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## Factors governing the pre-concentration of wastewater using forward osmosis for subsequent resource recovery

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## Factors governing the pre-concentration of wastewater using forward osmosis for subsequent resource recovery

### Abstract

This study demonstrated a technique using forward osmosis (FO) to pre-concentrate the organic matter in raw wastewater, thereby transforming low strength wastewater into an anaerobically digestible solution. The chemical oxygen demand (COD) of raw wastewater was concentrated up to approximately eightfold at a water recovery of 90%. Thus, even low strength wastewater could be pre-concentrated by FO to the range suitable for biogas production via anaerobic treatment. Excessive salinity accumulation in pre-concentrated wastewater was successfully mitigated by adopting ionic organic draw solutes, namely, sodium acetate, and EDTA-2Na. These two draw solutes are also expected to benefit the digestibility of the pre-concentrated wastewater compared to the commonly used draw solute sodium chloride. Significant membrane fouling was observed when operating at 90% water recovery using raw wastewater. Nevertheless, membrane fouling was reversible and was effectively controlled by optimising the hydrodynamic conditions of the cross-flow FO system.

### Keywords

governing, pre, forward, wastewater, factors, recovery, concentration, resource, subsequent, osmosis

### Disciplines

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16

17 **Abstract:** This study demonstrated a technique using forward osmosis (FO) to pre-  
18 concentrate the organic matter in raw wastewater, thereby transforming low strength  
19 wastewater into an anaerobically digestible solution. The chemical oxygen demand (COD) of  
20 raw wastewater was concentrated up to approximately eightfold at a water recovery of 90%.  
21 Thus, even low strength wastewater could be pre-concentrated using FO to the range suitable  
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23 concentrated wastewater was successfully mitigated by adopting ionic organic draw solutes,  
24 namely, sodium acetate and EDTA-2Na. These two draw solutes are also expected to benefit  
25 the digestibility of the pre-concentrated wastewater compared to sodium chloride. Significant  
26 membrane fouling was observed when operating at 90% water recovery using raw  
27 wastewater. Nevertheless, membrane fouling was reversible and was effectively controlled by  
28 optimising the hydrodynamic conditions of the cross-flow FO system.

29 **Keywords:** forward osmosis (FO); wastewater; pre-concentration; ionic organic draw  
30 solution; anaerobic digestion; membrane fouling.

31

## 32 **1. Introduction**

33 The shift from aerobic to anaerobic biological treatment processes is a necessary step to  
34 achieve energy efficient wastewater treatment and to facilitate resource recovery practices  
35 (Frijns et al., 2013; Verstraete et al., 2009; Wei et al., 2014). Anaerobic treatment has two  
36 major advantages over aerobic treatment, including energy recovery via methane production  
37 and reduced energy input, since aeration is not required (Appels et al., 2008). Furthermore,  
38 anaerobic effluent represents a practical platform for nutrient recovery (Ansari et al., 2016;  
39 Xie et al., 2014b).

40 In general, municipal wastewater is not suitable for direct anaerobic treatment. Indeed, given  
41 the low organic matter content of municipal wastewater (indicated by a chemical oxygen  
42 demand (COD) of usually less than 500 mg/L), the thermal energy and physical footprint  
43 required for anaerobic treatment can be excessive. Importantly, anaerobic treatment requires  
44 a feed solution in excess of 1,000 mg COD/L to ensure system stability and process  
45 efficiency (Khanal, 2009). An innovative approach to overcome the challenges associated  
46 with the anaerobic treatment of municipal wastewater involves the initial pre-concentration of  
47 organic matter prior to feeding the digester.

