

1 **Enhancing ammonium rejection in forward osmosis**
2 **for wastewater treatment by minimizing cation**
3 **exchange**

4 Khaled Almoalimi, Yong-Qiang Liu*

5 Faculty of Engineering and Physical sciences , University of Southampton, Southampton SO17 1BJ,
6 United Kingdom

7 *Corresponding author: Yong-Qiang Liu (Tel. +44 02380592843)

8 *E-mail address:* Y.Liu@soton.ac.uk

9 ABSTRACT

10 Ammonium permeation to draw solution (DS) is very common in forward osmosis (FO)
11 treatment due to the negative charge nature of the membrane, which restricts the application
12 of FO for wastewater treatment particularly with a purpose of ammonium recovery and water
13 reuse. Membrane modification by reducing the negative charge of membrane surface could
14 improve ammonium rejection. This study investigated ammonium rejection in the FO process
15 by selecting DSs with different physicochemical properties. Results show an increased
16 ammonium rejection rate with divalent cation-based DS (i.e. Mg^{2+}) due to larger hydrated
17 cation radius compared with monovalent cations such as Na^+ under the same osmotic
18 pressure. Non-ionic DSs such as glucose, glycine and ethanol are able to minimize ion
19 exchange across the membrane, leading to a 98.5-100% ammonium rejection. This indicates
20 that cation exchange is the critical factor for ammonium permeation. Real wastewater
21 treatment such as municipal wastewater and sludge digestate liquor by FO with NaCl and
22 glucose as DS, respectively, further confirms that minimizing cation exchange by selecting
23 appropriate DS could significantly improve ammonium rejection, which is not negatively
24 affected by the more complex nature of real wastewater. This study developed an alternative
25 method by selecting appropriate DS to increase ammonium rejection. Furthermore, it shed
26 light on the mechanism of enhanced ammonium rejection with different types of DSs, which
27 could provide general guidance on the selection of DS from the perspective of wastewater
28 treatment with ammonium considered.

29 Keywords: Forward osmosis; Ammonium rejection; Draw solution; Thin-film composite;
30 Municipal wastewater; Nutrient recovery

31 1. Introduction

32 With the more stringent environmental consents are being imposed to minimize eutrophication,
33 nutrients such as ammonium and phosphate in municipal wastewater need to be removed
34 from treatment [1, 2]. Meanwhile, ammonium and phosphorus in wastewater are important
35 resources that could be recovered as fertilizers. Thus, combining wastewater treatment with
36 nutrient recovery from wastewater has gained growing interest [3, 4]. Among different
37 technologies, the emerging forward osmosis (FO) technology appears promising due to the
38 high rejection rates of pollutants, simple process, potential of lower energy consumption, lower
39 membrane fouling propensity and possibilities for the direct recovery of nutrients from
40 wastewater by concentrating [5, 6].

41 In FO process, draw solution (DS) is believed to be the most critical because it affects water
42 flux, rejection of pollutants and the cost of DS including regeneration when necessary [7, 8].
43 An ideal DS should be able to generate higher water flux, lower reverse solute flux (RSF),
44 meanwhile, be easy to regenerate and preferred to have a low molecular weight and viscosity
45 to reduce the effect of concentration polarization (CP) [9, 10]. These requirements are usually
46 contradictory, and a compromise has to be made. This is one of the reasons that DS is being
47 studied intensively. However, there is little research on DS regarding the rejection of
48 ammonium, a major pollutant in wastewater.

49 It has been widely reported that ammonium in feed solution (FS) could easily permeate into
50 DS due to the nature of negative charge of FO membrane, positive charge of ammonium and
51 similar size with water [3, 11]. The permeation of ammonium from FS into DS could cause DS
52 contamination and the accumulation of ammonium in DS during the regeneration process [12].
53 In addition, the permeated and accumulated ammonium in DS could further escape into the
54 water when water recovery from DS is conducted [8, 13]. Thirdly, the escape of ammonium
55 from FS also results in less recovery efficiency when nutrient recovery from wastewater is

56 targeted. Thus, how to improve ammonium rejection in FO process for wastewater treatment
57 and resource recovery is very important.

58 So far, two types of FO membranes, i.e. cellulose triacetate (CTA) and thin-film composite
59 (TFC) membrane, have been developed. TFC, as the second generation of FO membrane,
60 becomes preferable to CTA due to higher water flux, lower RSF and lower biodegradable
61 tendency [14]. Although TFC FO membranes can achieve a more than 95% phosphate
62 rejection rate for different types of wastewaters such as municipal and industrial wastewaters
63 and sludge digestate [5, 12, 15–17], it shows a very poor ammonium rejection [13, 18]. In most
64 cases, ammonium in FS was even diluted with a lower concentration than the initial
65 concentration in FS. For example, for municipal wastewater treatment, a negative ammonium
66 concentration factor of -3 was reported by [17] with 0.6 M NaCl as DS and of -2.4 with seawater
67 as DS [3]. From the perspective of municipal wastewater treatment, this is unacceptable.

68 To tackle this critical issue, some researchers modified membrane surface by using poly
69 (ethylene glycol) diglycidyl ether or dicyclohexylcarbodiimide to create a positively charged
70 membrane surface to increase ammonium rejection [1, 19, 20]. Ammonium rejection rates of
71 99% for a synthetic solution with 50 mg/L NH_4^+ and of 89.3% for a return activated sludge
72 (RAS) were obtained after membrane surface modification [1]. When the membrane surface
73 was modified to be positively charged, however, the rejection of anions such as phosphate
74 and sulphate could be reduced. Akbari et al. [19] reported that a positively charged FO
75 membrane resulted in only 25% sulfate rejection. Phosphate rejection has not yet been
76 reported for the modified FO membranes [1, 19, 21], but creating a positively charged
77 membrane could negatively affect phosphate rejection. Levchenko and Freger [22] reported
78 that PO_4^{3-} rejection for the negatively charged nanofiltration (i.e. NF270) membrane was 95%,
79 while PO_4^{3-} rejection decreased significantly to 40% with a positively charged NF (p-NF)
80 membrane for the treatment of secondary wastewater. Thus, it is reasonable to speculate that
81 modifying the FO membrane surface to create a positively charged membrane might

82 negatively affect the rejection of phosphate or other small anions, which would increase the
83 contamination of DS and jeopardize the nutrient recovery efficiency from wastewater. Another
84 possible solution to increase ammonium rejection is to adjust the pH of FS to a lower value
85 such as 3.0. It was found by Engelhardt et al. [23] that ammonium rejection was increased
86 from around 52% at pH of 6 to more than 90% at pH 3 (with initial ammonium concentration
87 of 1 g/L as FS, and 0.5 M NaCl as DS for 80% water recovery rate). The pH effect could be
88 explained by the change in the membrane surface charge from more negative to less negative
89 due to more protonated carboxylic groups (COOH) at pH of 3 than deprotonated carboxylate
90 groups (COO⁻) at pH of 6. Thus, at lower pH, the forward ammonium flux and the RSF of Na⁺
91 were reduced, leading to the increase in ammonium rejection rate. We can see that adjusting
92 pH to increase ammonium rejection is essentially to change membrane surface charge as well.
93 Since wastewater is usually bulk and highly diluted, adjusting bulk solution pH is impractical.
94 Alternatively, an after-thought solution was proposed to overcome the DS contaminating
95 problem by removing permeated ammonium by microorganisms. For example, Rood et al. [13]
96 proposed to introduce an algal strain in the synthetic seawater DS to take up ammonium.
97 However, the proposed algal FO system was not very effective with only 35.4% ammonium
98 removal in total. In addition, introducing algae in DS could lead to potential membrane fouling
99 problems by forming biofilm on the membrane surface. Therefore, a cost-effective, efficient,
100 and easy-to-implement solution is badly desired for ammonium rejection without causing other
101 negative effects. It has been reported that different DSs could have different rejection rates for
102 a same type of contaminant [24, 25]. Hu et al. [26] investigated the impact of ionic DSs such
103 as NaCl and MgCl₂ on ammonium rejection by using the TFC FO membrane for treating
104 municipal wastewater. NH₄⁺-N concentration in the FS decreased during the FO process, i.e.,
105 not effectively rejected, with NaCl as DS while ammonium rejection rate reached between 58-
106 87% with MgCl₂ as DS. It was explained in the study that the higher diffusion coefficient of
107 NaCl than MgCl₂ resulted in a higher reverse Na⁺ than Mg²⁺ flux to FS, and thus caused more
108 forward ammonium permeation from the FS to the DS to maintain electroneutrality. Since this

109 study only investigated NaCl and MgCl₂ as DS, it is hard to draw a solid conclusion that
110 diffusion coefficient of DS plays a critical role for ammonium rejection. An investigation on
111 more different types of DSs is needed for the validation. Furthermore, multiple
112 physicochemical properties are changed when DS is different. Thus, it would be very beneficial
113 if the critical physicochemical properties of DS affecting ammonium rejection could be
114 identified. If so, a rule could be found to guide the selection of DS for ammonium rejection
115 without compromising the rejection of anions. In addition, we still do not know if other factors
116 such as wastewater quality and ammonium concentration in wastewater affect ammonium
117 rejection.

