsilon$ , of the TFC membrane was one

279 order of magnitude higher than that of the CTA membrane (Table 3). This significant  
280 difference in the active layer structure could result in a higher hindrance to solute transport by  
281 the TFC membrane compared to the CTA membrane (Nghiem et al. 2004, Schäfer et al.  
282 2011). In addition, the TFC membrane pores are hydrated due to the existence of charged  
283 functional groups within its polyamide active layer (Raghunathan and Aluru 2006). Such  
284 adsorption of water molecules within the membrane pore (i.e., the hydration of the membrane  
285 pore) could narrow the effective membrane pore size, thereby enhancing the solute hindrance.  
286 As a result, both the active layer structure and pore hydration likely play an important role in  
287 feed solute transport through the membrane. Indeed, the TFC membrane active layer with  
288 higher solute hindrance and narrowed membrane pore exhibited better separation  
289 performance (i.e., lower  $B$  value and reverse NaCl flux) compared with the CTA membrane.  
290 This hypothesis will be further examined by comparing the rejection of TrOCs by the CTA  
291 and TFC membranes in the following section.

292 **[Table 4]**

### 293 *3.2. Rejection of trace organic contaminants*

#### 294 *3.2.1 General behaviour*

295 Observed rejections of charged and neutral TrOCs by either the CTA or TFC  
296 membranes were markedly different for FO experiments at the same permeate water flux of 6  
297 L/m<sup>2</sup>h (or 1.68 μm/s) (Figure 2). Although the chemistry and intrinsic properties of the CTA  
298 and TFC membranes are different, rejection of charged TrOCs by both membranes were  
299 generally higher than those of neutral TrOCs, which is consistent with previous studies  
300 (Alturki et al. 2013, Valladares Linares et al. 2011, Xie et al. 2012b). These charged TrOCs  
301 may be rejected by both size exclusion and electrostatic repulsion arising from their hydrated  
302 molecular dimension and the negative surface charge of the membranes. On the other hand,  
303 there was no discernible difference in the rejection of charged TrOCs by the two membranes.  
304 Further, the TFC membrane exhibited substantially higher rejection of neutral TrOCs than the  
305 CTA membrane, despite its larger membrane pore size (Table 3). This observation was  
306 consistent with our hypothesis proposed in section 3.1.3 that the hydrated membrane pore  
307 surface induced by the existence of surface charge narrowed the effective membrane pore  
308 size, thereby enhancing the steric hindrance and resulting in better separation performance.  
309 This hypothesis will be further elaborated using the membrane pore hindrance transport  
310 model for a wide range of permeate water flux values in the following section.

311 **[Figure 2]**

312 *3.2.2 Modelling the rejection of trace organic contaminants*

313 The calculated membrane pore radii (Table 3) and the molecular radius of each  
314 compound can be used to simulate the rejection of TrOCs as a function of permeate water  
315 flux based on the membrane pore hindrance transport model (see section 2.3.2). This model  
316 was found to describe very well the real rejection of TrOCs by both the CTA and TFC  
317 membranes. Overall, the real rejection of TrOCs by both membranes increased as permeate  
318 flux increased, consistent with the phenomenon observed in pressure driven NF and RO  
319 processes (Nghiem et al. 2004).

320 Real rejections of charged TrOCs were above 90% for both CTA and TFC  
321 membranes (Figure 3). For negatively charged TrOCs, electrostatic repulsion arising from the  
322 negative surface charge of the membranes played an important role in their rejection. For  
323 example, despite similar molecular weight of sulfamethoxazole and linuron, real rejection of  
324 the negatively charged sulfamethoxazole (0.90 by the CTA membrane and 0.98 by the TFC  
325 membrane) was substantially higher than the neutral linuron (0.59 by the CTA membrane and  
326 0.82 by the TFC membrane). More significantly, there was marginal difference in real  
327 rejection of negatively charged TrOCs as their molecular weight increased. In aqueous  
328 solution, the charged TrOCs are hydrated and their hydrated radii are significantly larger than  
329 their apparent ionic radii (Nghiem et al. 2006). As a result, steric hindrance also governs the  
330 separation of both negatively and positively charged TrOCs. In summary, both electrostatic  
331 repulsion and steric hindrance govern the rejection of charged TrOCs in FO, thereby resulting  
332 in their high rejection.