48 The net energy recovery of anaerobic systems is theoretically proportional to the COD of the  
49 feed solution. Thus, pre-concentrating the organic matter in wastewater can significantly  
50 benefit the economics of anaerobic treatment processes. An ideal pre-concentration process  
51 would essentially separate water and non-aqueous components, to produce high quality water  
52 for reuse and a concentrate stream suitable for anaerobic treatment. Previously suggested  
53 methods include dynamic sand filtration, dissolved air flotation, and bio-flocculation (Frijns  
54 et al., 2013; Verstraete et al., 2009). However, these systems have limited organics retention  
55 capability and effluent from these processes still requires membrane filtration to produce  
56 water suitable for reuse. High rejection membrane processes such as nanofiltration (NF) and  
57 reverse osmosis (RO) can pre-concentrate the organic content of wastewater. Yet, they are  
58 not suitable for direct wastewater treatment and require extensive pre-treatment to control  
59 membrane fouling. Thus, the application of advanced separation technologies which can  
60 handle complex wastewater and achieve low energy treatment will be pivotal to developing  
61 sustainable wastewater treatment practices.

62 Forward osmosis (FO) is a membrane process with significant advantages when applied to  
63 wastewater treatment for fresh water production and resource recovery (Lutchmiah et al.,  
64 2014b; Xie et al., 2016). Unlike pressure driven membrane processes, the driving force of  
65 water permeation for FO is the osmotic pressure gradient between the feed solution  
66 (wastewater) and the draw solution (e.g. NaCl) (Cath et al., 2006). FO can directly pre-  
67 concentrate wastewater without significant external energy input (Alturki et al., 2013; Cath et  
68 al., 2006; Lutchmiah et al., 2014b). Furthermore, the nature of the driving force means that  
69 the process has a low fouling propensity and fouling can be highly reversible (Mi and  
70 Elimelech, 2010; Mi and Elimelech, 2013; She et al., 2016). Therefore, treatment of complex  
71 matrices such as wastewater by FO is feasible and key constituents including organic matter  
72 and nutrients can be retained in the concentrate. Fresh water can also be recovered from the  
73 draw solution by applying an additional desalination process such as NF (Nguyen et al.,  
74 2015), RO (Holloway et al., 2014; Luo et al., 2016), or membrane distillation (MD) (Nguyen  
75 et al., 2016; Xie et al., 2013). In particular, as a thermally driven desalination processes, MD  
76 presents a unique opportunity, as the required thermal energy could be supplied by solar  
77 thermal energy or from biogas co-generation produced from the subsequent anaerobic  
78 digestion of pre-concentrated wastewater (Duong et al., 2016).

79 FO is recognised as a promising approach to pre-concentrate wastewater prior to anaerobic  
80 treatment (Ansari et al., 2015; Lutchmiah et al., 2014a; Wei et al., 2014; Zhang et al., 2014),  
81 however this approach is yet to be fully explored. Recent studies have focused almost  
82 exclusively on the integration of FO and anaerobic treatment to form an anaerobic osmotic  
83 membrane bioreactor (An-OMBRs) (Chen et al., 2014; Gu et al., 2015; Yin Tang and Ng,  
84 2014) or to filter anaerobic effluent (Ding et al., 2014; Ding et al., 2016; Onoda et al., 2015).  
85 To date, very few studies have investigated the use of FO for direct treatment of municipal  
86 wastewater (Wang et al., 2016; Xie et al., 2013; Zhang et al., 2014). The FO wastewater pre-  
87 concentration concept allows for the simultaneous extraction of clean water for beneficial  
88 reuse while pre-concentrating wastewater to a higher strength suitable for anaerobic  
89 treatment. In this approach, a higher degree of control and accessibility exists for the FO  
90 component as it is not confined within a bioreactor, as is the case for An-OMBRs. In their  
91 recent work, Zhang et al. (2014) demonstrated the FO wastewater pre-concentration process,  
92 however due to the limitations of their experimental set-up, could only demonstrate a COD  
93 concentration factor of approximately three. Wang et al. (2016) presented the treatment  
94 performance of a spiral wound FO module to concentrate wastewater. Nevertheless, issues of

95 salinity accumulation and anaerobic treatment integration were not addressed by Wang et al.  
96 (2016).

