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## Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis

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1 **Comparison of the removal of hydrophobic trace organic**  
2 **contaminants by forward osmosis and reverse osmosis**

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**Water Research**

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## 16 **Abstract**

17 We compared the rejection behaviours of three hydrophobic trace organic contaminants,  
18 bisphenol A, triclosan and diclofenac, in forward osmosis (FO) and reverse osmosis (RO).  
19 Using erythritol, xylose and glucose as inert reference organic solutes and the membrane pore  
20 transport model, the mean effective pore size of a commercial cellulose-based FO membrane  
21 was estimated to be 0.74 nm. When NaCl was used as the draw solute, at the same water  
22 permeate flux of 5.4 L/m<sup>2</sup>·h (1.5 μm/s), the adsorption of all three compounds to the  
23 membrane in the FO mode was consistently lower than that in the RO mode. Rejection of  
24 bisphenol A and diclofenac were higher in the FO mode compared to that in the RO mode.  
25 Because the molecular width of triclosan was larger than the estimated mean effective  
26 membrane pore size, triclosan was completely rejected by the membrane and negligent  
27 difference between the FO and RO modes could be observed. The difference in the separation  
28 behaviour of these hydrophobic trace organics in the FO (using NaCl the draw solute) and  
29 RO modes could be explained by the phenomenon of retarded forward diffusion of solutes.  
30 The reverse salt flux of NaCl hinders the pore diffusion and subsequent adsorption of the  
31 trace organic compounds within the membrane. The retarded forward diffusion effect was not  
32 observed when MgSO<sub>4</sub> and glucose were used as the draw solutes. The reverse flux of both  
33 MgSO<sub>4</sub> and glucose was negligible and thus both adsorption and rejection of BPA in the FO  
34 mode were identical to those in the RO mode.

35 *Keywords:* Forward osmosis, reverse osmosis, bisphenol A, triclosan, diclofenac, mean  
36 effective membrane pore size, retarded forward diffusion.

37

## 38 **1. Introduction**

39 Water scarcity is a major global challenge and is being further exacerbated due to continuing  
40 population growth, industrialization, contamination of available fresh water sources, and  
41 increasingly irregular weather patterns. Utilising unconventional water resources such as  
42 reclaimed wastewater has been identified as an important avenue for augmenting water  
43 supply and alleviating water stress (Shannon et al. 2008). Extraction of clean water from  
44 unconventional sources, including seawater and municipal wastewater, is arguably feasible  
45 from both technical and economic points of view (Elimelech and Phillip 2011, Shannon et al.  
46 2008). However, the occurrence of trace organic contaminants in secondary treated effluent  
47 and sewage impacted water bodies in the range from a few nanogram per litre (ng/L) to  
48 several microgram per litre ( $\mu\text{g/L}$ ), is a major obstacle for the implementation of water reuse  
49 (Basile et al. 2011, Carballa et al. 2004, Snyder et al. 2003 ). Although the full extent of the  
50 impact of these trace organic contaminants on human health is still a subject of intense  
51 scientific debate, some of these compounds have been shown to cause serious adverse effects  
52 on a range of organisms at environmentally relevant concentrations (Cunningham et al. 2009,  
53 Hansen et al. 1998, Rodgers-Gray et al. 2000). As a result, numerous investigations have  
54 been conducted to enhance the removal capacity of current treatment processes or develop  
55 new technologies for better removal of these trace organic contaminants from domestic  
56 wastewater and other impaired water resources (Shannon et al. 2008).

57 Forward osmosis (FO) has recently re-emerged as a potential technology that can improve  
58 the energy efficiency of water purification (Cath et al. 2006). In FO, clean water is extracted  
59 from a contaminated feed under an osmotic pressure gradient generated by the draw solution.  
60 Membrane fouling in the FO process has been shown to be less severe and more reversible  
61 than that with nanofiltration (NF) and reverse osmosis (RO) processes (Lee et al. 2010, Mi  
62 and Elimelech 2010, Ng and Elimelech 2004, Tang et al. 2010, Zou et al. 2011). Even when  
63 membrane fouling does occur, it is largely reversible and can be easily controlled by a simple  
64 physical cleaning technique such as increasing the shear force (cross flow velocity) at the  
65 membrane surface (Mi and Elimelech 2010). Consequently, there have been several  
66 successful demonstrations of FO for the treatment of wastewater with high fouling propensity  
67 with no or limited pretreatment, such as landfill leachate (Herron 1997), anaerobic digester  
68 concentrate (Holloway et al. 2007), activated sludge solution (Achilli et al. 2009, Cornelissen  
69 et al. 2008), and domestic wastewater (Cath et al. 2005, Valladares Linares et al. 2011).

70 Cath et al. (2010) proposed a novel hybrid system that combined the FO and RO processes  
71 for simultaneous water reuse and seawater desalination. In this hybrid system, domestic  
72 wastewater is first treated by an FO membrane and clean water is transported into a seawater  
73 draw solution. The diluted draw solution is subsequently desalinated by RO to produce clean  
74 water. This novel approach provides a double treatment barrier particularly for trace organic  
75 contaminants with a potentially lower energy footprint compared to current practice  
76 (Elimelech and Phillip 2011, Yangali-Quintanilla et al. 2011). Another system that combines  
77 FO and RO processes is the osmotic MBR (Achilli et al. 2009, Cornelissen et al. 2011). In  
78 this process, the wastewater passes through two semipermeable membranes in the FO  
79 processes and the RO process that used to separate and recycle the draw solution, thus  
80 providing a dual barrier for trace organic contaminants. Hence, it is of paramount importance  
81 to better understand the removal of trace organic contaminants in the FO process and  
82 compare the removal behaviour to that of RO.

83 The structure of the selective barrier of FO membranes is similar to that of RO membranes.  
84 However, the filtration behaviour of FO and NF/RO may not be the same because these  
85 processes operate in two distinctive filtration modes: one is osmotically driven while the  
86 other is hydraulic pressure driven. Significant differences in membrane fouling between FO  
87 and RO modes have been noticed. Lee et al. (2010) compared the fouling behaviours in FO  
88 and RO modes, and reported that the thickness and compactness of the fouling layers during  
89 FO and RO filtration were significantly different. Mi and Elimelech (2010) reported that the  
90 fouling layer formed in the FO process was loose and could be easily removed by increasing  
91 shear force. Therefore, it hypothesized herein that the solute mass transfer characteristics in  
92 FO and RO may not be the same, thereby influencing the separation behaviours of trace  
93 organic contaminants in FO and RO.

94 In this study, we compare the separation of hydrophobic trace organic contaminants by a  
95 commercially available FO membrane in the FO and RO modes at the same permeate flux.  
96 The mean effective pore size of the membrane was estimated to facilitate the understanding  
97 of separation behaviour using reference organic solutes and the steric hindrance pore  
98 transport model. Adsorption of the hydrophobic trace organic contaminants to the membrane  
99 was quantified and related to their rejection in the FO and RO modes. Solute mass transfer in  
100 the FO and RO modes was compared and delineated to elucidate the mechanisms governing  
101 the removal of trace organic contaminants in FO and RO modes.

## 102 **2. Materials and methods**

### 103 *2.1. Forward osmosis membrane and membrane characterization*

104 An asymmetric FO membrane acquired from Hydration Technologies Innovation (HTI,  
105 Albany, OR) was used in this investigation. The FO membrane, embedded in a polyester  
106 mesh for mechanical support, has a dense, moderately hydrophilic cellulose triacetate active  
107 layer. More details on the FO membrane are provided elsewhere (Cath et al. 2006,  
108 McCutcheon and Elimelech 2008).

109 Contact angle measurement was conducted by a Rame-Hart goniometer (Model 250,  
110 Rame-Hart, Netcong, NJ) using the standard sessile drop method. Room temperature was  
111 maintained at 21-22 °C during the measurement. An FO membrane coupon was submerged  
112 into Milli-Q water and shaken overnight before drying in a desiccator for contact angle  
113 measurement. Contact angles on both sides of the membrane were measured. At least ten  
114 droplets on each membrane sample were analysed.