118 Thus, the objective of this study was to evaluate what properties of DS could be used to
119 enhance ammonium rejection with TFC FO membrane for wastewater treatment. The
120 investigated DSs included ionic DSs such as NaCl, MgCl₂, MgSO₄, Na₂SO₄ and non-ionic DSs
121 such as glucose, glycine and ethanol. The effects of FS chemistry on ammonium rejection
122 were also investigated by using synthetic wastewater, real municipal wastewater and sludge
123 digestate.

124 **2. Materials and methods**

125 **2.1 Forward osmosis membrane and experimental setup**

126 Hollow fibre TFC membranes developed by the Singapore Membrane Technology Centre with
127 an effective membrane area of 90 cm² were used in this study. Each hollow fibre membrane
128 module contains 15 fibres with the inner and outer diameters of the hollow fibre as 870 and
129 1180 µm, respectively. According to the method reported by Kim et al. [27] and Cath et al. [28],
130 the pure water permeability, the solute permeability, and the structural parameter of the FO
131 membranes used in this study were measured as 1.65 L/m²·hr·bar, 0.16 L/m²·hr, and 242 µm,
132 respectively.

133 A lab-scale cross-flow FO membrane system was run with the orientation of active layer facing
134 FS. Counter-current recirculation of the FS and DS was applied on each side of the FO
135 membrane via two peristaltic pumps with a cross-flow velocity of 13.4 cm/s. The FS tank was
136 placed on a digital balance (Kern, Germany), and the water flux was calculated based on the
137 recorded weight changes during the experiment periods. Before each experiment, DI water
138 was recirculated on both sides of the FO membrane for at least 30 min. After each experiment,
139 the FO membrane module was flushed with DI water for more than 10 min at a normal flow
140 rate. Furthermore, the hollow fibre modules were stored in fresh DI water at 5 °C and the DI
141 water was replaced at least once a week to avoid microorganism growth when membrane
142 modules were not in use.

143 **2.2 Feed solution and draw solution**

144 Two different types of synthetic wastewater were used in this study. To investigate the effects
145 of DS type in FS on ammonium rejection, synthetic water containing only ammonium with a
146 concentration of 34.30 ± 0.61 mg/L ammonium-N (with $(\text{NH}_4)_2\text{SO}_4$ for N) was used. To
147 investigate ammonium rejection with the presence of other main pollutants in municipal
148 wastewater, a synthetic municipal wastewater was prepared to simulate municipal wastewater
149 that was reported by Metcalf and Eddy [29] with 497 mg/L COD (with NaAc. $3\text{H}_2\text{O}$ as COD),
150 9 mg/L $\text{PO}_4^{3-}\text{-P}$ (with KH_2PO_4 for P), 38 mg/L ammonium-N (with $(\text{NH}_4)_2\text{SO}_4$ for N), 9mg/L Ca^{2+} ,
151 8 mg/L Mg^{2+} , 9 mg/L K^+ .

152 Two different $\text{NH}_4^+\text{-N}$ concentrations, i.e., 18 and 1294 mg/L, respectively, in synthetic
153 wastewater were used to simulate $\text{NH}_4^+\text{-N}$ concentration in municipal wastewater and sludge
154 digestate for the study of effects of initial ammonium concentration in FS on ammonium
155 rejection in the TFC FO process.

156 In addition, real municipal wastewater and sludge digestate were tested with 0.6 M NaCl and
157 1.2 M glucose as DSs, respectively, under the same osmotic pressure of 29 bar. Both

158 municipal wastewater after the treatment by primary settlement tank and sludge digestate from
159 anaerobic digester were collected from the Millbrook Municipal Wastewater Treatment plant,
160 Southampton, UK. To avoid the FO hollow fibre membrane clogging from suspended solids
161 [30], both real municipal wastewater and sludge digestate were pre-treated [31] by
162 centrifugation and filtration to minimize suspended solid concentration. Specifically, the
163 municipal wastewater was centrifuged (Sorvall Legend T, Sorvall) for 10 min at 4100 g/min,
164 followed by filtration with 1.2 μm filter (Whatman, UK) and finally with 0.45 μm filter (Whatman,
165 UK). The same procedure was used to filter the sludge digestate with the addition of chemical
166 coagulant such as aluminium chloride prior to the filtration. The filtered municipal wastewater
167 contained 119.96 ± 3.39 mg/L COD, 2.26 ± 0.12 mg/L $\text{PO}_4^{3-}\text{-P}$, 16.74 ± 0.16 mg/L $\text{NH}_4^+\text{-N}$,
168 63.83 ± 0.49 mg/L Ca^{2+} , 13.07 ± 0.27 mg/L Mg^{2+} and 17.16 ± 1.41 mg/L K^+ mg/L, while the
169 filtered sludge digestate consisted of 959.70 ± 33.93 mg/L COD, 1 ± 0.02 mg/L $\text{PO}_4^{3-}\text{-P}$,
170 1255.13 ± 87.56 mg/L $\text{NH}_4^+\text{-N}$, 21.02 ± 0.32 mg/L Ca^{2+} , 18.96 ± 0.82 mg/L Mg^{2+} , and $93.38 \pm$
171 2.36 mg/L K^+ mg/L.

172 Four different types of inorganic salts such as NaCl, MgCl_2 , MgSO_4 and Na_2SO_4 were used as
173 DSs due to their different diffusion coefficient, molecular size and hydrated cation radius. Non-
174 ionic chemicals such as glucose, glycine and ethanol with different molecular weight and
175 diffusion coefficient were chosen as three types of DSs with minimal cation exchange potential.
176 The main physicochemical properties of DSs were summarized in Table S1. In addition, Table
177 S2 shows the estimated transport parameters, atomic weight and estimated cation hydrated
178 radius in the inorganic DSs. Different DS concentrations were prepared by dissolving the
179 osmotic agents in deionized (DI) water to rule out the effects of other ions from DSs.

180 **2.3 Operation of the experimental systems**

181 The water flux performance of the TFC membrane with three different types of DSs (i.e. NaCl,
182 MgCl_2 and glucose) was evaluated by using the lab-scale, hollow fibre FO system to determine

183 water flux (J_w) and RSF (J_s). These DSs were chosen as a reference to evaluate the effect of
184 DS physicochemical properties (i.e. diffusion coefficient, molecular weight and viscosity) on
185 the FO water flux and RSF. The solute was dissolved in DI water to prepare DSs with different
186 concentrations, which corresponded to different osmotic pressure i.e. 24, 48, 96 and 144 bar,
187 respectively. The molar concentration of 6 M glucose as DS to obtain 144 bar osmotic
188 pressure wasn't evaluated in this study as this concentration exceeds its solubility limit in
189 water. To determine the RSF of the DS in the FO process, the conductivity (Hanna HI700
190 instrument, HI7639 probe, UK) of the FS was measured every 15 min when using ionic salts
191 as DSs and DI water as FS, while a 10 mL sample was withdrawn from the FS tank every 15
192 min for the subsequent COD analysis when non-ionic DSs were used. All FO experiments to
193 determine water flux and RSF were lasted for at least 2 hr.

194 FO experiments were run until 50% water recovery rate to investigate the effect of DS type on
195 ammonium rejection by TFC FO membrane. The initial FS and DS volumes were set as 1 L
196 for the effect of DS type on ammonium rejection, while the initial volumes for synthetic
197 wastewater and real wastewater were set as 0.7 and 0.7 L, respectively, for the investigation
198 of ammonium rejection in different types of wastewater. To investigate the effects of other ions
199 on ammonium rejection, a synthetic municipal wastewater was used as FS (2 L) with 1M of
200 glucose (2 L) as DS until 90% water recovery. Unless otherwise stated, the pH of both FS and
201 DS were adjusted to around 7 by using sodium hydroxide (NaOH) or hydrochloric acid (HCl)
202 prior to each experiment.

203 Before the membrane experiments for synthetic or real wastewater, baseline tests were
204 conducted with DI water as FS and 1 M NaCl DS to determine the baseline water flux. After
205 the membrane experiments for synthetic or real wastewater, the flux was tested again with DI
206 water to determine the water flux decline extent by comparing it with the baseline flux. After
207 this, two different physical methods were used to clean the membrane, which are i) normal
208 flushing by replacing FS and DS with DI water with flow rates of 0.6 L/min for 30 min, and ii)

209 osmotic backwashing by substituting DS with DI water and FS with 1 M NaCl with active layer
210 facing DS for 30 min at flow rates of 0.6 L/min to induce opposite crossflow to remove foulants
211 on/in the membrane.

212 **2.4 Analytical methods**

213 COD, ammonium, and phosphate were measured in accordance with standard methods by
214 American Public Health Association (APHA). Conductivity was measured by using Hanna
215 HI700 instrument and HI7639 probe (Hanna, UK). pH was measured using the pH probe from
216 Jenway 3010 meter (Bibby Scientific Ltd, UK). The concentration of cations such as Ca²⁺, Mg²⁺
217 and K⁺ were analyzed using ion chromatography (882 Compact IC plus, Metrohm,
218 Switzerland).