97 Although there is growing interest in the application of FO for wastewater pre-concentration  
98 and subsequent energy/resource recovery, the assessment of key performance factors has not  
99 been systematically investigated to date. Several challenges must be addressed for the  
100 implementation of the proposed FO wastewater pre-concentration process. Firstly, salinity  
101 accumulation is a major problem for high retention membrane systems such as FO, and  
102 particularly when combined with a sensitive biological process (Lay et al., 2010; Luo et al.,  
103 2014; Nawaz et al., 2013). Secondly, membrane fouling remains a prominent challenge for  
104 the sustained wastewater filtration of such complex wastewater solutions (Lutchmiah et al.,  
105 2011; Valladares Linares et al., 2013; Xie et al., 2013; Zhang et al., 2014).

106 This study aims to elucidate the key factors governing FO membrane performance during  
107 wastewater pre-concentration. The effectiveness of FO at pre-concentrating wastewater was  
108 examined by evaluating the ability of the FO membrane to retain COD at different water  
109 recoveries. Next, we evaluated the use of ionic organic draw solutes to mitigate salinity build-  
110 up. The effect of the selected draw solution on the produced clean water flux, COD, and pH  
111 of the concentrated wastewater was also investigated. Lastly, the extent of membrane fouling  
112 was assessed and hydrodynamic conditions were optimised. Both batch and continuous flow  
113 experiments were conducted to observe FO membrane fouling behaviour with real  
114 wastewater under intense pre-concentration conditions. Overall, this study proposes the  
115 importance of draw solution selection and optimised hydrodynamic conditions for the  
116 application of FO for wastewater pre-concentration.

## 117 **2. Materials and Methods**

### 118 *2.1 Materials and chemicals*

119 Cellulose triacetate (CTA) membrane with a non-woven support was used in this study and  
120 was acquired from Hydration Technologies Innovation (Albany, Oregon, USA). The overall  
121 thickness of this non-woven CTA membrane is 144  $\mu\text{m}$ . The average pore size is expected to  
122 be similar to that of a CTA membrane with embedded support which has been reported to be  
123 0.37  $\mu\text{m}$  by Xie et al. (2014a). Experiments were conducted with analytical grade draw  
124 solutes, at a constant osmotic pressure of 60 bar. The concentration of each draw solution at  
125 this pressure was calculated using OLI Stream Analyzer (OLI Systems, Inc., Morris Plains,

126 New Jersey, USA). Sodium chloride, sodium acetate, and EDTA-2Na were used as draw  
127 solutions and the concentrations corresponding to 60 bar osmotic pressure were 1.27, 1.49,  
128 and 0.61 M, respectively.

129 Primary effluent (i.e. wastewater after primary sedimentation) was obtained from  
130 Wollongong Wastewater Treatment Plant (Wollongong, Australia). All batch experiments  
131 were conducted using both low and moderate strength wastewater, to represent the variability  
132 of municipal wastewater influent quality. Moderate strength wastewater was obtained during  
133 a dry weather period. Low strength wastewater was obtained immediately after a wet weather  
134 period.

## 135 2.2 *Forward osmosis system*

136 A lab-scale, cross-flow FO membrane system was used. The membrane cell had two  
137 symmetric flow channels both with length, width, and height of 250, 50, and 2 mm,  
138 respectively, resulting in an effective membrane area of 125 cm<sup>2</sup>. The feed and draw  
139 solutions were continuously circulated through each flow channel by two variable speed gear  
140 pumps (Micropump, Vancouver, Washington, USA). The flow rate was regulated by two  
141 rotameters and was adjusted to achieve the desired cross-flow velocity. The majority of  
142 experiments were operated with 1 L/min (corresponding to a cross-flow velocity of 16.7  
143 cm/s). A spacer was placed on the draw solution side of the membrane to improve mixing.

144 The draw solution reservoir was positioned on a digital balance (Mettler-Toledo Inc.,  
145 Hightstown, New Jersey, USA) and weight changes were recorded to calculate permeate  
146 water flux. A reservoir containing a highly concentrated stock solution (5 M) was also placed  
147 on the digital balance and was automatically dosed into the draw solution to maintain a  
148 constant osmotic pressure during experiments. The conductivity of the draw solution was  
149 monitored using a conductivity probe (Cole-Parmer, Vernon Hills, Illinois, USA), and was  
150 connected to a controller and a peristaltic pump to automatically regulate the draw solution  
151 concentration (control accuracy of  $\pm 0.1$  mS/cm).