### 115 *2.2. Representative trace organic contaminants*

116 Bisphenol A (endocrine disrupting compound), triclosan (antibacterial and antifungal agent),  
117 and diclofenac (non-steroidal anti-inflammatory drug) were selected as representative  
118 hydrophobic trace organic contaminants. These hydrophobic compounds are ubiquitous trace  
119 organic contaminants in secondary treated effluent and non-potable recycled water. They  
120 were selected primarily because of their suitable molecular dimensions and physicochemical  
121 properties to provide variable ‘solute-membrane’ interactions and subsequent removal  
122 behaviour. Their key physicochemical properties and molecular structures are presented in  
123 Table 1. The compounds were purchased from Sigma–Aldrich (St. Louis, MO) and their  
124 reported purity is 99% or higher. The trace organic contaminants were first dissolved in pure  
125 methanol to make up stock solutions of 2 g/L. The stock solutions were stored at -18 °C and  
126 were used within one month.

127 **[Table 1]**

### 128 *2.3. Forward osmosis and reverse osmosis laboratory systems*

129 FO experiments were conducted using a closed-loop bench-scale FO membrane system  
130 (Supplementary Data, Figure S1). The membrane cell was made of acrylic plastic and had  
131 channel dimensions of 13 cm long, 9.5 cm wide, and 0.2 cm deep. The total effective  
132 membrane area was 123.5 cm<sup>2</sup>.

133 Two variable speed gear pumps (Micropump, Vancouver, WA) were used to circulate the  
134 feed and draw solutions. Flow rates of the feed and draw solutions were monitored using  
135 rotameters and kept constant at 1 L/min (corresponding to a cross flow velocity of 9 cm/s).  
136 The draw solution reservoir was placed on a digital balance (Mettler Toledo Inc., Hightstown,  
137 NJ) and weight changes were recorded by a computer to calculate the permeate water flux.  
138 The conductivity of the draw solution was continuously measured using a conductivity probe  
139 with a cell constant of 1 cm<sup>-1</sup> (Cole-Parmer, Vernon Hills, Illinois). To maintain constant  
140 draw solution concentration, a peristaltic pump was regulated by a conductivity controller to  
141 intermittently dose a small volume of a concentrated draw solution (6 M of NaCl or 4 M  
142 MgSO<sub>4</sub> depending on the draw solution type) into the draw solution reservoir (control  
143 accuracy was ± 0.1 mS/cm). The concentrated draw solution makeup reservoir was also  
144 placed on the same digital balance. This setup ensured that the transfer of liquid between the  
145 two reservoirs did not interfere with the measurement of permeate water flux and that the  
146 system could be operated at a constant osmotic pressure driving force during the experiment.  
147 Manual control of draw solution concentration was applied when neutral glucose was used as  
148 draw solute in the FO experiment. A concentrated glucose (6 M) was manually added into the  
149 draw solution reservoir every two hours to minimize the dilution of the draw solution and the  
150 decline of osmotic pressure driving force.

151 A laboratory-scale cross-flow RO system with a rectangular stainless-steel crossflow cell  
152 was used in this study (Supplementary Data, Figure S2). The cell had an effective membrane  
153 area of 40 cm<sup>2</sup> (4 cm × 10 cm) with a channel height of 0.2 cm. The unit was equipped with a  
154 Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN). The temperature of the feed  
155 solution was kept constant using a chiller/heater (Neslab RTE 7) equipped with a stainless  
156 steel heat exchanger coil, which was submerged into a stainless steel reservoir. Permeate flow  
157 was measured by a digital flow meter (Optiflow 1000, Agilent Technologies, Palo Alto, CA)  
158 connected to a PC, and the cross flow rate was monitored using a rotameter.

#### 159 *2.4. Characterisation of membrane pore size*

160 Three reference organic solutes, namely erythritol, xylose, and glucose (Sigma-Aldrich, Saint  
161 Louis, MO), were employed to estimate the mean effective pore size of the membrane. A  
162 feed solution containing 40 mg/L (as total organic carbon, TOC) of each organic solute in  
163 Milli-Q water was used. The membrane was pre-compacted at 18 bar for 1 hour in the RO  
164 system, and experiments were conducted at pressure of 8, 10, 12, 14, and 16 bar at a constant

165 crossflow velocity of 25 cm/s. After adjusting the pressure, the crossflow RO filtration  
166 system was run for 1 hour before taking permeate and feed samples for analysis.

167 We used the pore transport model that incorporates steric (size) exclusion and hindered  
168 convection and diffusion to estimate the membrane pore size from the rejection data of the  
169 reference organic solutes (López-Muñoz et al. 2009, Nghiem et al. 2004, Tsuru et al. 1995).  
170 In this model, the ratio of solute radius ( $r_s$ ) to the membrane pore radius ( $r_p$ ),  $\lambda = r_s/r_p$ , is  
171 linked by the distribution coefficient  $\phi$  when only steric interactions are considered:

$$172 \quad \phi = (1 - \lambda)^2 \quad (1)$$

173 The real rejection of the reference organic solutes ( $R_r$ ) is determined from:

$$174 \quad R_r = 1 - \frac{c_L}{c_o} = 1 - \frac{\phi K_c}{1 - \exp(-Pe)(1 - \phi K_c)} \quad (2)$$

175 where  $c_o$  and  $c_L$  are the solute concentration just outside the pore entrance and pore exit,  
176 respectively;  $Pe$  is the membrane Peclet number;  $\phi$  is the distribution coefficient for hard-  
177 sphere particles when only steric interactions are considered; and  $K_c$  is the hydrodynamic  
178 hindrance coefficient. Details on the calculation of  $Pe$  and  $K_c$  are given elsewhere (Bungay  
179 and Brenner 1973, Nghiem et al. 2004).

180 The real rejection in Equation (2) relates to the solute permeate concentration at the  
181 membrane surface, which is different from the bulk concentration due to concentration  
182 polarization. We applied film theory to account for concentration polarization, and relate the  
183 observed rejection  $R_o$  to the real rejection by:

$$184 \quad \ln \frac{(1 - R_r)}{R_r} = \ln \frac{(1 - R_o)}{R_o} - \frac{J_v}{k_f} \quad (3)$$

185 where  $k_f$  is the mass transfer coefficient, and  $J_v$  is the volumetric permeate flux.

186 The mass transfer coefficient ( $k_f$ ) was experimentally determined using the method  
187 described by Sutzkover et al. (2000). Experiments were first conducted at a crossflow  
188 velocity of 25 cm/s by measuring the pure water flux, followed by adding NaCl into the feed  
189 reservoir to make up a feed salt concentration of 2000 mg/L, and measuring the permeate  
190 water flux and permeate salt concentration. This protocol was carried out at two different  
191 applied pressures of 10 and 16 bar. Knowing the permeate and feed salt concentrations (and  
192 thus, the corresponding osmotic pressures based on van't Hoff equation,  $\pi_p$  and  $\pi_b$ ,  
193 respectively), the applied pressure ( $\Delta P$ ), the pure water flux ( $J_w$ ), and the permeate flux with



194 the 2000 mg/L NaCl solution ( $J_{salt}$ ) enables the evaluation of the salt concentration at the  
195 membrane surface. This membrane surface concentration is used in the film model for  
196 concentration polarization to determine the mass transfer coefficient (Sutzkover et al. 2000):

$$197 \quad k_f = \frac{J_{salt}}{\ln \left[ \frac{\Delta P}{\pi_b - \pi_p} \left( 1 - \frac{J_{salt}}{J_w} \right) \right]} \quad (4)$$

198 To estimate the membrane pore size, the following optimization process was applied. First,  
199 the parameters  $\phi K_c$  and  $Pe/J_v$  that are uniquely related to  $R_r$ , were determined by fitting the  
200 reference organic solute rejection data to the model (Equation 2) using an optimization  
201 procedure (Solver, Microsoft<sup>®</sup> Excel). The parameters  $\phi K_c$  and  $Pe/J_v$  are a function of solely  
202 the variable  $\lambda$  (ratio of solute radius to membrane pore radius,  $r_s/r_p$ ) and thus were used to  
203 obtain  $\lambda$  for each organic solute and the membrane. With the determined value of  $\lambda$  and the  
204 given solute radius  $r_s$ , the membrane average pore radius was readily calculated for each  
205 reference organic solute rejection data.

### 206 2.5. Trace organic contaminant rejection experiments

207 Bisphenol A, triclosan, or diclofenac were spiked into a background electrolyte solution (20  
208 mM NaCl and 1 mM NaHCO<sub>3</sub>) to obtain a feed solution concentration of 500 µg/L of one  
209 specific trace organic contaminant. Either HCl (1 M) or NaOH (1 M) was introduced into the  
210 feed tank to adjust the initial pH value of the feed solution to pH 7. Analytical grade NaCl,  
211 MgSO<sub>4</sub>, and glucose (Fisher Scientific, Pittsburgh, PA) were used to prepare the draw  
212 solutions in Milli-Q water.