219 **2.5 Calculations**

220 Water flux across the FO membranes was determined by using equation 1:

$$221 \quad J_w = \frac{\Delta V}{\Delta t * A_m} \quad \text{Equation 1}$$

222 Where J_w (L/m²·hr) is the water flux, ΔV (L) is the volume change of the FS, Δt (hr) is the time
223 elapsed and A_m (m²) is the effective membrane area. To obtain the FS volume, FS weight was
224 divided by the density, which was assumed to be 1 kg/L.

225 The concentration factor (equation 2) (CF) was calculated as the ratio between the FS
226 concentration at time t (C_t) after FO experiment and the initial FS concentration (C_0) at time 0:

$$227 \quad CF = \frac{C_t}{C_0} \quad \text{Equation 2}$$

228 Contaminant rejection rate (R) was calculated based on the mass balance between FS and
229 DS (equation 3):

230
$$R = \left(1 - \frac{V_{df} \cdot C_{df}}{V_{fi} \cdot C_{fi}}\right) \times 100\%$$
 Equation 3

231 Where V_{df} (L) is the final volume of the DS, C_{df} (mg/L) is the final contaminate concentration in
 232 the DS, V_{fi} (L) is the initial FS volume, C_{fi} (mg/L) the initial contaminate concentration in the
 233 FS.

234 The RSF (J_s) was calculated from the following formula (equation 4):

235
$$J_s = \frac{V_{Ft2} \cdot C_{Ft2} - V_{Ft1} \cdot C_{Ft1}}{\Delta t \cdot A_m}$$
 Equation 4

236 Where J_s (g/m²·hr) is the RSF, V_{Ft2} (L) is the volume of FS at recording time interval t_2 , V_{Ft1}
 237 (L) is the FS volume at recording time interval t_1 , C_{Ft2} (g/L) is the solute mass concentration in
 238 FS at t_2 , C_{Ft1} (g/L) is the solute mass concentration in FS at t_1 . The salt concentration in the
 239 FS due to RSF was obtained by measuring conductivity of FS at different times according to
 240 the calibration curve between salt concentration and conductivity of solution. The
 241 concentration of reverse non-ionic solute was obtained by measuring COD of FS at different
 242 times according to the calibration curve between non-ionic solute concentration and COD.

243 The osmotic pressures for different DSs at different concentrations were calculated using Van't
 244 Hoff equation 5 [32–36]:

245
$$\Pi = iMRT$$
 Equation 5

246 Where Π (bar) is the osmotic pressure, i is the van't Hoff factor of the solute, M (mol/L) is the
 247 molar concentration, R is the universal gas constant (0.08206 L.atm/mol.K) and T is the
 248 absolute temperature in K.

249 The saturation index (SI) was calculated by using Visual MINTEQ (v. 3.1) software to estimate
 250 potential precipitates in the concentrated FS. The SI for synthetic municipal wastewater FS

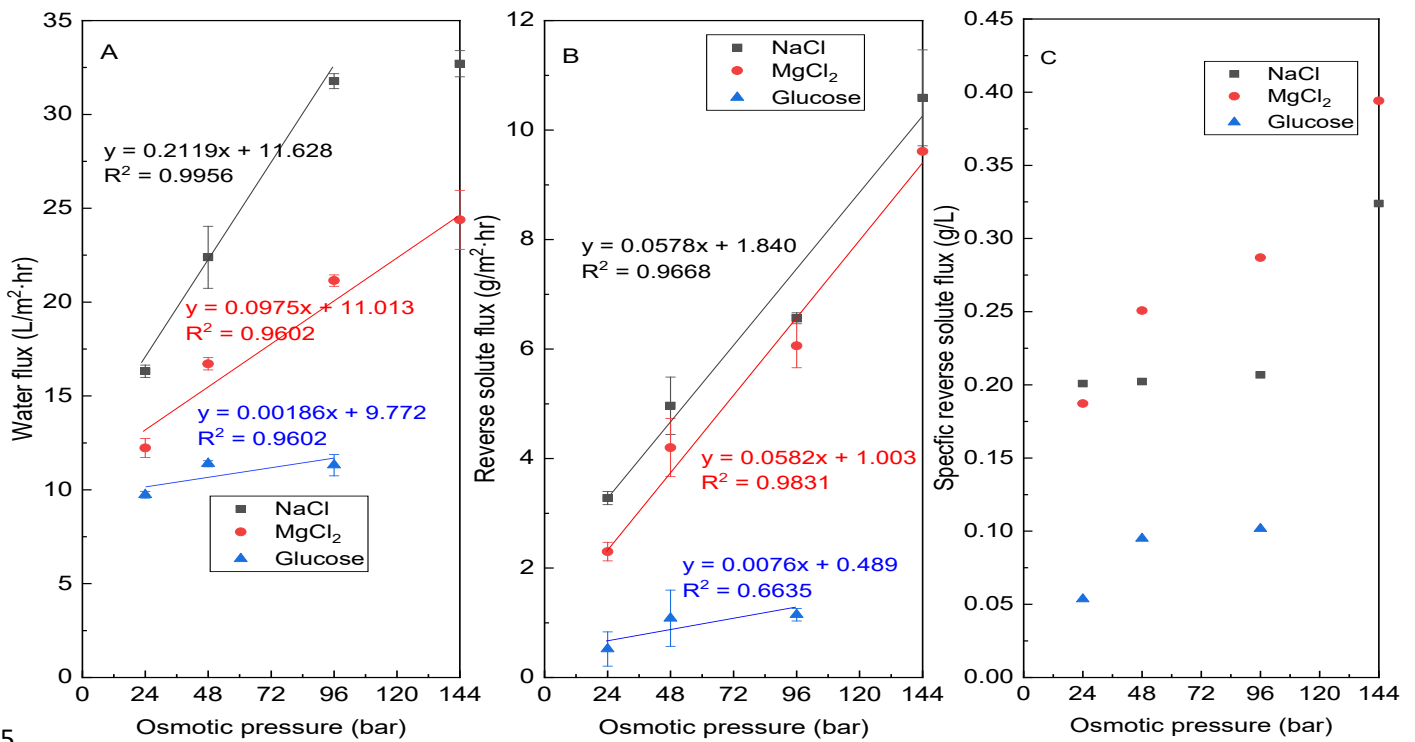
251 and 1 M glucose DS was calculated at 90% water recovery rate, while SI for real municipal
252 wastewater and sludge digestate was calculated at 50% water recovery rate.

253 **3. Results and discussion**

254 **3.1 Effects of draw solution type on water flux and reverse solute** 255 **flux**

256 Fig. 1 shows the effects of DS type, e.g. monovalent, divalent inorganic and non-ionic organic
257 DS, on water flux and RSF under different osmotic pressures. It can be seen that water flux
258 increased linearly with the increase in the osmotic pressure of three different types of DSs,
259 however, the water flux increased with the highest rate of 0.21 L/m²·hr·bar when using NaCl
260 as DS, followed by MgCl₂ with a rate of 0.098 L/m²·hr·bar and glucose with a rate of nearly 0.
261 This indicates that enhancing water flux by simply increasing the osmotic pressure of DS is
262 not always workable, which instead highly depends on the type of DS. Among DSs such as
263 NaCl, MgCl₂ and glucose used in this experiment, diffusion coefficients are 1.47 x 10⁻⁹, 1.07
264 x 10⁻⁹ and 0.67 x 10⁻⁹ m²/s, respectively, and viscosity of liquid under the same osmotic
265 pressure are 0.94, 1.14 and 1.45 cP, respectively, and molecular size of solute are 58.44,
266 95.21 and 180.16 g/mol, respectively [37–42]. It has been reported that lower diffusion
267 coefficient, higher viscosity and larger molecule size of DS could increase severity of both
268 internal (ICP) and external concentration polarization (ECP) [43, 44] since solute molecules in
269 DS are unable to quickly diffuse from the bulk solution to the diluted zone in the support layer
270 of membrane facing DS. This would reduce effective driving force created by osmotic pressure
271 difference between FS and DS, lowering water flux. Thus, glucose results in the lowest water
272 flux due to the most severe ICP caused by the highest viscosity and the lowest diffusivity
273 coefficient under the same osmotic pressure compared with NaCl and MgCl₂. When the
274 concentration of DS increases, viscosity further increases. The positive impact from the

275 increased osmotic pressure of glucose is likely offset by the negative impact from more severe
 276 ICP, leading to negligible water flux increase as shown in Fig. 1A. Although no quantitative
 277 relationship could be obtained between water flux and draw solution's viscosity, and diffusivity
 278 coefficient and molecular size of solute, physicochemical properties of DS such as diffusion
 279 coefficient, viscosity and molecular size could be used to qualitatively estimate water flux and
 280 corresponding water flux increase with the concentration of DS. This is helpful for the selection
 281 of DS for different application scenarios. In addition, it should be noted that draw solution's
 282 viscosity and diffusivity coefficient could be significantly changed for an increased water flux
 283 at higher temperature as reported in our previous study [45]. Thus, besides what mentioned
 284 above, temperature should be also considered when selecting DS.