333 Generally, the TFC membrane exhibited higher rejection of hydrophilic neutral  
334 (caffeine and atrazine) and hydrophobic neutral (linuron and pentachlorophenol) TrOCs with  
335 low molecular weights (Figure 4). As the molecular weight increased, there was no  
336 discernible difference in the rejection of neutral hydrophilic and hydrophobic TrOCs by  
337 either the CTA or TFC membranes. This molecular-weight dependent rejection behaviour  
338 suggests that steric hindrance governs the rejection of neutral TrOCs in an FO process.  
339 However, it is noteworthy that despite its larger effective pore size compared to that of the  
340 CTA membrane, the TFC membrane exhibited higher rejection of neutral TrOCs with low  
341 molecular weight than the CTA membrane.

342 **[Figure 3]**

343

[Figure 4]

### 344 3.2.3 *Relating trace organic rejection to membrane properties*

345 Structure of the membrane active layer plays an important role in the rejection of TrOCs.  
346 Active layer structures of the CTA and TFC membranes differed significantly. The TFC  
347 membrane has a higher  $l/\epsilon$  parameter and thus exhibits higher hindrance to TrOC diffusion in  
348 comparison to the CTA membrane. The higher solute hindrance of the TFC membrane is also  
349 consistent with its lower  $B$  value, which can be described by the “solution–diffusion”  
350 mechanism in the FO process (Hancock et al. 2011a, Yong et al. 2012).

351 Pore hydration induced by membrane surface charge also attributed to the higher TrOC  
352 rejection by the TFC membrane. Pore hydration exists in both the CTA and TFC membranes,  
353 which is manifested by a layer of water molecules permanently attached to the negatively  
354 charged membrane surface via hydrogen bonding (Raghunathan and Aluru 2006). However,  
355 the degrees of pore hydration of the CTA and TFC membranes were likely different when  
356 they are operated in FO mode because of the difference in reverse NaCl permeation (Figure  
357 5). Specifically, the CTA membrane possessed less surface charge (Figure 1) and exhibited  
358 an order of magnitude higher reverse NaCl flux than the TFC membrane (Table 4). Thus,  
359 pore hydration of the CTA membrane was substantially suppressed due to the elevated ionic  
360 strength in the membrane pore (Nghiem et al. 2006). By contrast, the TFC membrane has a  
361 much lower reverse NaCl salt flux due to a more negative membrane surface charge in  
362 comparison to the CTA membrane. Thus, TFC membrane pores remain highly hydrated in  
363 FO mode, resulting in a higher TrOC rejection when compared to the CTA membrane.

364

[Figure 5]

365 Results reported here have significant implications for the fabrication of next  
366 generation FO membranes. The separation performance of FO membranes could be improved  
367 substantially by tuning both the active layer structure and surface charge. Fabricating an  
368 active layer with superior transport properties is important in achieving better TrOC  
369 rejections (Tiraferri et al. 2011), such as high  $A$  and low  $B$  values, and high  $l/\epsilon$  value.  
370 Imparting surface charge to the membrane could offer enhanced steric hindrance without  
371 compromising water diffusion. In a recent study, Flanagan and Escobar (2013) modified a  
372 neutral polybenzimidazole based membrane using different functional agents to impart  
373 negative surface charges and reported higher water flux and NaCl rejection than unmodified  
374 PBI membrane. However, the possible detrimental effects of carboxyl groups on the

375 membrane resistance to organic fouling should be considered (Mo et al. 2012), which  
376 requires optimization of charge density and type of functional groups.

#### 377 **4. Conclusions**

378 We have systematically characterised key properties of the CTA and TFC membranes  
379 and compared their rejection of 12 TrOCs as a function of permeate flux using the membrane  
380 pore hindrance transport model. The TFC membrane has a higher  $A$  value, lower  $B$  and  $S$   
381 values and higher surface charge than those of the CTA membrane. As a result, the TFC  
382 membrane exhibited a higher water flux and lower reverse NaCl flux than the CTA  
383 membrane. More importantly, the calculated membrane pore radii of the CTA and TFC  
384 membranes were 0.37 and 0.42 nm, respectively. The calculated active layer structure factor,  
385  $l/\varepsilon$ , of the CTA and TFC membranes were 0.11 and 2.12  $\mu\text{m}$ , respectively.