213 For the FO experiments, the initial volumes of the feed and draw solutions were 4 L and 1  
214 L, respectively. The draw solutions used for the various experiments were 0.5 M NaCl, 3 M  
215 glucose, or 2.5 M MgSO<sub>4</sub>. Temperatures of the feed and draw solutions were kept constant at  
216 25±1 °C using a temperature control unit (Thermo Fisher Scientific, Waltham, MA). A new  
217 FO membrane coupon was used for each experiment. Approximately 1 mL of samples from  
218 both the feed and draw solutions were taken at specific time intervals for HPLC analysis.

219 For the RO experiments, the initial volume of the feed solution was 4 L. The temperature  
220 of the feed solution was kept constant at 25±1 °C using a chiller/heater (Neslab RTE 7). The  
221 membrane was pre-compacted at 18 bar with deionised water for one hour prior to trace  
222 organic contaminant rejection experiments. To simulate a similar flux pattern as that in the  
223 FO mode, the permeate in the RO mode was not recirculated into the feed reservoir.

224 Experiments were conducted at a constant permeate flux (corresponding to an operating  
225 pressure of 10 bar) and at a constant crossflow velocity of 25 cm/s.

226 The rejection of trace organic contaminants in the RO is defined as

$$227 \quad R_{RO} = \left(1 - \frac{C_{p(t)}}{C_{f(t)}}\right) 100\% \quad (5)$$

228 where,  $C_{p(t)}$  and  $C_{f(t)}$  are the concentration of target solute in the permeate and feed solution at  
229 time  $t$ , respectively. Unlike the RO process, the permeate concentration in the FO process is  
230 diluted by the draw solution. Hence, the actual (corrected) concentration of the target solute,  
231  $C_{s(t)}$ , can be obtained by taking into account the dilution using a mass balance:

$$232 \quad C_{s(t)} = \frac{C_{ds(t)} V_{ds(t)} - C_{ds(t-1)} V_{ds(t-1)}}{V_{w(t)}} \quad (6)$$

233 Here,  $V_{w(t)}$  is the permeate volume of water to the draw solution at time  $t$ ,  $V_{ds(t-1)}$  is the volume  
234 of draw solution at time  $(t-1)$ ,  $V_{ds(t)}$  is the volume of draw solution at time  $t$ ,  $C_{ds(t)}$  is the  
235 measured concentration of target solute in the draw solution at time  $t$ , and  $C_{ds(t-1)}$  is the  
236 measured concentration of target solute in the draw solution at time  $(t-1)$ . Subsequently, the  
237 solute rejection is calculated using the actual permeate concentration, yielding:

$$238 \quad R_{FO} = \left(1 - \frac{C_{s(t)}}{C_{f(t)}}\right) 100\% \quad (7)$$

239 where  $C_{f(t)}$  is the concentration of the target solute in the feed solution at  $t$  time.

240 The amount of trace organic contaminant adsorbed to the membrane was experimentally  
241 determined using an extraction procedure. At the completion of each FO or RO experiment,  
242 the membrane was removed from the membrane cell. Excess liquid on the membrane surface  
243 was allowed to drain off by gently tilting the membrane coupon. A predetermined size of  
244 membrane coupon (2.5 cm × 3 cm) was submerged in 10 mL of pure methanol in a sealed  
245 conical flask, which was placed on a shaker at a speed of 120 rpm at 20 °C for 12 hours.  
246 Aliquot sample of approximately 1 mL was taken at the end of the extraction procedure for  
247 HPLC analysis to quantify the amount of trace organic contaminant adsorbed onto the  
248 membrane. The amount of trace organic contaminant absorbed to the membrane was also  
249 determined by a mass balance calculation.

250 The reverse flux of draw solute in FO mode was determined using mass balance  
251 calculation:

252 
$$J_{\text{salt}} = \frac{(C_t V_t - C_0 V_0)}{At} \quad (8)$$

253 where  $C_0$  and  $C_t$  are the concentration of the draw solute in the feed at time 0 and  $t$ ,  
254 respectively;  $V_0$  and  $V_t$  are the volume of the feed at time 0 and  $t$ , respectively;  $A$  is the  
255 membrane area, and  $t$  is the operating time of the FO experiment. Draw solute concentrations  
256 of NaCl and MgSO<sub>4</sub> in the feed solution were determined using electric conductivity  
257 measurement based on the calibration curves of NaCl and MgSO<sub>4</sub>, and that of glucose was  
258 determined using TOC measurement.

## 259 2.6. Analytical methods

260 A Shimadzu TOC analyser (TOC-V<sub>CSH</sub>) was used to analyze the permeate concentration of  
261 the reference organic solutes. Concentration of glucose in the feed solution was also  
262 measured for the calculation of the reverse draw solute flux using the same TOC analyser.  
263 For trace organic contaminants rejection experiments, a Shimadzu HPLC system (Shimadzu,  
264 Kyoto, Japan) equipped with a Supelco Drug Discovery C-18 column (with diameter, length,  
265 and pore size of 4.6 mm, 150 mm, and 5 μm, respectively) and a UV–Vis detector was used  
266 to measure the concentrations of the trace organic contaminants in the feed and permeate (or  
267 draw solution) samples. A detection wavelength of 280 nm was employed. The mobile phase  
268 used for gradient elution was Milli-Q water buffered with 25 mM KH<sub>2</sub>PO<sub>4</sub> and acetonitrile,  
269 and was delivered at 1 mL/min through the column. Calibration generally yielded standard  
270 curves with coefficients of determination ( $R^2$ ) greater than 0.99 within the range of  
271 experimental concentrations used. The analysis was carried out immediately upon the  
272 conclusion of each experiment. A sample injection volume of 50 μL was used considering the  
273 salt tolerance of the C18 column. The quantification limit for all the analytes under  
274 investigation using these conditions was approximately 10 μg/L.

## 275 3. Results and discussion

### 276 3.1. Membrane pore size

277 Real rejection ( $R_r$ ) of the reference organic solutes by the membrane at different permeate  
278 fluxes (Supplementary Data, Figure S3) was obtained from observed rejection ( $R_o$ ) by  
279 accounting for concentration polarization (Equation 3). The real rejections data of the  
280 reference organic solutes were used to estimate the mean effective membrane pore size using  
281 the membrane pore transport model (Equation 2). The mean effective membrane pore radius

282 was determined to be 0.37 nm (equivalent to the mean effective membrane pore size of 0.74  
283 nm) based on the obtained  $\lambda$  and molecular radii of three reference organic solutes (Table 2).

284 The pore size of the membrane is comparable to that of a “tight” nanofiltration membrane  
285 such as the NF 90. Using the same membrane pore transport model, the average pore radius  
286 of the NF 90 was determined to be 0.34 and 0.38 nm by Nghiem et al. (2004) and López-  
287 Muñoz et al. (2009), respectively. In comparison, the membrane has a considerably smaller  
288 pore radius than “loose” NF membranes, such as the NF 270 with a pore radius of 0.42 – 0.44  
289 nm (López-Muñoz et al. 2009, Nghiem et al. 2004) and the BQ01 with a pore radius of 0.80  
290 nm (Seidel et al. 2001). Based on the pore transport model, rejection of trace organic  
291 contaminants by the HTI FO membrane is expected to be higher than that of a typical NF  
292 membrane.

293 It is noteworthy that the active layer of the HTI FO membrane is made of cellulose  
294 triacetate whereas the skin layer of most commercially available NF and RO membranes is  
295 made of polyamide or its derivatives. Therefore, the intrinsic separation property of the FO  
296 membrane may differ from that of a typical NF membrane. In fact, the HTI FO membrane  
297 has a much lower permeability and a slightly higher NaCl rejection in comparison to most NF  
298 membranes (Gray et al. 2006, Lee et al. 2010, Mi and Elimelech 2008). The measured pure  
299 water permeability and NaCl rejection of the HTI FO membrane measured in the RO mode  
300 were 1.1 L/ (m<sup>2</sup>·h·bar) and 92.8 %, respectively. In comparison, it was reported that the pure  
301 water permeability and NaCl rejection of the NF90 (which is known to be a tight NF  
302 membrane) were 6.4 L/ (m<sup>2</sup>·h·bar) and 85%, respectively (Nghiem et al. 2008).