286 Fig. 1. The dependence of water flux, reverse solute flux and specific reverse solute flux on the osmotic
 287 pressure of draw solutions such as NaCl, MgCl₂ and glucose and DI water as FS.

288 RSF is another important factor which needs to be considered for the selection of DSs. It can
 289 be seen from Fig. 1B that RSF increased linearly with the rise of the osmotic pressure of NaCl,
 290 MgCl₂ and glucose, but RSF of NaCl and MgCl₂ were much higher than that of glucose. Again,
 291 RSF could depend on diffusion coefficient, molecular size of solute in DS, and viscosity. The

292 larger effective diameter of hydrated Mg^{2+} (i.e. $800 \cdot 10^{-12}$ m, almost two times of Na^+ [36]) and
293 lower diffusivity of Mg^{2+} might result in the lower passage of Mg^{2+} ion through the FO
294 membrane compared with Na^+ . Glucose has the larger molecular size as non-ionic organic
295 and lower diffusivity coefficient, leading to the lowest RSF. These results are in good
296 agreement with previous studies with NaCl, magnesium acetate, $MgCl_2$, sodium acetate and
297 glucose as DSs, whereby DSs with lower diffusion coefficient have a lower water flux and RSF
298 [43, 46–48]. In addition, it is found that the RSF from NaCl and $MgCl_2$ changed at a similar
299 rate of $0.058 \text{ g/m}^2\cdot\text{hr}\cdot\text{bar}$ with the osmotic pressure, which is different from water flux. From
300 this perspective, NaCl is better than $MgCl_2$ as DS.

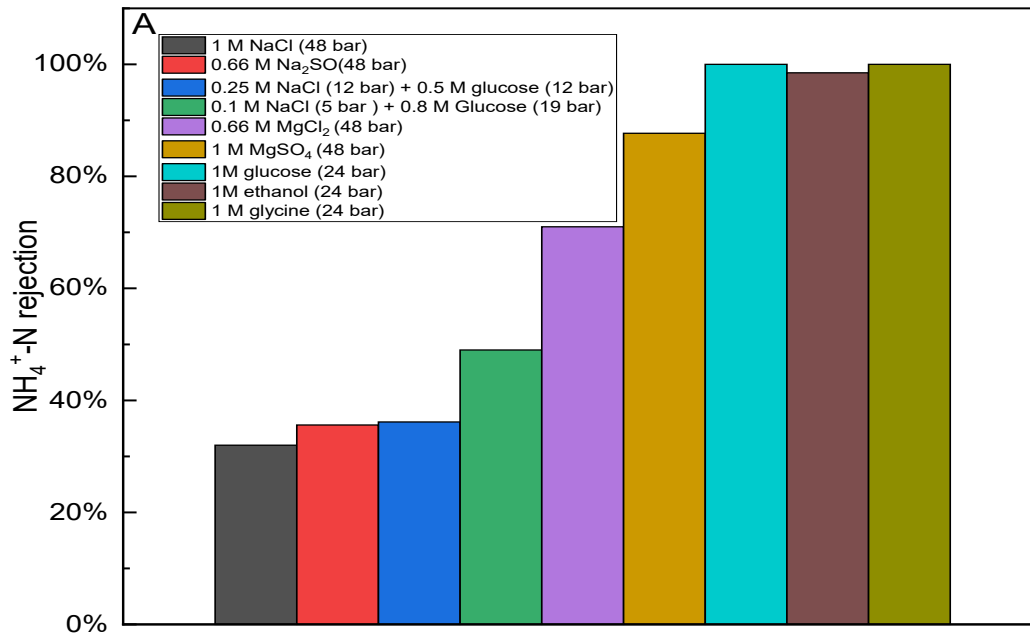
301 When considering DS loss (or replenishment demand) or total contamination of FS by the
302 solutes of DS after a certain operation period, specific reverse solute flux (J_s/J_w), i.e. how much
303 solute loss from DS due to RSF for per liter permeate, is a more useful parameter than RSF.
304 As shown in Fig. 1C, glucose had the lowest specific reverse solute flux at 24, 48 and 96 bar
305 compared with NaCl and $MgCl_2$. However, $MgCl_2$ demonstrates higher specific reverse flux
306 than NaCl although it has lower RSF than NaCl as the increasing rate of RSF was higher than
307 the increasing rate of water flux. As shown in Table S3, the replenishment cost of glucose is
308 lower than NaCl and $MgCl_2$ at the osmotic pressure of 24 bar, however, with the increase in
309 osmotic pressure, NaCl becomes more economic than glucose and $MgCl_2$. From the practical
310 point of view, seawater or brine could be obtained for free particularly in the regions close to
311 coasts. However, with the development of saccharification from organic wastes, glucose or
312 sugar solutions could be available at an acceptable cost. In this case, an FO process with
313 sugar solution as DS could be integrated with a fermentation process to reduce the cost of
314 sugar.

315 **3.2 Effects of draw solution type on ammonium rejection**

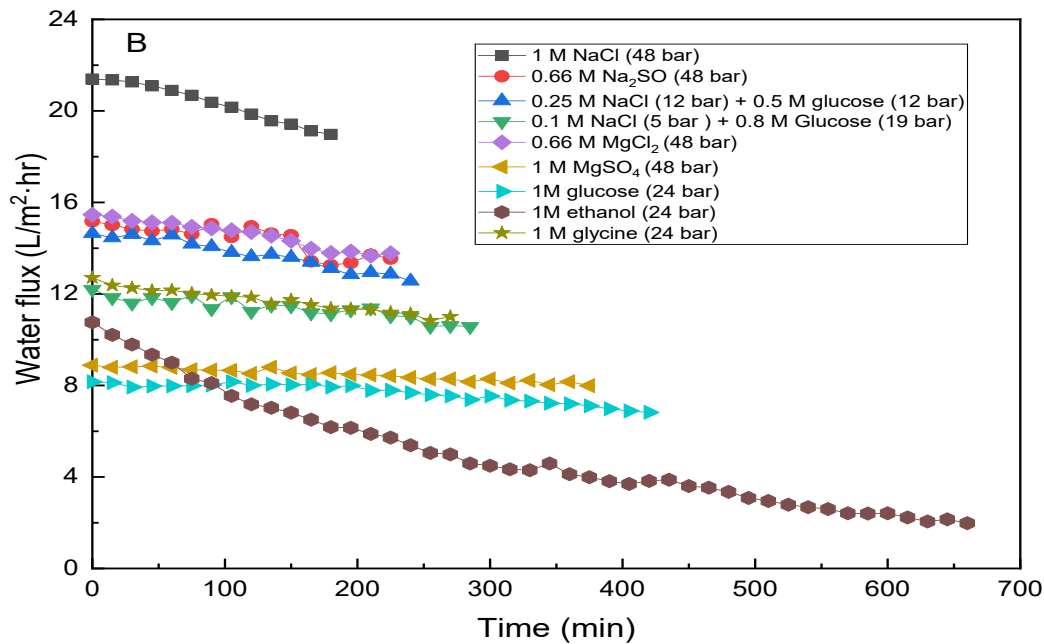
316 Unlike COD and phosphate, ammonium is usually ineffectively rejected by the TFC FO
317 membrane due to the negative charge of membrane surface. Pre-tests of DSs of NaCl, MgCl₂
318 and glucose showed ammonium rejection rates as 32.46%, 70.72% and 100%, respectively
319 (Fig 2A). From this result, it can be known that selecting appropriate DSs could be an
320 alternative to the modification of membrane surface from negative to positive charge as
321 reported to selectively reject ammonium.

322 To better understand which physicochemical properties of solute of DS affect ammonium
323 rejection most, two additional ionic DSs (i.e. Na₂SO₄ and MgSO₄), and two neutral DSs (i.e.
324 glycine and ethanol) were further investigated for ammonium rejection. Glycine and ethanol
325 were selected because they are neutral at the studied pH but with higher diffusion coefficient
326 than that of glucose while Na₂SO₄ and MgSO₄ were selected as they are ionic as NaCl but
327 with different diffusion coefficients and hydrated cation radius. 9 DSs for the study could be
328 classified into groups for the comparison of different hydrated cation radius such as Na⁺ and
329 Mg²⁺, different diffusion coefficients with the same cation such as between NaCl and Na₂SO₄,
330 MgCl₂ and MgSO₄, different diffusion coefficients for neutral chemicals such as glycine,
331 ethanol and glucose. Fig. 2 shows ammonium rejection and water flux with 9 different DSs. It
332 can be seen that sodium-based DSs have higher water flux than magnesium-based DSs but
333 with lower ammonium rejection. Neutral chemicals as DSs have ammonium rejection rates of
334 100% or close to 100% with middle-range or low-range water flux.

335



336



337

338 Fig. 2. Water flux and $\text{NH}_4^+\text{-N}$ rejection rate in the synthetic FS with different DSs during the TFC FO
339 process until 50% water recovery with 34.30 ± 0.61 mg/L of initial $\text{NH}_4^+\text{-N}$.