## 152 2.3 *Experimental protocol*

153 All experiments were conducted in FO mode (i.e. active layer facing the feed solution).  
154 Analytical grade solutes were dissolved in DI water at concentrations corresponding to an  
155 osmotic pressure of 60 bar. Water flux was measured according to the standard procedure



156 previously described by (Cath et al., 2013). Water recovery was used to represent the FO  
157 water extraction rate and was calculated based on the ratio of the cumulative permeate  
158 volume and the initial feed solution volume.

159 For batch experiments, the FO system was used to process primary effluent until a water  
160 recovery of 90% had been achieved. The initial volume of primary effluent (i.e. feed  
161 solution) was 2 L, and the solution was continuously filtered until 90% of the feed solution  
162 had permeated through the membrane (i.e. permeate volume of 1.8 L). Water flux was  
163 continuously monitored. The conductivity, pH, and temperature of each solution were also  
164 regularly measured. A 10 mL sample was withdrawn from the feed solution at specific time  
165 intervals for COD analysis as a measure of the strength of the wastewater or concentrated  
166 solution. All batch experiments were conducted in duplicate.

167 A continuous flow experiment was also conducted whereby 5 L of primary effluent was  
168 firstly processed to achieve 90% water recovery, leaving 0.5 L of pre-concentrated solution.  
169 At this point, the membrane was flushed with DI water to remove the fouling layer. The  
170 system was then continuously operated using a feeding and concentrate withdrawal regime  
171 (maintaining 90% water recovery). Two Masterflex peristaltic pumps (Cole-Parmer, Vernon  
172 Hills, Illinois, USA) were used to supply fresh primary effluent into the feed solution  
173 reservoir and to withdraw concentrate. The experiment was terminated approximately 90  
174 hours after membrane flushing, when the water flux had reduced to half of the initial water  
175 flux. Sodium chloride was used as the draw solution for all continuous flow experiments.

176 Detailed reverse solute flux experiments were conducted to elucidate solute transport  
177 behaviours of the ionic organic draw solutes. The feed solution consisted of 3 L of DI water  
178 and the respective draw solution had a constant osmotic pressure of 60 bar. The conductivity,  
179 pH, and temperature of solutions were measured hourly. The reverse draw solute flux of each  
180 draw solution was measured by monitoring the changes of conductivity in the feed solution  
181 over time. A 20 mL sample was also withdrawn from the DI water feed solution reservoir for  
182 subsequent analysis of sodium and total organic carbon (TOC) to determine the reverse solute  
183 flux of sodium, and acetate and EDTA, respectively.

#### 184 *2.4 Analytical methods*

185 Key water quality parameters of the primary effluent were measured according to standard  
186 methods. COD was measured using a Hach DRB200 COD Reactor and Hach DR3900

187 spectrophotometer (program number 435 COD HR) following the US-EPA Standard Method  
188 5220. Adequate dilutions and adjustments were made to minimise chloride interference  
189 during sample measurements. A Shimadzu analyser (TOC-V<sub>CSH</sub>) was used to determine TOC  
190 concentration. An inductively coupled plasma – optical emission spectroscopy (ICP-OES)  
191 system (ICP-OES 710, Agilent, Australia) was used to determine the sodium ion  
192 concentration in the samples. Temperature, pH, and electrical conductivity were measured  
193 using an Orion 4-Star pH/conductivity meter (Thermo Scientific, Waltham, MA).

### 194 **3. Results and discussion**

#### 195 *3.1 FO pre-concentration of organic matter in wastewater*

196 Low strength wastewater can be pre-concentrated by FO up to the range suitable for  
197 anaerobic digestion (i.e. approximately 1,000 mg COD/L). In this study, both low strength  
198 ( $137\pm 8$  mg COD/L), and moderate strength wastewater ( $356\pm 13$  mg COD/L) were pre-  
199 concentrated until 90% water recovery was achieved (Figure 1A). The FO process  
200 predominantly extracted clean water, therefore enriching the concentration of organic matter  
201 in the feed solution. Results show that the FO process consistently pre-concentrated COD up  
202 to approximately eightfold, independent of the initial wastewater COD. The low and  
203 moderate strength wastewater COD concentrations were increased up to  $982\pm 61$  and  
204  $2,893\pm 70$  mg/L, respectively. These results demonstrate the suitability of FO for pre-  
205 concentrating wastewater, and its robustness for treating wastewater with variable influent  
206 quality. Furthermore, pre-concentrating wastewater with FO produces a reduced solution  
207 volume (i.e. ten times reduction at 90% water recovery) that is rich in organics and is  
208 arguably more amenable to anaerobic digestion compared to directly digesting raw  
209 wastewater.