303 The estimated mean effective membrane pore size allows for a systematic investigation of  
304 the transport behaviours of the three selected hydrophobic trace organic contaminants. It is  
305 noted that the molecular width of both bisphenol A and diclofenac (Table 1) is smaller than  
306 the membrane pore size, while that of triclosan (Table 1) is larger than the membrane pore  
307 size. In the following section, we explored the different removal behaviours of these  
308 hydrophobic compounds in the FO and RO modes.

309 **[Table 2]**

## 310 3.2. Removal behaviour of hydrophobic trace organics in FO and RO modes

### 311 3.2.1 Bisphenol A

312 Bisphenol A is a hydrophobic compound with a distribution coefficient ( $\log D$ ) value of 3.64  
313 (at experimental pH of 7) (Table 1). The measured contact angle of the HTI FO membrane in  
314 this study was  $62.8 \pm 3.9^\circ$ , which is similar to the value of  $60.2 \pm 3.4^\circ$  previously reported by  
315 McCutcheon and Elimelech (2008), indicating that the membrane is also moderately  
316 hydrophobic. Adsorption of bisphenol A to the membrane was observed in both the FO and  
317 RO modes as evident by the decrease in the feed concentration of the compound as the  
318 filtration process progressed (Figure 1). In fact, adsorption of hydrophobic trace organics to  
319 NF/RO membranes has been widely reported in the literature (Braeken et al. 2005, Schäfer et  
320 al. 2011).

321 When NaCl was used as the draw solution, there was a remarkable difference in the  
322 filtration behaviour of bisphenol A in the FO and RO modes (Figure 1). Even though the  
323 adsorption of bisphenol A to the membrane occurred in both the FO and RO modes, the  
324 adsorption process reached a quasi equilibrium state faster in the FO mode compared to the  
325 RO mode. In the FO mode, the feed concentration of bisphenol A decreased from 500 to 470  
326  $\mu\text{g/L}$  within the first 100 minutes. The small increase in the feed concentration of bisphenol  
327 A after 100 minutes of filtration can be explained by the continuous reduction in volume of  
328 the feed solution as water permeated through the membrane to the draw solution. In contrast,  
329 in the RO mode, it took almost 200 minutes for the feed concentration of bisphenol A to  
330 reach a stable value of approximately 420  $\mu\text{g/L}$ . Both mass balance calculation and extraction  
331 measurement consistently showed that the amount of bisphenol A adsorbed to the membrane  
332 in the RO mode was significantly higher than that in the FO mode (Table 3).

333 It is notable that the rejection of bisphenol A in the FO mode was higher than that in the  
334 RO mode at the same permeate water flux (Figure 1). The bisphenol A rejection in the FO  
335 mode was comparable to the value previously reported by Hancock et al (2011) who  
336 examined the rejection of bisphenol A by the same membrane using similar concentration  
337 and type of draw solution, feed solution and experimental set-up. The rejection of bisphenol  
338 A in FO mode (Figure 1) was higher than that reported by Valladares Linares et al (2011).  
339 However, it is noted that unlike our study and that by Hancock et al (2011), in the study by  
340 Valladares Linares et al (2011), the FO membrane cell was submerged in the feed solution  
341 similar to a dead-end filtration configuration.

342 Rejection value of bisphenol A in the RO mode also agreed well with the estimated pore  
343 radius of the membrane, whose pore size is larger than that of the NF270 membrane and  
344 slightly smaller than that of the NF90 membrane. The rejection obtained by the membrane in  
345 the RO mode was 75%. In comparison, bisphenol A rejection by the NF270 and NF90  
346 membrane in the RO mode was 30 and 90%, respectively (Nghiem et al. 2008).

347 The higher rejection of bisphenol A in the FO mode compared to the RO mode when  
348 operated at the same permeate water flux can be explained by the higher adsorption of this  
349 compound to the membrane in the RO mode (Table 3). It has been previously established that  
350 the adsorption of hydrophobic trace organic contaminants to the membrane can subsequently  
351 facilitate their transport by diffusion through the membrane polymeric matrix (Nghiem et al.  
352 2004). The molecular size of bisphenol A is slightly smaller than the mean effective  
353 membrane pore size (Tables 1 and 2) and diffusive transport of this compound through the  
354 membrane polymeric matrix is expected to be significant.

355 **[Figure 1]**

356 **[Table 3]**

### 357 3.2.2 *Triclosan*

358 Significant adsorption of triclosan, which has a log  $D$  value of 5.28 at pH 7 (Table 1), to the  
359 membrane was also observed. The feed concentration of triclosan decreased significantly as  
360 the filtration experiments progressed in both the FO and RO modes (Figure 2). In good  
361 agreement with the results reported above for bisphenol A, the adsorption of triclosan to the  
362 membrane reached a quasi equilibrium state faster in the FO mode than in the RO mode as  
363 seen from the triclosan feed concentration profiles. It is also notable that the amount of  
364 triclosan adsorbed to the membrane in the RO mode was significantly higher than that in the  
365 FO mode (Table 4). However, because the molecular width of triclosan (0.75 nm) was larger  
366 than the estimated mean effective pore size of the membrane (0.74 nm), a near complete  
367 rejection of this compound was observed in both the FO and RO modes (Figure 2). In a  
368 previous study, Hancock et al (2011) reported complete rejection of triclosan by the same  
369 membrane. Similarly, near complete rejection of triclosan by the NF270 membrane which is  
370 a loose NF membrane has also been reported by Nghiem and Coleman (2008).

371 **[Figure 2]**

372 **[Table 4]**

### 373 3.2.3 Diclofenac

374 Adsorption of diclofenac to the membrane (Table 5) was much smaller than bisphenol A and  
375 triclosan consistent with its low Log  $D$  value (1.77 at pH 7, Table 1). Because the feed  
376 volume continuously decreased in the FO mode, the feed concentration of diclofenac  
377 gradually increased as a function of time (Figure 3). In the RO mode, the adsorption of  
378 diclofenac to the membrane was higher than that in the FO mode (Table 5), which explains  
379 only slight increase in its feed concentration. It is also notable that diclofenac rejection was  
380 almost complete in the FO mode and was only approximately 90 % in the RO mode (Figure  
381 3). The high rejection of diclofenac in both RO and FO modes is expected given its molecular  
382 dimension. It is noteworthy that although diclofenac has a similar molecular weight  
383 compared to triclosan, the shape of this compound is cylindrical (molecular modelling). The  
384 molecular width of diclofenac is slightly smaller than the estimated mean effective pore size  
385 of the membrane (Table 1). Consequently, it was possible to observe the difference in the  
386 rejection of diclofenac between the FO and RO modes at the same permeate flux (Figure 3).

387 **[Figure 3]**

388 **[Table 5]**

### 389 3.3. Reverse draw solute permeation retards the forward transport of 390 hydrophobic organics

391 The marked difference in the separation behaviour of hydrophobic trace organics in the FO  
392 and RO modes discussed above could be attributed to their steric hindrance by the draw  
393 solute permeating through the membrane in the opposite direction. In the RO process, water  
394 permeates through the membrane under a hydraulic pressure gradient across the membrane  
395 and mass transfer can only occur in one direction from the feed side towards the permeate  
396 side of the membrane. In the FO process, water permeates from the feed solution to the draw  
397 solution under an osmotic pressure gradient generated by the concentrated draw solution  
398 across the membrane. As a result, the transport of water through the membrane in FO is  
399 coupled with the transport of the draw solute in the opposite direction (Figure 4).

400 **[Figure 4]**

401 The reverse NaCl flux in the FO experiments was significant (Table 6). We also note that  
402 the hydrated radii of Na<sup>+</sup> (0.36 nm) and Cl<sup>-</sup> (0.33 nm) (Israelachvili 2010) were comparable  
403 to that of the membrane pore radius as well as the molecular dimensions of hydrophobic

404 organic contaminants investigated in this study. Thus, the reverse salt flux could hinder the  
405 pore forward diffusion of the trace organic solute, leading to a lower adsorption of  
406 hydrophobic trace organic within the membrane and subsequently higher rejection in the FO  
407 mode than that in the RO mode.