340 Different from the mechanism of ammonium rejection by modified membrane surface with
341 repulsion between ammonium and positive charge on the membrane surface, the higher
342 ammonium rejection rates with magnesium-based DSs and neutral chemicals as DSs are
343 most likely due to reduced cation exchange between ammonium in the FS and cations in the
344 DS. Irvine et al. [49] reported solute-solute interaction via ion exchange could have a dramatic

345 impact on the permeation of solutes through dense polymeric membranes and they found that
346 identity of anions in DS had a significant impact on forward nitrate permeation from FS. In our
347 study, we focused on forward ammonium permeation. We found that the identity of cation such
348 as Na^+ and Mg^{2+} have significant impact on forward ammonium permeation via cation
349 exchange with magnesium based DS having higher ammonium rejection. It is known that
350 divalent Mg^{2+} has a larger hydrated radius than that of monovalent Na^+ (i.e. 0.428 nm for Mg^{2+}
351 and 0.358 nm for Na^+ , respectively) [36, 50]. Cheng et al. [51] also reported that divalent draw
352 cations with larger hydrated radius could reduce cation exchange compared with monovalent
353 draw cations when studying K^+ in the FS. Thus, it could be concluded that divalent draw cation
354 is better for cation rejection in FS, and it is reasonable to speculate that trivalent draw cation
355 could be even better than divalent cation regarding ammonium rejection.

356 Secondly, it is found from Fig. 2A that the lower diffusion coefficient of DS led to higher
357 ammonium rejection when the cation identity was same. For example, Na_2SO_4 with lower
358 diffusion coefficient resulted in a 3% higher ammonium rejection rate than NaCl with higher
359 diffusion coefficient. MgSO_4 with lower diffusion coefficient achieved more than 15%r
360 ammonium rejection rate than MgCl_2 with higher diffusion coefficient . This suggests that to
361 enhance the ammonium rejection rate, it is better to use a multivalent cation-based DS with a
362 lower diffusion coefficient.

363 Regarding neutral chemicals as DS without ion dissociation, it is found from Fig. 2A that
364 ammonium was almost 100% rejected. The comparison of diffusion coefficient of ionic and
365 non-ionic DSs used in this study in Table S1 shows that ethanol and glycine have much higher
366 diffusion coefficient than Na_2SO_4 and MgSO_4 , but ammonium rejection rates from ethanol and
367 glycine are almost 100%. In addition, when NaCl concentration in the DS with a mixture of
368 NaCl and glucose was higher than 0.25 M, ammonium rejection rate was slightly higher (i.e.
369 3%) than that with 1 M NaCl as DS. When NaCl concentration in the DS with a mixture of NaCl
370 and glucose was reduced to 0.1 M, ammonium rejection rate was improved by 15% compared

371 with 1 M NaCl due to the reduced Na^+ in DS and thus reduced reverse Na^+ permeation for
372 cation exchange although the osmotic pressure of DS was controlled at the same level.
373 Therefore, we can see that ammonium rejection rate does not rely on osmotic pressure but is
374 negatively related with NaCl concentration. In addition, it is found from Fig. 2B that the water
375 flux of ethanol decreased more steeply compared with other DSs. The ethanol concentration
376 in the DS after 50% water recovery rate was 19.41 g/L, lower than the theoretical ethanol
377 concentration of 30.71 g/L assuming no ethanol transport to other solution or phases. The
378 mass balance calculation by measuring COD in the FS after 50% water recovery rate indicates
379 that 20.06% of the initial ethanol amount in DS transferred from the DS to the FS by RSF while
380 around 4% of the initial ethanol was evaporated during the 11 hr FO operation given that
381 ethanol was highly volatile. The more reverse ethanol permeation from DS to FS is the main
382 reason for the steeper drop of water flux compared with other types of DSs. The significant
383 loss of ethanol to the FS observed in this study is in agreement with [52] who showed that
384 RSF obtained for ethanol DS was $240 \text{ g/m}^2\cdot\text{hr}$, and was 40 times higher than $6 \text{ g/m}^2\cdot\text{hr}$ for
385 NaCl DS at the same osmotic pressure of 46.7 bar. This is mainly due to the small size of
386 ethanol molecules and high diffusion coefficient. Even with such high reverse ethanol flux,
387 there is almost no forward ammonium permeation. These results further confirm that cation
388 exchange between DS and FS is the most critical factor for forward ammonium permeation
389 while diffusion coefficient of DS might only play a minor role when ionic DS is used.

390 Apart from ammonium exchange with cations in DS, H^+ as a smaller positively charged ion
391 could be more easily exchanged when ionic DSs are used, leading to pH change in both FS
392 and DS. It can be seen from Fig. S1 that a notable pH increase was observed in FS with NaCl,
393 MgCl_2 and glucose as DSs during the period of the first 10% water recovery rate. After that,
394 the pH of FS increased most with MgCl_2 as DS, while slightly with NaCl as DS and slightly
395 decreased with glucose as DS. This is probably because that one Mg^{2+} needs roughly 2 H^+ to
396 exchange to maintain electroneutrality, and thus lead to higher pH increase in FS. The pH
397 increase in the FS was observed in both synthetic and real wastewater during the FO process

398 with different DSs [53–56]. Ansari et al. [56] reported that the pH of the FS increased from 6.5
399 to 8.0 with 1.27 M NaCl as DS after achieving 90% water recovery rate during the CTA FO
400 process. Another study by Kumar et al. [50] showed that the pH of the FS with either NaCl or
401 MgCl₂ as DSs at a 90 bar osmotic pressure was increased from 7 to 8 and 8.2, respectively.
402 The pH change validates the ion exchange between DS and FS.

403 When DS is selected for enhanced ammonium rejection, water flux has to be considered as
404 well because higher water flux can reduce membrane surface area required for specific
405 treatment demand. From Fig. 2, it can be seen that for ionic DSs, it is difficult to find a type of
406 DS with both relatively higher water flux and ammonium rejection rate. Since all neutral
407 chemicals used in this study achieved almost 100% ammonium rejection rate, we just need to
408 select a neutral chemical with the highest water flux as DS. Glycine is less practical as DS
409 given its cost, but the findings in this study could be used as a guidance to select more suitable
410 DS to meet the requirement of high ammonium rejection for wastewater treatment.

411 **3.3 Concentrating synthetic municipal wastewater with glucose** 412 **as draw solution until 90% water recovery rate**

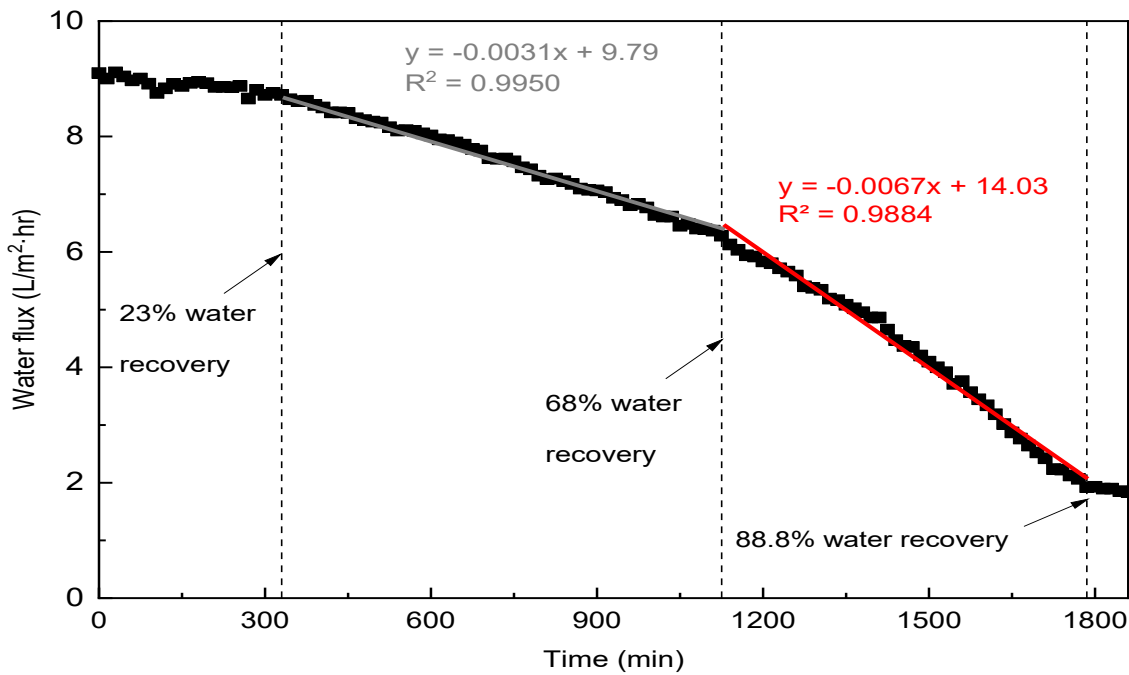
413 To further investigate if ammonium rejection with neutral chemicals as DS would be negatively
414 affected by other ions and chemicals in wastewater, synthetic wastewater with multiple ions
415 and chemicals was investigated with glucose as DS for 90% water recovery rate. As shown in
416 Table 1, COD concentration was increased from 496.82 ± 34.78 to 6419.29 ± 69.57 mg/L with
417 a concentration factor of 12.92. The final COD concentration was higher than the theoretical
418 value for a complete COD rejection, i.e. 10 of concentration factor. Obviously, the extra COD
419 was due to reverse solute permeation from DS. Although reverse glucose flux results in the
420 cost for replenishment, the glucose lost to FS can be recovered as methane when
421 concentrated municipal wastewater goes through post-treatment such as anaerobic digestion.
422 No PO₄³⁻ and NH₄⁺ were detected in the DS after 90% recovery rate, indicating 100%