386 The pore hindrance transport model can be used to describe the rejection of TrOCs by  
387 the FO process. Rejection of charged TrOCs by both the CTA and TFC membranes was  
388 generally high and was governed by both electrostatic interaction and steric hindrance. In  
389 contrast, the TFC membrane exhibited higher rejection of neutral TrOCs with low molecular  
390 weight than the CTA membrane, albeit that the TFC membrane pore size was larger than that  
391 for the CTA membrane. We attribute the observed higher rejection of neutral TrOCs by the  
392 TFC membrane to a more favourable active layer structure as indicated by the larger active  
393 layer thickness to porosity ratio parameter,  $l/\varepsilon$ , and the negative membrane surface charge  
394 that induced pore hydration.

#### 395 **5. Acknowledgements**

396 The authors would like to thank Hydration Technology Innovations and Oasys Water  
397 for providing membrane samples. University of Wollongong is acknowledged for the  
398 provision of a doctoral scholarship to Ming Xie.

#### 399 **6. References**

- 400 Alturki, A.A., McDonald, J.A., Khan, S.J., Price, W.E., Nghiem, L.D. and Elimelech, M.  
401 (2013) Removal of trace organic contaminants by the forward osmosis process. *Separation*  
402 *and Purification Technology* 103, 258-266.
- 403 Basile, T., Petrella, A., Petrella, M., Boghetich, G., Petruzzelli, V., Colasuonno, S. and  
404 Petruzzelli, D. (2011) Review of Endocrine-Disrupting-Compound Removal Technologies in  
405 Water and Wastewater Treatment Plants: An EU Perspective. *Industrial & Engineering*  
406 *Chemistry Research* 50(14), 8389-8401.



407 Bungay, P.M. and Brenner, H. (1973) The motion of a closely-fitting sphere in a fluid-filled  
408 tube. *International Journal of Multiphase Flow* 1(1), 25-56.

409 Carballa, M., Omil, F., Lema, J.M., Llompart, M.a., García-Jares, C., Rodríguez, I., Gómez,  
410 M. and Ternes, T. (2004) Behavior of pharmaceuticals, cosmetics and hormones in a sewage  
411 treatment plant. *Water Research* 38(12), 2918-2926.

412 Cartinella, J.L., Cath, T.Y., Flynn, M.T., Miller, G.C., Hunter, K.W. and Childress, A.E.  
413 (2006) Removal of Natural Steroid Hormones from Wastewater Using Membrane Contactor  
414 Processes†. *Environmental Science & Technology* 40(23), 7381-7386.

415 Cath, T.Y., Adams, D. and Childress, A.E. (2005) Membrane contactor processes for  
416 wastewater reclamation in space: II. Combined direct osmosis, osmotic distillation, and  
417 membrane distillation for treatment of metabolic wastewater. *Journal of Membrane Science*  
418 257(1-2), 111-119.

419 Cath, T.Y., Childress, A.E. and Elimelech, M. (2006) Forward osmosis: Principles,  
420 applications, and recent developments. *Journal of Membrane Science* 281(1-2), 70-87.

421 Cath, T.Y., Elimelech, M., McCutcheon, J.R., McGinnis, R.L., Achilli, A., Anastasio, D.,  
422 Brady, A.R., Childress, A.E., Farr, I.V., Hancock, N.T., Lampi, J., Nghiem, L.D., Xie, M.  
423 and Yip, N.Y. (2013) Standard Methodology for Evaluating Membrane Performance in  
424 Osmotically Driven Membrane Processes. *Desalination* 312, 31-38.

425 Cath, T.Y., Hancock, N.T., Lundin, C.D., Hoppe-Jones, C. and Drewes, J.E. (2010) A multi-  
426 barrier osmotic dilution process for simultaneous desalination and purification of impaired  
427 water. *Journal of Membrane Science* 362(1-2), 417-426.

428 Childress, A.E. and Elimelech, M. (1996) Effect of solution chemistry on the surface charge  
429 of polymeric reverse osmosis and nanofiltration membranes. *Journal of Membrane Science*  
430 119(2), 253-268.

431 Elimelech, M., Chen, W.H. and Waypa, J.J. (1994) Measuring the zeta (electrokinetic)  
432 potential of reverse osmosis membranes by a streaming potential analyzer. *Desalination* 95(3),  
433 269-286.

434 Elimelech, M. and O'Melia, C.R. (1990) Effect of electrolyte type on the electrophoretic  
435 mobility of polystyrene latex colloids. *Colloids and Surfaces* 44, 165-178.

436 Elimelech, M. and Phillip, W.A. (2011) The Future of Seawater Desalination: Energy,  
437 Technology, and the Environment. *Science* 333(6043), 712-717.