408 **[Table 6]**

409 Our results are consistent with the “retarded forward diffusion” phenomenon suggested by  
410 Hancock and Cath (2009) who examined the coupled diffusion of solutes in osmotically  
411 driven membrane processes. They reported that the permeation of dissolved silica ( $\text{SiO}_2$ )  
412 from the feed to the draw solution was lower when  $\text{NH}_4\text{HCO}_3$  was used as the draw solute  
413 instead of  $\text{NaCl}$  or  $\text{MgCl}_2$ . Hancock and Cath (2009) explained their observation by the  
414 higher reverse flux of  $\text{NH}_4\text{HCO}_3$  compared to that of both  $\text{NaCl}$  and  $\text{MgCl}_2$  at the same  
415 osmotic pressure of the draw solution. The results reported in this study and those observed  
416 by Hancock and Cath suggest that the “retarded forward diffusion” phenomenon can be more  
417 profound for hydrophobic trace organic contaminants because of their much lower  
418 concentration in the feed solution and their ability to transport through the membrane via the  
419 sorption-diffusion mechanism.

420 When the reverse draw solute flux is negligible, one would expect that the retarded  
421 forward diffusion phenomenon would diminish. To verify this hypothesis, the adsorption and  
422 rejection of BPA were examined at the same permeate water flux as that in the RO mode (i.e.,  
423  $5.4 \text{ L/m}^2\cdot\text{h}$  ( $1.5 \mu\text{m/s}$ )) using glucose and  $\text{MgSO}_4$  as the draw solutes. Glucose has a low  
424 diffusion coefficient ( $6.9 \times 10^{-10} \text{ m}^2/\text{s}$ ) and a Stokes radius of 0.32 nm which is comparable to  
425 the membrane mean effective pore radius.  $\text{MgSO}_4$  has a considerably low diffusion  
426 coefficient ( $3.5 \times 10^{-10} \text{ m}^2/\text{s}$ ) and the hydration radii of  $\text{Mg}^{2+}$  (0.43 nm) and  $\text{SO}_4^{2-}$  (0.40 nm)  
427 (Israelachvili 2010) are larger than the membrane pore size. As a result, the reverse flux of  
428 both glucose and  $\text{MgSO}_4$  was negligible (Table 6). In the absence of substantial reverse flux  
429 of the draw solute, the pore transport and the adsorption of BPA to the membrane in both FO  
430 and RO modes were almost identical (Table 6). The rejections of BPA using glucose (77 %)   
431 and  $\text{MgSO}_4$  (76 %) as the draw solutes in the FO mode (Figure 5) were comparable to that in  
432 the RO mode (76 %).

433 **[Figure 5]**



#### 434 **4. Conclusion**

435 Rejection of three hydrophobic trace organic contaminants, namely bisphenol A, triclosan,  
436 and diclofenac, by a commercially available FO membrane was investigated in both the FO  
437 and RO modes. The separation behaviour of the trace organic compounds in the FO mode,  
438 when NaCl was used as the draw solute, differed from that in the RO mode. At the same  
439 water permeate flux of 5.4 L/m<sup>2</sup>·h (or 1.5 μm/s), adsorption of all three compounds to the  
440 membrane in the FO mode was consistently lower than that in the RO mode. In addition, the  
441 rejections of bisphenol A and diclofenac were higher in the FO mode compared to the RO  
442 mode. Because the molecular width of triclosan were larger than the estimated mean effective  
443 membrane pore size, the rejection of triclosan by the membrane was close to 100 % and  
444 negligible difference between the FO and RO modes could be observed. The difference in the  
445 separation behaviour of these hydrophobic trace organics in the FO (when NaCl was used as  
446 the draw solute) and RO modes could be explained by the retarded forward diffusion of feed  
447 solutes within the membrane pore. The relatively high reverse NaCl flux hinders the  
448 adsorption and diffusion of these trace organic compounds within the membrane pore matrix.  
449 The retarded forward diffusion phenomenon was verified by conducting experiments using  
450 draw solutions with much lower reverse salt flux, namely MgSO<sub>4</sub> and glucose. With these  
451 draw solutes, the adsorption and rejection of BPA in the FO mode were identical to that those  
452 in the RO mode.

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455 Australian government and the university postgraduate award (UPA) provided by the  
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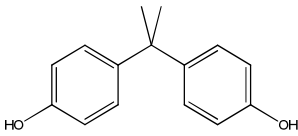
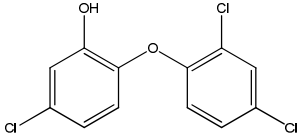
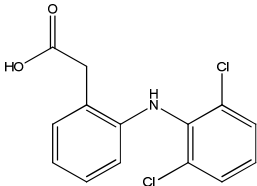
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- 569
- 570

571 **Table 1:** Key physicochemical properties of bisphenol A, triclosan, and diclofenac.

Compound	Bisphenol A	Triclosan	Diclofenac
Molecular structure			
Molecular weight (g/mol)	228.3	289.5	296.2
$pK_a$ <sup>a</sup>	10.3	7.8	4.18
Log <i>D</i> (at pH 7) <sup>a</sup>	3.64	5.28	1.77
Log $K_{ow}$ <sup>a</sup>	3.64	5.34	4.55
Molecular dimension (nm) <sup>b</sup>	Height	0.383	0.693
	Length	1.068	1.419
	Width	0.587	0.748

572 <sup>a</sup> Source: SciFinder Scholar, data calculated using Advanced Chemistry Development (ACD/Labs)  
 573 Software V8.14 for Scholaris (1994-2007 ACD/Labs)

574 <sup>b</sup> Calculated using Molecular Modelling Pro Version 6.25 (ChemWS)

575 **Table 2:** Estimated mean effective membrane pore radius obtained from reference organic  
 576 solute experiments

Organic solute	Stokes radius <sup>a</sup> $r_s$ (nm)	$\lambda=r_s/r_p$	Mean effective membrane pore radius $r_p$ (nm)
Erythritol	0.26	0.79	0.33
Xylose	0.29	0.76	0.38
Glucose	0.32	0.80	0.40
Average			0.37

<sup>a</sup> Calculated using the Stokes-Einstein equation

577 **Table 3:** BPA mass adsorption in FO and RO modes (permeate water flux = 5.4 L/m<sup>2</sup>·h (1.5  
 578  $\mu\text{m/s}$ )).

Operating mode	Normalised by membrane area ( $\mu\text{g/cm}^2$ )	
	Mass balance calculation	Direct extraction measurement
FO	1.25	1.41
RO	2.07	2.24

579

580 **Table 4:** Triclosan mass adsorption in FO and RO modes (permeate water flux = 5.4 L/m<sup>2</sup>·h  
 581 (1.5  $\mu\text{m/s}$ )).

Operating mode	Normalised by membrane area ( $\mu\text{g/cm}^2$ )	
	Mass balance calculation	Direct extraction measurement
FO	4.64	4.42
RO	9.18	8.81

582

583

584 **Table 5:** Diclofenac mass adsorption in FO and RO modes (permeate water flux = 5.4 L/m<sup>2</sup>·h  
 585 (1.5 μm/s)).

Operating mode	Normalised by membrane area (μg/cm <sup>2</sup> )	
	Mass balance calculation	Direct extraction measurement
FO	0.196	0.173
RO	0.764	0.422

586 **Table 6:** BPA mass balance in FO (NaCl, MgSO<sub>4</sub>, and glucose draw solutions) and RO  
 587 modes (permeate water flux = 5.4 L/m<sup>2</sup>·h (1.5 μm/s)).

Operating mode	Draw solution	Reverse solute flux (g/m <sup>2</sup> ·h)	Normalised by membrane area (μg/cm <sup>2</sup> )	
			Mass balance calculation	Direct extraction measurement
FO	NaCl	4.28	1.25	1.41
	MgSO <sub>4</sub>	0.06	1.98	2.01
	Glucose	0.28	1.82	1.89
RO	Not applicable	0	2.07	2.24

588

589 LIST OF FIGURES

590 **Figure 1:** BPA concentration in feed and permeate and rejection as a function of time in the  
591 (a) FO mode and (b) RO mode at the same permeate water flux of  $5.4 \text{ L/m}^2 \cdot \text{h}$  ( $1.5 \text{ } \mu\text{m/s}$ ). The  
592 FO experimental conditions were as follows: the initial concentrations of BPA in the feed =  
593  $500 \text{ } \mu\text{g/L}$ ,  $\text{pH} = 7$ , the background electrolyte contained  $20 \text{ mM NaCl}$  and  $1 \text{ mM NaHCO}_3$ ,  
594 draw solution =  $0.5 \text{ M NaCl}$ , cross flow rate =  $1 \text{ L/min}$  for both sides, and cross flow velocity  
595 =  $9 \text{ cm/s}$ . The temperature =  $25 \pm 1 \text{ } ^\circ\text{C}$  for both sides. The error bars represent standard  
596 deviation of data obtained from two independent experiments. The RO experimental  
597 conditions were as follows: the initial concentrations of BPA in the feed =  $500 \text{ } \mu\text{g/L}$ ,  $\text{pH} = 7$ ,  
598 the background electrolyte contained  $20 \text{ mM NaCl}$  and  $1 \text{ mM NaHCO}_3$ . Operating pressure  
599  $10 \text{ bar}$ , cross flow rate =  $1 \text{ L/min}$ , cross flow velocity =  $25 \text{ cm/s}$ , temperature =  $25 \pm 1 \text{ } ^\circ\text{C}$ .