423 ammonium and phosphate rejection. However, as shown in Table 2, concentration factors of
 424 soluble $\text{PO}_4^{3-}\text{-P}$ and $\text{NH}_4^+\text{-N}$ in FS were 8.48 and 7.92, respectively, lower than theoretical
 425 value 10 for 100% rejection rate. At the end of the FO experiment with 90% water recovery
 426 rate, precipitates were observed in the concentrated FS, proving that a tiny proportion of
 427 soluble ammonium and phosphate were precipitated due to increased pollutant concentrations
 428 and pH. The SI values of struvite or hydroxyapatite at increased concentrations of $\text{PO}_4^{3-}\text{-P}$,
 429 $\text{NH}_4^+\text{-N}$, Ca^{2+} and Mg^{2+} and pH from 6.7 to 7.1 became positive, implying high potential for the
 430 formation of precipitates (Table S4). 100% rejection of $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ by DS glucose can
 431 avoid forward nutrient permeation to contaminate DS and downstream recovered water and
 432 meanwhile guarantees maximum nutrient recoveries in the post-treatment. The final $\text{PO}_4^{3-}\text{-P}$
 433 concentration of 73.77 mg/L in the concentrated FS at 90% water recovery rate could be
 434 directly precipitated as struvite or hydroxyapatite precipitation for phosphorus recovery by
 435 adjusting pH to 9-11. In addition, since NH_4^+ and K^+ have the same hydrated radii [58] as 3.3
 436 Å, similar rejection rates of NH_4^+ and K^+ were expected. However, it was noted that K^+ was
 437 enriched by just 4 fold from 8.75 to 35.04 mg/L. This indicates the complexity of forward
 438 permeability of small ions through membrane. The higher concentration factors reported in
 439 this study for Mg^{2+} and Ca^{2+} compared with K^+ align with previous studies in that monovalent
 440 cations are more permeable than divalent cations through FO membranes [5].

441 Table 1: Summary of initial and final concentrations of pollutants in synthetic wastewater as feed
 442 solution and 1 M glucose as draw solution, and concentration factors of each pollutant with a 90% water
 443 recovery rate after TFC hollow fibre FO membrane.

Pollutants	Initial concentration in FS (mg/L)	Final concentration in FS (mg/L)	Concentration factor	Theoretical concentration in FS assuming 100% rejection (mg/L)
COD	496.82 ± 34.78	6419.29 ± 69.57	12.92	4968.20
$\text{PO}_4^{3-}\text{-P}$	8.72 ± 0.43	73.77 ± 0.09	8.48	87.20
$\text{NH}_4^+\text{-N}$	38.33 ± 1.10	303.53 ± 2.86	7.92	383.30
Ca^{2+}	8.57 ± 0.24	66.20 ± 1.83	7.72	85.70
Mg^{2+}	7.75 ± 0.16	64.21 ± 0.95	8.28	77.50
K^+	8.75 ± 0.39	35.04 ± 1.14	4	87.50

444 Fig. 3 shows the dynamic water flux during FO process. Water flux decreased continuously
445 mainly because of the reduced driving force between FS and DS by concentrating ions and
446 chemicals in the FS and diluting DS. Fig. 3 shows varied water flux reduction rate, indicating
447 membrane fouling could be involved in FO process, especially in the latter part of the process.
448 Based on the varying slopes of water flux reduction, the membrane process could be divided
449 into four distinct periods, i.e. the first 330 min with water recovery rate from 0 to 23%, the
450 period from 330 to 1125 min with water recovery rate from 23 to 68%, the period from 1125 to
451 1785 min with water recovery rate from 68 to 88.8%, and the last period from 1785 to 1860
452 min with water recovery from 88.8 to 90%. In the first and last periods, water fluxes were
453 relatively stable with little water reduction. This is because a certain time (i.e. 330 min) was
454 needed for the development of membrane fouling, while in the last period (i.e. 88.8-90%), the
455 fouling layer grew slowly. However, in the second period, water flux declined with a rate of
456 0.0031 L/m²·hr per min from 8.72 to 6.28 L/m²·hr while it became 0.0067 L/m²·hr per min, a
457 doubled declining rate, from 68% to 88.8% water recovery rate where the flux dropped by
458 69.4% from 6.28 to 1.92 L/m²·hr. The increased water flux decline in the 2nd and 3rd periods
459 should be from membrane fouling. Since the synthetic wastewater used in this study mainly
460 contained sodium acetate, ammonium, phosphate Ca²⁺, Mg²⁺, and K⁺, it could be speculated
461 the membrane fouling was mainly caused by inorganic scaling from the phosphate precipitates
462 instead of organic fouling or biofilm fouling. It is interesting to note that water flux decline rate
463 was two times higher in the third period with water recovery rate above 68%, indicating that
464 inorganic membrane fouling passed a tipping point. From this point of view, it would be better
465 to operate FO process with a water recovery rate below 68% to maintain an acceptable water
466 flux and treating capacity of FO system. It needs to point out that the recommended specific
467 water recovery rate should be different for different wastewater with different fouling potential
468 and different DSs, which should be obtained by monitoring water flux over the time.



469

470 Fig. 3. Water flux behaviour with synthetic municipal wastewater as feed solution and 1 M glucose as
 471 draw solution for the TFC FO membrane until 90% water recovery rate.

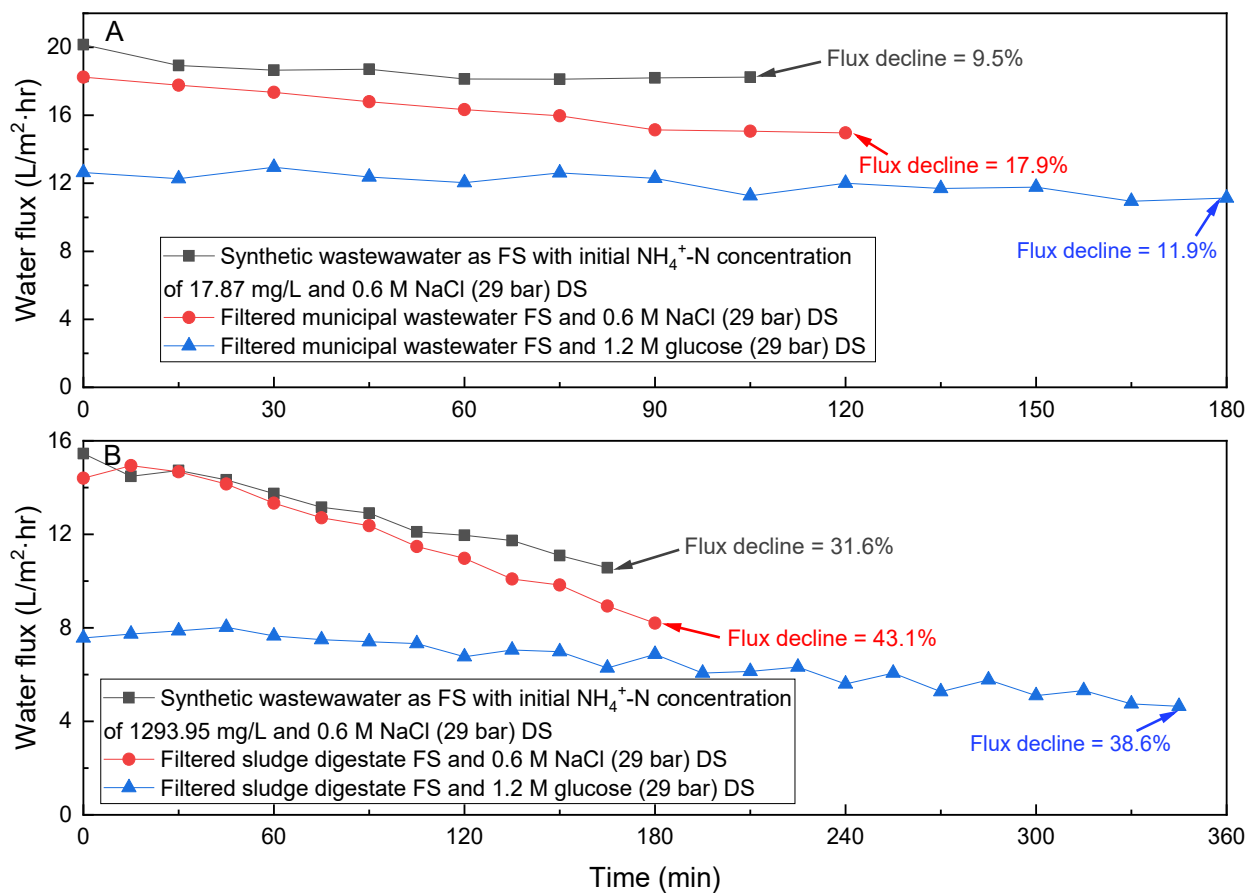
472 After synthetic municipal wastewater treatment with 90% water recovery rate, the water flux
 473 was tested with DI water. It was found that water flux declined by around 34.5% as shown in
 474 Fig. S2. This further validated membrane fouling during the FO treatment. After osmotic
 475 backwashing for 30 min, around 99% of the initial water flux was restored, suggesting the
 476 reversibility of the TFC FO membrane after inorganic fouling.