438 Flanagan, M.F. and Escobar, I.C. (2013) Novel Charged and Hydrophilized  
439 Polybenzimidazole (PBI) Membranes for Forward Osmosis. *Journal of Membrane Science*  
440 434, 85-92.

441 Grant, S.B., Saphores, J.-D., Feldman, D.L., Hamilton, A.J., Fletcher, T.D., Cook, P.L.M.,  
442 Stewardson, M., Sanders, B.F., Levin, L.A., Ambrose, R.F., Deletic, A., Brown, R., Jiang,  
443 S.C., Rosso, D., Cooper, W.J. and Marusic, I. (2012) Taking the “Waste” Out of “Wastewater”  
444 for Human Water Security and Ecosystem Sustainability. *Science* 337(6095), 681-686.

445 Hancock, N.T., Phillip, W.A., Elimelech, M. and Cath, T.Y. (2011a) Bidirectional  
446 Permeation of Electrolytes in Osmotically Driven Membrane Processes. *Environmental*  
447 *Science & Technology* 45(24), 10642-10651.

448 Hancock, N.T., Xu, P., Heil, D.M., Bellona, C. and Cath, T.Y. (2011b) Comprehensive  
449 Bench- and Pilot-Scale Investigation of Trace Organic Compounds Rejection by Forward  
450 Osmosis. *Environmental Science & Technology* 45(19), 8483-8490.

451 Hoover, L.A., Phillip, W.A., Tiraferri, A., Yip, N.Y. and Elimelech, M. (2011) Forward with  
452 Osmosis: Emerging Applications for Greater Sustainability. *Environmental Science &*  
453 *Technology* 45(23), 9824-9830.

454 Martinetti, C.R., Childress, A.E. and Cath, T.Y. (2009) High recovery of concentrated RO  
455 brines using forward osmosis and membrane distillation. *Journal of Membrane Science*  
456 331(1-2), 31-39.

457 McCutcheon, J.R. and Elimelech, M. (2008) Influence of membrane support layer  
458 hydrophobicity on water flux in osmotically driven membrane processes. *Journal of*  
459 *Membrane Science* 318(1-2), 458-466.

460 McCutcheon, J.R., McGinnis, R.L. and Elimelech, M. (2005) A novel ammonia—carbon  
461 dioxide forward (direct) osmosis desalination process. *Desalination* 174(1), 1-11.

462 McGinnis, R.L. and Elimelech, M. (2007) Energy requirements of ammonia—carbon dioxide  
463 forward osmosis desalination. *Desalination* 207(1-3), 370-382.

464 McGinnis, R.L., Hancock, N.T., Nowosielski-Slepowron, M.S. and McGurgan, G.D. (2013)  
465 Pilot demonstration of the NH<sub>3</sub>/CO<sub>2</sub> forward osmosis desalination process on high salinity  
466 brines. *Desalination* 312, 67-74.

467 Mi, B. and Elimelech, M. (2010) Gypsum Scaling and Cleaning in Forward Osmosis:  
468 Measurements and Mechanisms. *Environmental Science & Technology* 44(6), 2022-2028.

469 Mo, Y., Tiraferri, A., Yip, N.Y., Adout, A., Huang, X. and Elimelech, M. (2012) Improved  
470 Antifouling Properties of Polyamide Nanofiltration Membranes by Reducing the Density of  
471 Surface Carboxyl Groups. *Environmental Science & Technology* 46(24), 13253-13261.

472 Nghiem, L.D., Schafer, A.I. and Elimelech, M. (2006) Role of electrostatic interactions in the  
473 retention of pharmaceutically active contaminants by a loose nanofiltration membrane.  
474 *Journal of Membrane Science* 286(1-2), 52-59.

475 Nghiem, L.D., Schäfer, A.I. and Elimelech, M. (2004) Removal of Natural Hormones by  
476 Nanofiltration Membranes: Measurement, Modeling, and Mechanisms. *Environmental*  
477 *Science & Technology* 38(6), 1888-1896.

478 Petersen, R.J. (1993) Composite reverse osmosis and nanofiltration membranes. *Journal of*  
479 *Membrane Science* 83(1), 81-150.

480 Raghunathan, A.V. and Aluru, N.R. (2006) Molecular Understanding of Osmosis in  
481 Semipermeable Membranes. *Physical Review Letters* 97(2), 024501.

482 Schäfer, A.I., Akanyeti, I. and Semião, A.J.C. (2011) Micropollutant sorption to membrane  
483 polymers: A review of mechanisms for estrogens. *Advances in Colloid and Interface Science*  
484 164(1-2), 100-117.