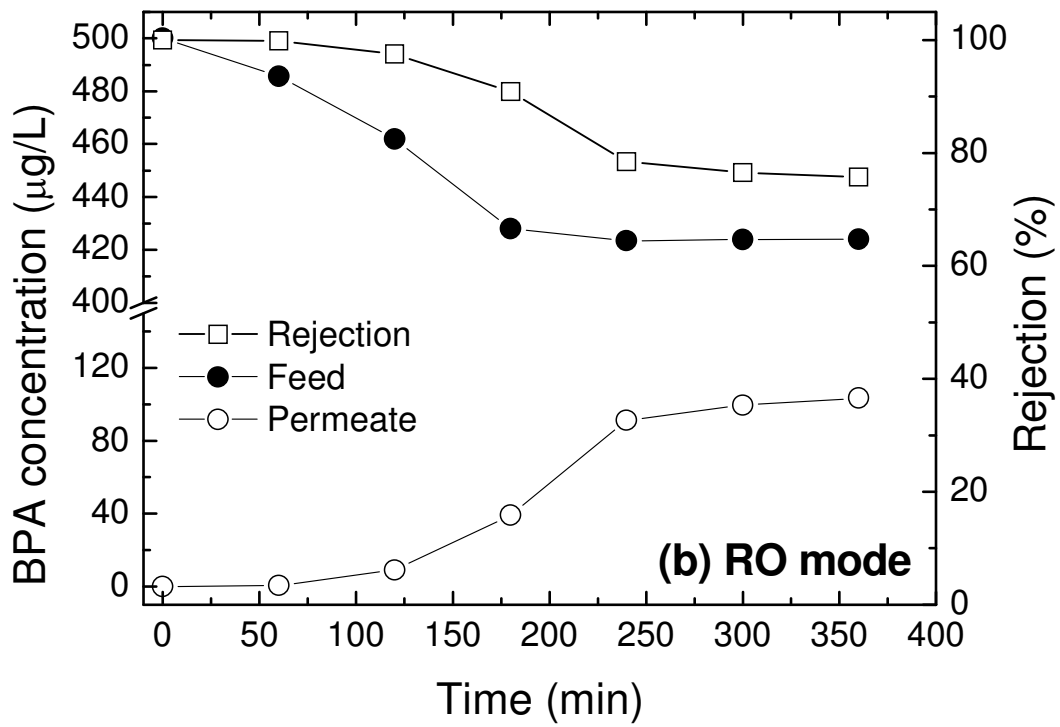
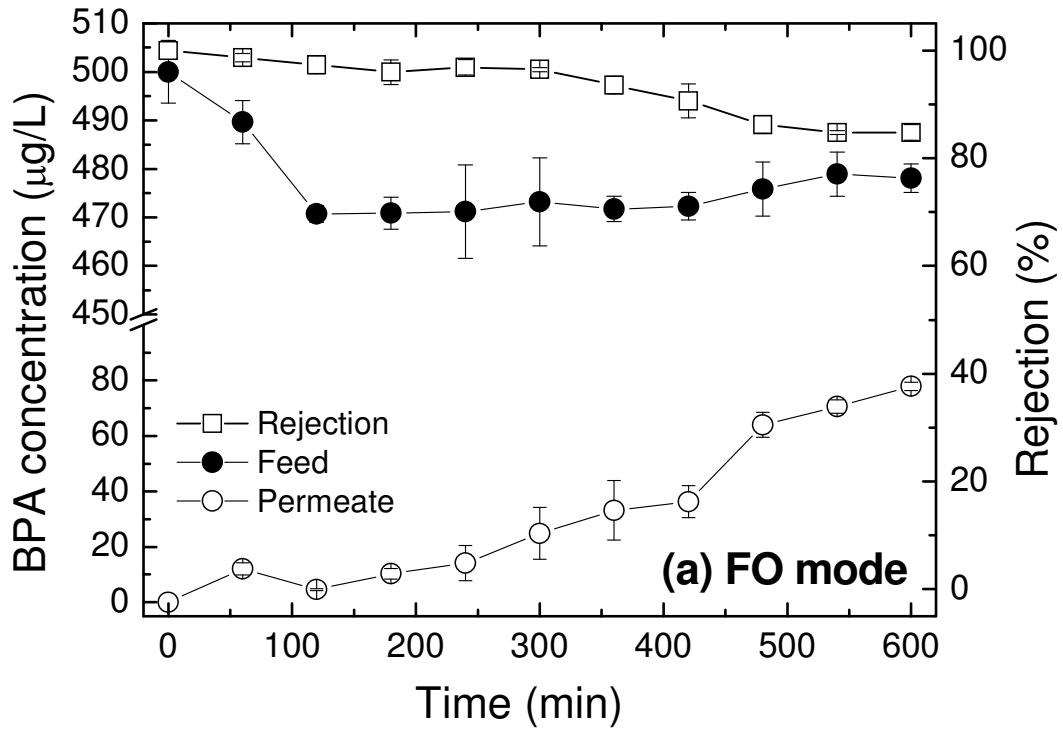
600 **Figure 2:** Triclosan concentration in feed and permeate and rejection as a function of time in  
601 (a) FO mode and (b) RO mode. The initial concentration of triclosan in the feed =  $500 \text{ } \mu\text{g/L}$   
602 both in the FO and RO experiments. Other experimental conditions were described in Figure  
603 1.

604 **Figure 3:** Diclofenac concentration in feed and permeate and rejection as a function of time  
605 in (a) FO mode and (b) RO mode. The initial concentration of diclofenac in the feed =  $500$   
606  $\mu\text{g/L}$  both in the FO and RO experiments. Other experimental conditions were described in  
607 Figure 1.

608 **Figure 4:** Schematic diagram representing the retarded forward diffusion of feed solutes in  
609 the FO process by the reverse draw solutes.