477 **3.4 Effect of initial ammonium concentration on ammonium**
 478 **rejection with NaCl and glucose as draw solutions**

479 Real wastewater might contain different ammonium concentrations. In addition, real
 480 wastewater is more complex with more types of ions and chemicals. More tests were
 481 conducted to further investigate effects of ammonium concentration on ammonium rejection
 482 and enhanced ammonium rejection by neutral chemicals with different ammonium
 483 concentrations. Firstly, synthetic wastewater containing only ammonium was tested with NaCl
 484 as DS to study the effect of initial NH_4^+ -N concentration on cation exchange (i.e. Na^+ and

485 ammonium) during the FO process. Then, real municipal wastewater (i.e. sewage) and sludge
486 digestate were tested with 0.6 M NaCl and 1.2 M glucose as DSs, respectively, under the
487 same osmotic pressure. In practice, seawater could be used as a cost-effective DS, thus, the
488 osmotic pressure of 29 bar was chosen in this section to simulate seawater [12].

489 As shown in Fig. 4, higher ammonium concentration resulted in lower water flux due to the
490 reduced driving force. In addition, water fluxes for treating synthetic wastewater with both initial
491 17.9 mg/L $\text{NH}_4^+\text{-N}$ and 1294.0 mg/L $\text{NH}_4^+\text{-N}$ were slightly higher than for treating real
492 wastewater when NaCl was used as DS. Meanwhile, water flux decline percentages for real
493 wastewater were higher than synthetic wastewater for achieving 50% water recovery rate.
494 This is expected because the presence of other soluble organic or inorganic pollutants in real
495 wastewater could result in reduced driving force across membrane and cause more severe
496 membrane fouling than synthetic wastewater. In addition, it is found that water fluxes with
497 NaCl as DS were much higher than glucose even at the same osmotic pressure. This is closely
498 related with ICP and ECP that specific type of DS creates. Due to higher viscosity, lower
499 diffusion coefficient and larger molecular weight, glucose can create much higher ICP and
500 ECP than NaCl. It is very interesting to note that water flux decline extents with glucose as DS
501 were around 6% lower than NaCl for both real municipal and sludge digestate liquor although
502 there was much longer FO duration process. To further investigate if this was due to less
503 membrane fouling, water flux was measured with DI water as FS.



504

505 Fig. 4. Water flux decline with NaCl and glucose DSs at 29 bar osmotic pressure for the TFC FO
 506 membrane until 50% water recovery rate: A) with low initial ammonium concentration and B) with high
 507 initial ammonium concentration.

508 Relative water flux can be used to indicate the change of membrane performance. To

509 understand how much flux drop at the end of each experiment was caused by membrane

510 fouling, base-line water flux was measured with DI water as FS and NaCl as DS after each

511 FO experiment and results were shown in Fig 5. It can be seen that relative water fluxes after

512 the treatment of real wastewater are similar for DS with NaCl and glucose, which was around

513 0.96 for filtered municipal wastewater and 0.98 for filtered sludge digestate liquor. This result

514 indicates that sludge digestate liquor did cause slightly more serious membrane fouling due

515 to higher concentration of foulants than municipal wastewater, but the same level of relative

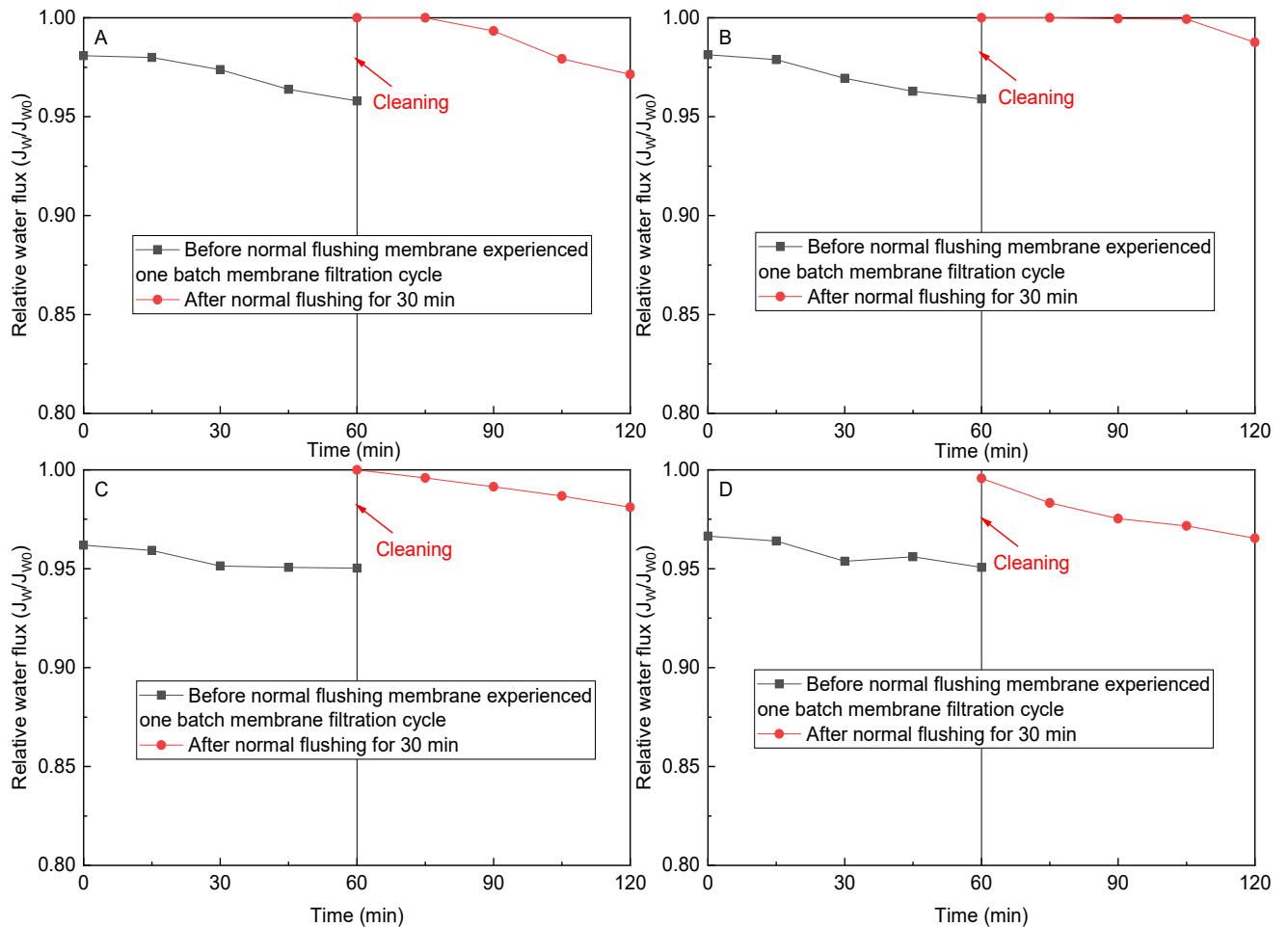
516 water fluxes for the same type of wastewater with either NaCl or glucose as DS suggested

517 that the less flux decline extent with glucose as DS could be caused by other factors. In

518 addition, the complete recovery of water flux after the normal flushing indicates that membrane

519 fouling is fully reversible even for real wastewater with 50% water recovery rate and pre-

520 treatment by 0.45 μm membrane filtration to remove suspended solids. This is highly in
 521 agreement with other FO studies on membrane fouling for treating filtered wastewater at a
 522 lower water recovery rate with NaCl as DS [59–61]. 100% membrane recoverability with
 523 glucose as DS also suggests that the membrane fouling and flux recoverability are not closely
 524 related with physical properties of DS.