485 Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., von Gunten,  
486 U. and Wehrli, B. (2006) The Challenge of Micropollutants in Aquatic Systems. *Science*  
487 313(5790), 1072-1077.

488 Shaffer, D.L., Yip, N.Y., Gilron, J. and Elimelech, M. (2012) Seawater desalination for  
489 agriculture by integrated forward and reverse osmosis: Improved product water quality for  
490 potentially less energy. *Journal of Membrane Science* 415-416, 1-8.

491 Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Marinas, B.J. and Mayes, A.M.  
492 (2008) Science and technology for water purification in the coming decades. *Nature*  
493 452(7185), 301-310.

494 Snyder, S.A., Westerhoff, P., Yoon, Y. and Sedlak, D.L. (2003 ) Pharmaceuticals, Personal  
495 Care Products, and Endocrine Disruptors in Water: Implications for the Water Industry.  
496 *Environmental Engineering Science* 20(5), 449-469.

497 Sutzkover, I., Hasson, D. and Semiat, R. (2000) Simple technique for measuring the  
498 concentration polarization level in a reverse osmosis system. *Desalination* 131(1-3), 117-127.

499 Tiraferri, A. and Elimelech, M. (2012) Direct quantification of negatively charged functional  
500 groups on membrane surfaces. *Journal of Membrane Science* 389, 499-508.

501 Tiraferri, A., Yip, N.Y., Phillip, W.A., Schiffman, J.D. and Elimelech, M. (2011) Relating  
502 performance of thin-film composite forward osmosis membranes to support layer formation  
503 and structure. *Journal of Membrane Science* 367(1-2), 340-352.

504 Valladares Linares, R., Yangali-Quintanilla, V., Li, Z. and Amy, G. (2011) Rejection of  
505 micropollutants by clean and fouled forward osmosis membrane. *Water Research* 45(20),  
506 6737-6744.

507 Wang, R., Shi, L., Tang, C.Y., Chou, S., Qiu, C. and Fane, A.G. (2010) Characterization of  
508 novel forward osmosis hollow fiber membranes. *Journal of Membrane Science* 355(1-2),  
509 158-167.

510 Wei, J., Qiu, C., Tang, C.Y., Wang, R. and Fane, A.G. (2011) Synthesis and characterization  
511 of flat-sheet thin film composite forward osmosis membranes. *Journal of Membrane Science*  
512 372(1-2), 292-302.

513 Wilke, C.R. and Chang, P. (1955) Correlation of diffusion coefficients in dilute solutions.  
514 *AIChE Journal* 1(2), 264-270.

515 Xie, M., Nghiem, L.D., Price, W.E. and Elimelech, M. (2012a) Comparison of the removal of  
516 hydrophobic trace organic contaminants by forward osmosis and reverse osmosis. *Water*  
517 *Research* 46(8), 2683-2692.

518 Xie, M., Price, W.E. and Nghiem, L.D. (2012b) Rejection of pharmaceutically active  
519 compounds by forward osmosis: Role of solution pH and membrane orientation. *Separation*  
520 *and Purification Technology* 93, 107-114.

521 Xie, M., Price, W.E., Nghiem, L.D. and Elimelech, M. (2013) Effects of feed and draw  
522 solution temperature and transmembrane temperature difference on the rejection of trace  
523 organic contaminants by forward osmosis. *Journal of Membrane Science* 438, 57-64.

524 Yangali-Quintanilla, V., Li, Z., Valladares, R., Li, Q. and Amy, G. (2011) Indirect  
525 desalination of Red Sea water with forward osmosis and low pressure reverse osmosis for  
526 water reuse. *Desalination* 280(1-3), 160-166.

527 Yip, N.Y., Tiraferri, A., Phillip, W.A., Schiffman, J.D. and Elimelech, M. (2010) High  
528 Performance Thin-Film Composite Forward Osmosis Membrane. *Environmental Science &*  
529 *Technology* 44(10), 3812-3818.

530 Yong, J.S., Phillip, W.A. and Elimelech, M. (2012) Coupled reverse draw solute permeation  
531 and water flux in forward osmosis with neutral draw solutes. *Journal of Membrane Science*  
532 392-393, 9-17.

533 Zhao, S., Zou, L., Tang, C.Y. and Mulcahy, D. (2012) Recent developments in forward  
534 osmosis: Opportunities and challenges. *Journal of Membrane Science* 396, 1-21.