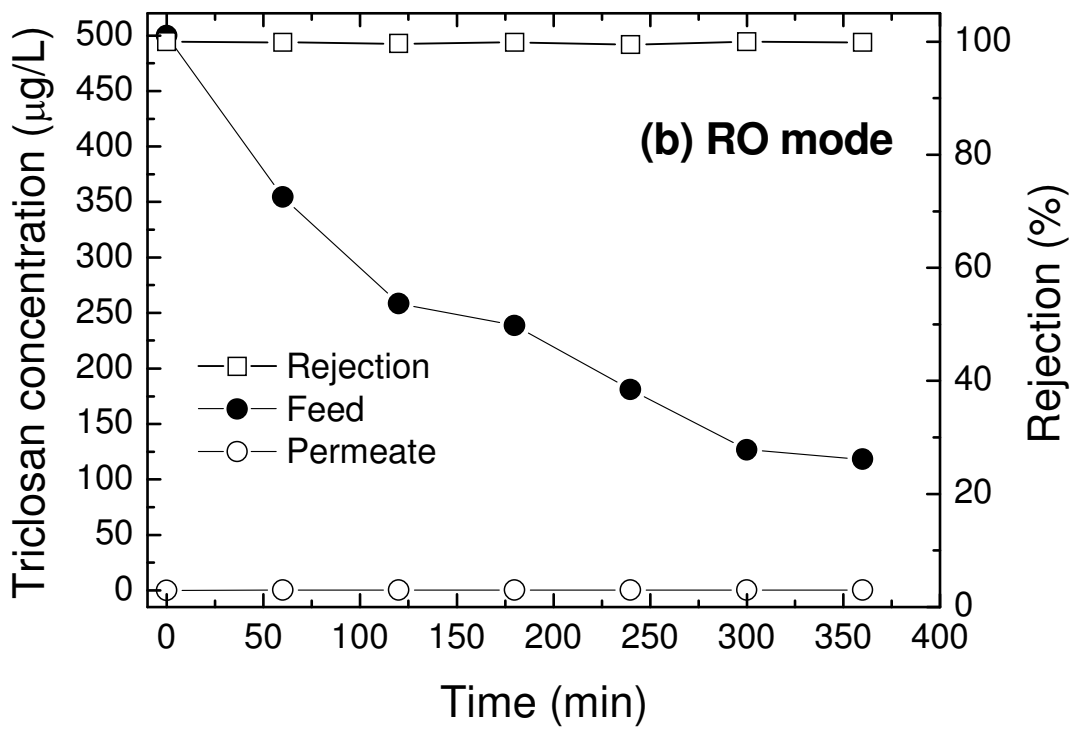
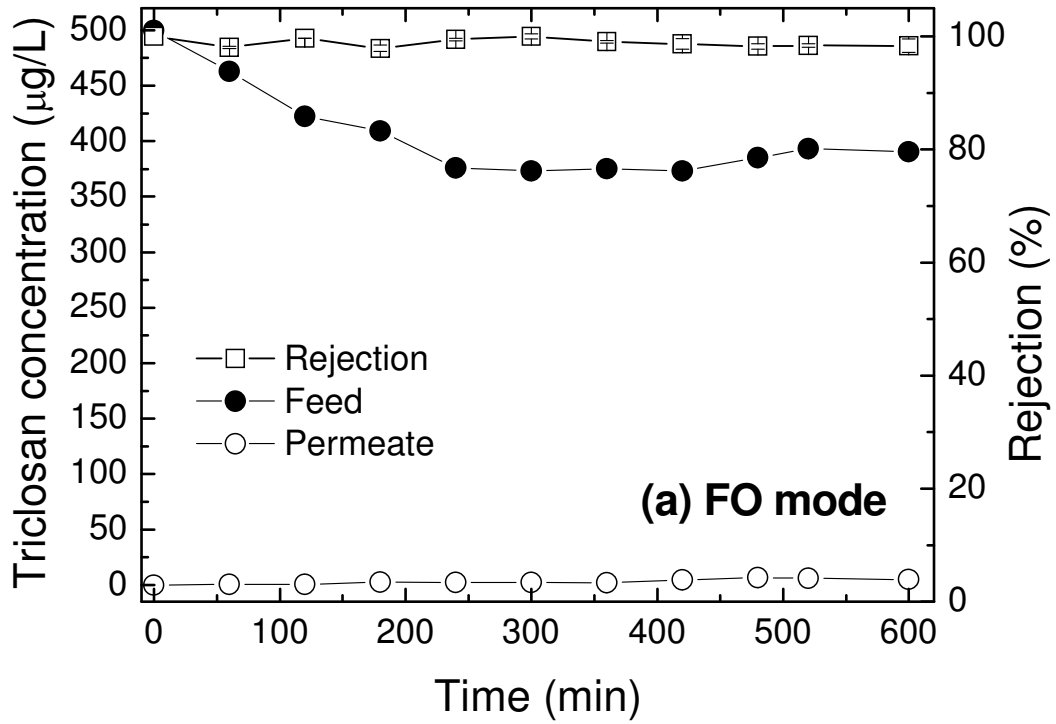
610 **Figure 5:** BPA concentration in feed and permeate and rejection as a function of time in the  
611 FO mode using approximately (a)  $3 \text{ M glucose}$  and (b)  $2.5 \text{ M MgSO}_4$  as draw solution. The  
612 permeate water flux was  $5.4 \text{ L/m}^2 \cdot \text{h}$  ( $1.5 \text{ } \mu\text{m/s}$ ). Other FO experimental conditions were as  
613 described in Figure 1.





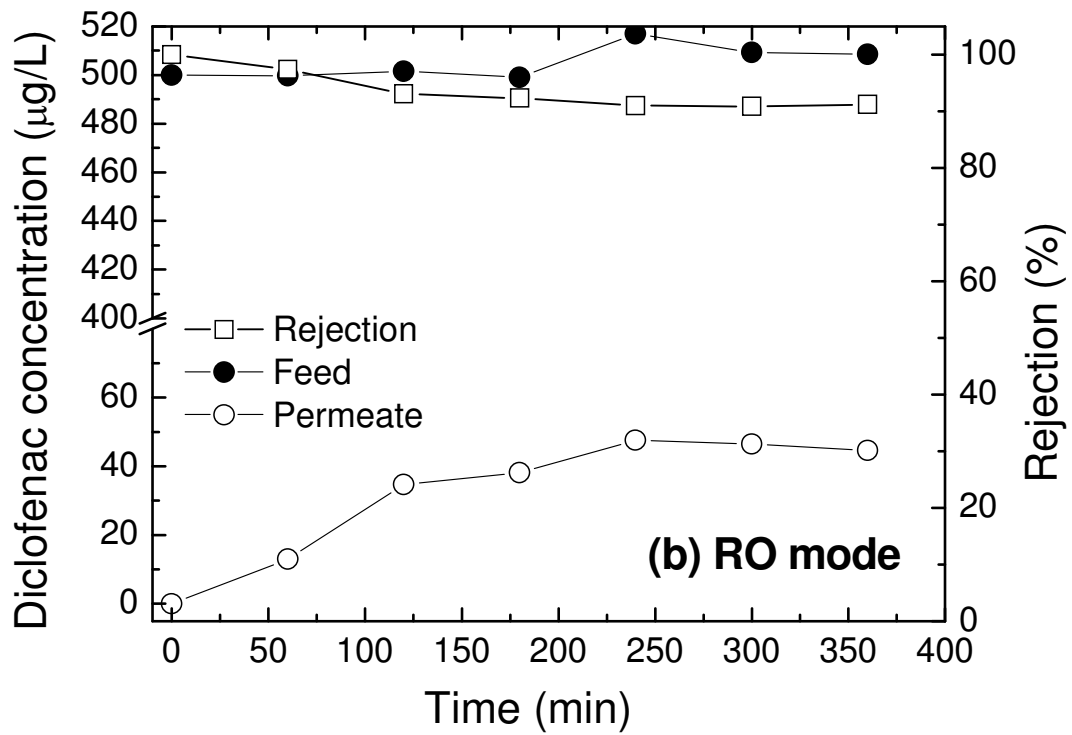
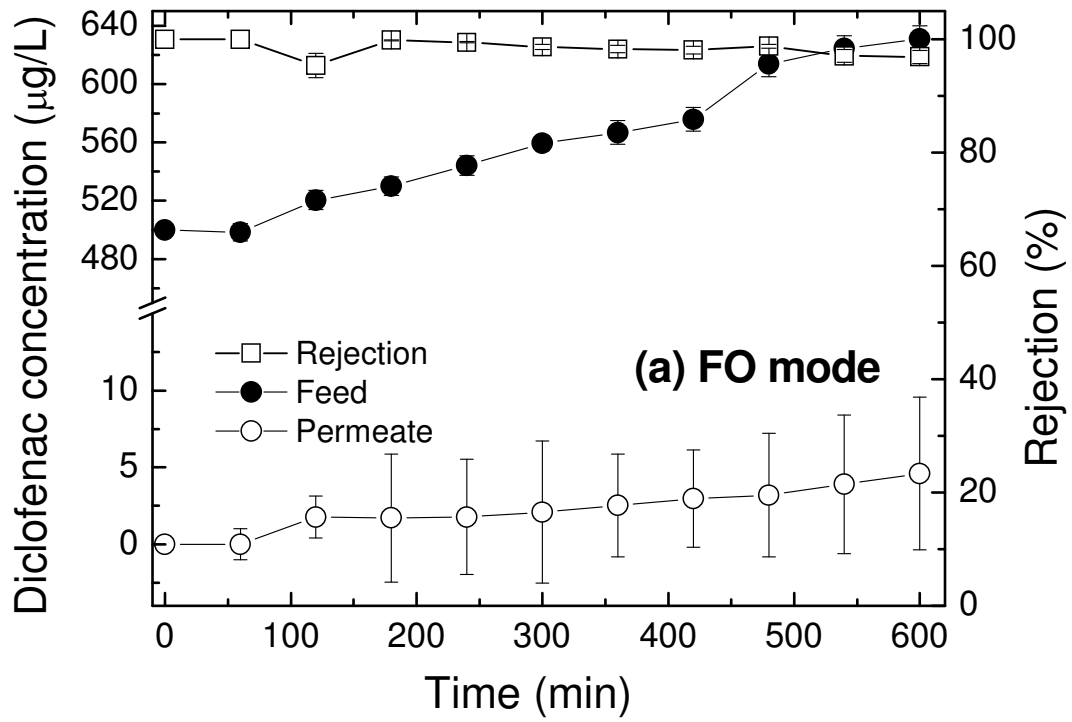
614