525

526 Fig. 5. Relative water fluxes before and after normal DI water flushing to clean FO membrane following
 527 each FO batch cycle with 50% water recovery rate A) filtered municipal wastewater and C) filtered
 528 digestion sludge as FS, respectively with and 0.6 M NaCl as DS, B) filtered municipal wastewater and
 529 D) as filtered digestion sludge as FS, respectively, and 1.2 M glucose as DS

530 When synthetic wastewater with only ammonium was used as FS with 50% water recovery, it
 531 is found that ammonium rejection rate highly depended on initial ammonium concentration in
 532 FS (Table 2). For example, when the initial $\text{NH}_4^+\text{-N}$ concentration was 17.87 mg/L, the final
 533 $\text{NH}_4^+\text{-N}$ concentration dropped to only 6.72 mg/L with a rejection rate of 19.3% when NaCl
 534 was used as DS. However, when the initial $\text{NH}_4^+\text{-N}$ concentration was 1293.95 mg/L,

535 ammonium rejection rate reached 79.2% with a final $\text{NH}_4^+\text{-N}$ concentration of 2044.89 mg/L.
 536 From the perspective of concentrating ammonium in FS, FO performs better with higher initial
 537 ammonium concentration. However, the actual ammonium permeated to DS at initial $\text{NH}_4^+\text{-N}$
 538 concentration of 1293.95 mg/L reached 188.27 mg while it was only 10.10 mg at initial $\text{NH}_4^+\text{-N}$
 539 N concentration of 17.87 mg/L, causing more ammonium pollution to DS or possible problem
 540 for downstream water recovery from DS. In addition, higher ammonium permeation from FS
 541 to DS implies that more Na^+ in DS permeates to FS by cation exchange across membrane
 542 between NH_4^+ and Na^+ to maintain electroneutrality, resulting in high RSF. Cheng et al. [51]
 543 also reported that more cation exchange occurred for higher K^+ concentration in the FS in the
 544 TFC FO process when NaCl was used as DS. Thus, selecting appropriate DS to fully reject
 545 ammonium in FS or to be used for other benefits such as fertilisers.

546 Table 2: Summary of initial and final $\text{NH}_4^+\text{-N}$ concentrations in the FS, rejection rate and final $\text{NH}_4^+\text{-N}$
 547 mass in the DS with 0.6 M NaCl as draw solution with a 50% water recovery rate after TFC hollow fibre
 548 FO treatment for treating synthetic wastewater with only ammonium.

Initial $\text{NH}_4^+\text{-N}$ concentration in FS (mg/L)	Final $\text{NH}_4^+\text{-N}$ concentration in FS (mg/L)	Rejection rate (%)	Final $\text{NH}_4^+\text{-N}$ mass in the DS (mg)
17.87 ± 0.15	6.72 ± 0.15	19.3	10.10 ± 0.82
1293.95 ± 10.68	2044.89 ± 1.53	79.2	188.27 ± 1.65

549 Table 3 shows the performance of wastewater treatment with FO. Due to the use of coagulant
 550 $\text{Al}_2(\text{SO}_4)_3$ for enhanced suspended solid removal during the pre-treatment, phosphate
 551 concentration in filtered sludge digestate liquor was reduced to only 1 mg/L $\text{PO}_4^{3-}\text{-P}$. But for
 552 other dominant pollutants, their concentrations in sludge digestate liquor were much higher
 553 than municipal wastewater. It can be seen that glucose as DS obtained higher rejection rates
 554 of dominant pollutants and metal ions than NaCl for either municipal wastewater or sludge
 555 digestate liquor. Regarding ammonium, similar to results obtained with synthetic wastewater,
 556 ammonium in municipal wastewater with lower initial ammonium concentration was diluted
 557 while it was concentrated in sludge digestate liquor as FS with higher initial ammonium
 558 concentration with NaCl as DS. But ammonium rejection was still close to 100% for glucose
 559 as DS. Although glucose always resulted in better rejection than NaCl for any pollutants

560 measured in this study as shown in Table 3, it was noted that concentration factors of NH_4^+
561 and PO_4^{3-} in sludge digestate liquor were lower than those in municipal wastewater. In addition,
562 pH of FS increased from 7.0 to around 7.7-7.8. Due to the higher concentrations of pollutants
563 and higher pH in FS during FO treatment period, it is possible for highly concentrated
564 chemicals especially ammonium, phosphate, calcium and magnesium in FS to form inorganic
565 precipitates such as calcium phosphate or struvite. To validate this assumption, pHs of the
566 concentrated municipal wastewater and sludge digestate liquor were adjusted from 7.7-7.8 to
567 5.5 and PO_4^{3-} concentrations were measured again. As shown in Table 3, concentration
568 factors of PO_4^{3-} -P increased to around 1.92 or higher due to the release of phosphorus from
569 possible precipitates [62], suggesting inorganic phosphate precipitates at pH 7.7-7.8. In
570 addition, SI, used as an indicator of possible mineral precipitation, of the concentrated FS at
571 50% water recovery rate showed oversaturation of phosphate precipitates for both municipal
572 wastewater and sludge digestate liquor as FSs even at this PO_4^{3-} -P concentration level (i.e.
573 1.5-3.72 mg/L) (Table S5). However, concentration factor of 1.92 is still lower than the
574 theoretical concentration factor of 2 although no phosphate was detected in DS. Thus, it is
575 speculated that part of phosphate precipitates could be attached to the TFC membrane
576 surface. For real wastewater treatment, it was found that higher pHs as shown in Table 3 were
577 reached than DI water as FS as shown in Fig. S1. Higher pH results in higher possibility for
578 inorganic precipitates, which contributes to membrane fouling. Unlike DI water, municipal
579 wastewater and digestate FSs are more complex [63] suggesting that the wastewater pH was
580 greatly dependent on the physicochemical characteristics of wastewater. Therefore, it was
581 speculated that the higher pH increase for the concentrated municipal wastewater and
582 digestate in this study was due to the complex nature of real wastewater compared with DI
583 water.

584 Table 3: Summary of initial and final concentrations of pollutants in municipal wastewater and digestion sludge wastewaters as feed solutions and 0.6 M NaCl
 585 and 1 M glucose as draw solutions, and concentration factors of each pollutant with a 50% water recovery rate after TFC hollow fibre FO membrane treatment.

		pH	NH ₄ ⁺ -N	COD	PO ₄ ³⁻ -P	Ca ²⁺	Mg ²⁺	K ⁺		
			mg/L							
Municipal wastewater	0.6 M NaCl	Initial	7 ± 0.03	16.74 ± 0.16	119.96 ± 3.39	2.26 ± 0.12	63.83 ± 0.49	13.07 ± 0.27	17.16 ± 1.41	
		Final	7.83	8.44 ± 0.56	239.93 ± 13.35	3.50 ± 0.06	110.67 ± 3.34	24.28 ± 0.61	18.96 ± 0.95	
		CF	-	-1.98	2	1.55	1.74	1.86	1.07	
	1.2 M glucose	0.6 M NaCl	Final	5.5	-	-	4.36 ± 0.23	-	-	-
			CF	-	-	-	1.93	-	-	-
			Final	7.71	33.54 ± 0.25	263.92 ± 23.12	3.72 ± 0.17	116.43 ± 1.18	24.63 ± 1.46	26.33 ± 1.26
		1.2 M glucose	CF	-	2	2.2	1.65	1.81	1.89	1.63
			Final	5.5	-	-	4.38 ± 0.16	-	-	-
			CF	-	-	-	1.94	-	-	-
Sludge digestate	0.6 M NaCl	Initial	7.01 ± 0.02	1255.13 ± 87.56	959.70 ± 33.93	1 ± 0.05	21.02 ± 0.32	18.96 ± 0.82	93.38 ± 2.36	
		Final	7.84	1422.31 ± 3.75	1919.38 ± 33.9	1.51 ± 0.04	38.08 ± 1.40	35.92 ± 0.89	128.19 ± 3.65	
		CF	-	1.13	2	1.51	1.81	1.89	1.37	
	1.2 M glucose	0.6 M NaCl	Final	5.5	-	-	1.92 ± 0.04	-	-	-
			CF	-	-	-	1.92	-	-	-
			Final	7.82	2409.82 ± 34.24	2159.34 ± 67.86	1.53 ± 0.06	40.24 ± 1.49	37.53 ± 0.75	172.51 ± 3.43
		1.2 M glucose	CF	-	1.92	2.25	1.53	1.91	1.98	1.81
			Final	5.5	-	-	1.93 ± 0.04	-	-	-
			CF	-	-	-	1.93	-	-	-

586

587 4. Conclusion

588 This study investigated the enhancement of ammonium rejection by the TFC FO for
589 wastewater treatment by selecting appropriate DS. The following conclusions can be drawn:

- 590 • Lower reverse cation flux in DS resulted in higher ammonium rejection because
591 ammonium rejection is related with the exchange of cation in DS and ammonium.
- 592 • Cation exchange between cation in DS and ammonium is the critical factor leading
593 to lower ammonium rejection in FS. DS with multivalent cation and a larger
594 hydrated radius resulted in higher ammonium rejection and non-ionic DSs led to
595 almost a complete ammonium rejection.
- 596 • Other physical properties of DS such as viscosity, molecular weight, and diffusion
597 coefficient did not affect ammonium rejection very much. But for the same cation,
598 (such as NaCl-Na₂SO₄ and MgCl₂-MgSO₄), ammonium rejection increased when
599 the anion's diffusion coefficient was lower.
- 600 • More absolute ammonium in FS permeated to DS at higher initial ammonium
601 concentration in the FS with ionic DS, but ammonium rejection rate increased.
- 602 • Concentration of ammonium, phosphate and other ions in FS as well as pH
603 increase of FS due to cation exchange across membrane between H⁺ and Na⁺, led
604 to more inorganic precipitates for membrane fouling. However, physical cleaning
605 for 30 min could fully recover FO membrane fouled from one batch cycle for the
606 treatment of synthetic municipal wastewater, real municipal wastewater and sludge
607 digestate liquor with microfiltration pre-treatment.

608

609

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