615 **Figure 1**



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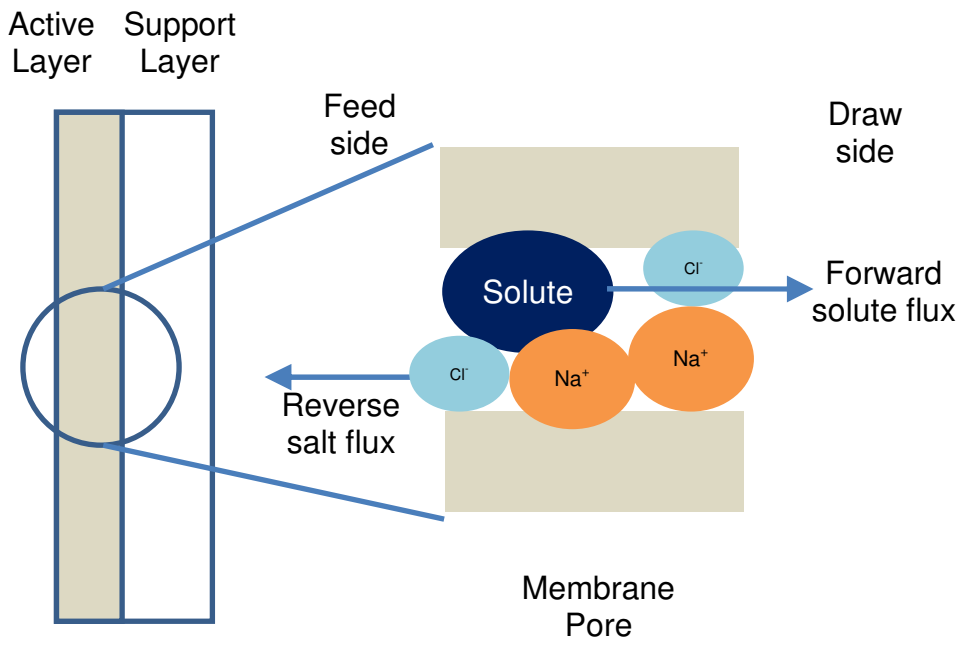
617 **Figure 2**



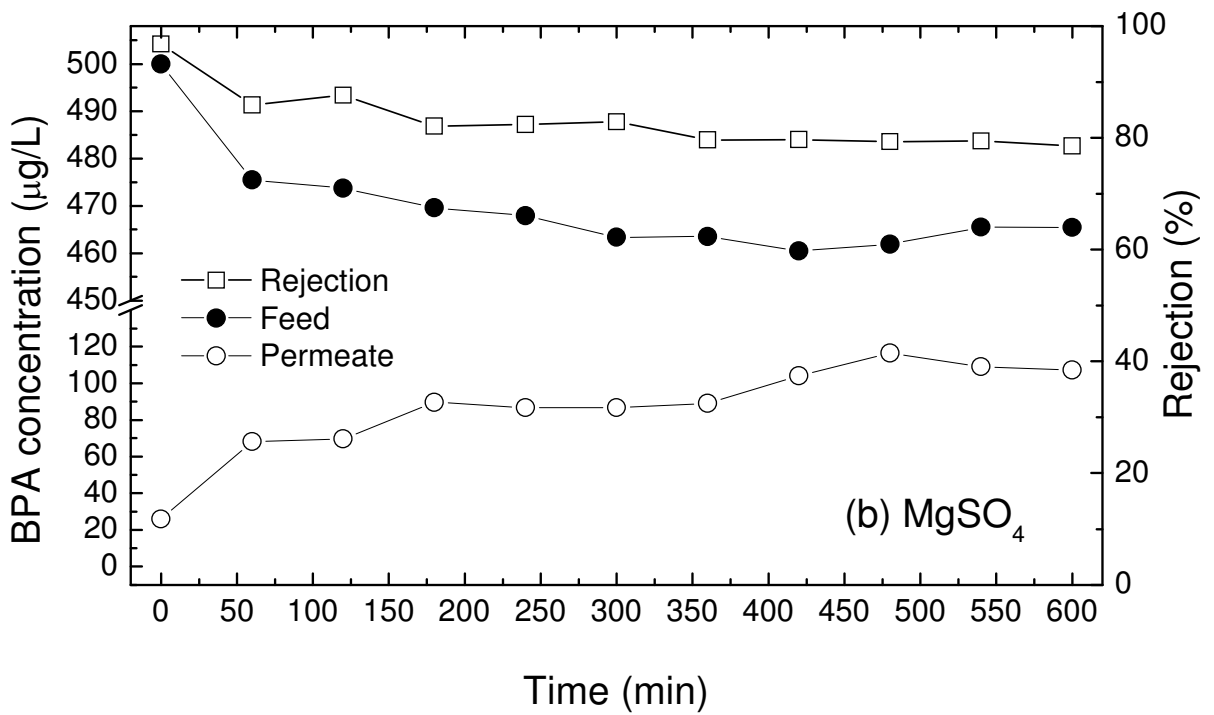
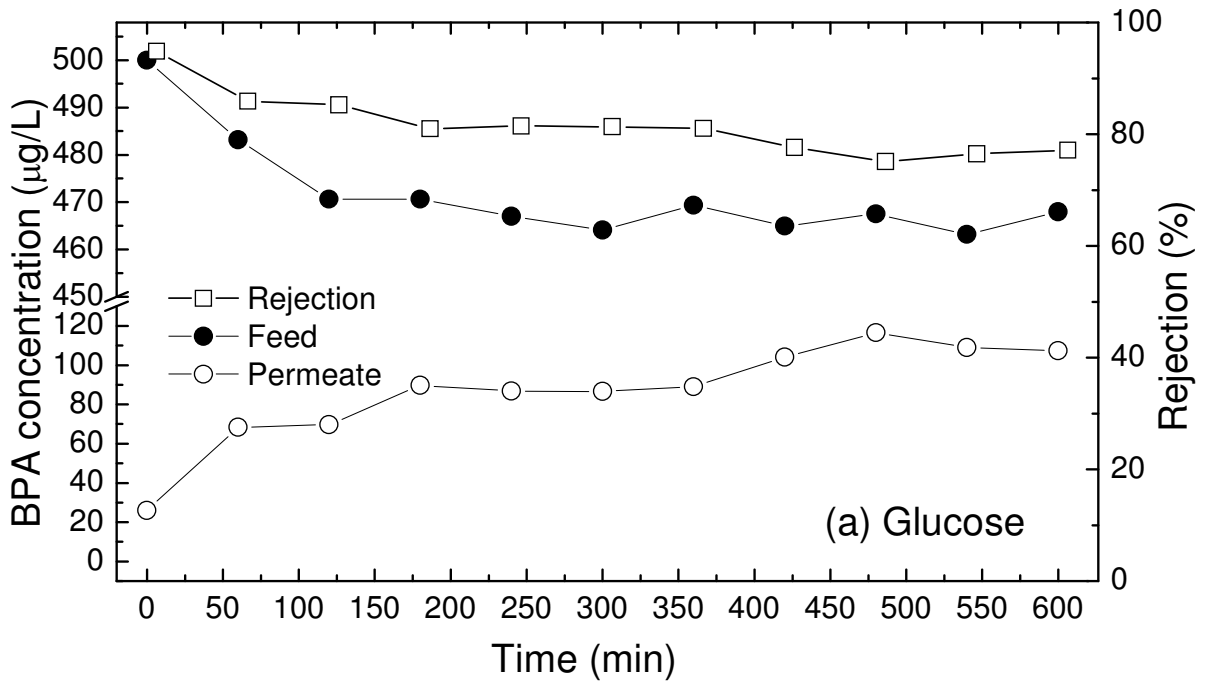
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619 **Figure 3**

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638 **Figure 4**



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640 **Figure 5**