210 The concentration of COD in wastewater increased proportionally with the FO system water  
211 recovery (Figure 1B). The FO membrane effectively retained a large proportion of organic  
212 matter in the feed solution, shown by the comparability of the experimental COD  
213 concentration with the calculated mass balance (i.e. assuming 100% COD retention in the  
214 feed solution). The experimental results were only slightly lower than values obtained from  
215 mass balance calculation and this observation can possibly be explained by the accumulation  
216 of solid organics within the membrane cell. In other words, a portion of the bulk pre-  
217 concentrated wastewater COD gradually formed a cake layer on the membrane surface.

218 Therefore, the measured feed solution COD concentration was lower than expected,  
219 particularly at high water recoveries where solids content was high. To a lesser degree, the  
220 observed COD pre-concentration behaviour may also relate to the incomplete rejection of  
221 COD by the FO membrane (i.e. 99% rejection) (Valladares Linares et al., 2013).  
222 Theoretically, the COD concentration factor could be further maximised by increasing water  
223 recovery, or when higher strength wastewater is used as the feed solution (i.e. >500 mg  
224 COD/L), yet this would further exacerbate the issues of salinity accumulation (Section 3.2.1)  
225 and membrane fouling (Section 3.3). The eightfold concentration of COD achieved in this  
226 study is substantially higher than previous studies (i.e. three-fold COD concentration) (Zhang  
227 et al., 2014) and is attributed to the longer process filtration time and potentially the lower  
228 initial COD of the wastewater.

229

### [FIGURE 1]

230 The enhanced organic content of FO concentrated wastewater can enable this solution to be  
231 fed into an anaerobic digester, and is arguably more effective when compared to direct  
232 anaerobic digestion of dilute wastewater. The net energy recovery from an anaerobic digester  
233 is theoretically proportional to the feed COD concentration, and therefore the FO system  
234 water recovery (Wei et al., 2014). Thus, the increased COD concentration of FO pre-  
235 concentrated wastewater would increase energy recovery per unit volume of digestate.  
236 Furthermore, since 90% of the initial water content has been extracted by the FO process for  
237 further treatment, the volume of feed that requires heating to optimum mesophilic conditions  
238 (i.e. 35 °C) during anaerobic treatment is lowered ten-fold (when compared with raw  
239 wastewater). In addition, when the FO process is combined with other desalination processes,  
240 high quality water can be reclaimed for reuse (Chekli et al., 2016). Overall, FO presents a  
241 direct and robust approach to wastewater treatment, by focussing on pre-concentrating  
242 organic matter to facilitate subsequent anaerobic digestion for energy recovery.

243 *3.2 Ionic organic draw solutes for wastewater pre-concentration*

244 *3.2.1 Salinity accumulation*

245 Salinity accumulation is a major hindrance for high retention membrane systems such as FO,  
246 particularly when coupled with a biological process (Luo et al., 2014). Intensive pre-  
247 concentration of wastewater by FO leads to the accumulation of salinity in the feed solution  
248 via two mechanisms. Firstly, the natural salinity of wastewater is retained by the FO

249 membrane, and therefore the salt concentration increases proportionally to the system water  
250 recovery. Secondly, salt leaks from the draw solution into the feed solution (i.e. reverse draw  
251 solute flux) and can also significantly contribute to salinity accumulation (Cath et al., 2006).  
252 Salinity accumulation in FO systems can have detrimental effects on water flux, as the  
253 osmotic pressure of the feed solution is increased, thereby reducing the effective osmotic  
254 driving force. More importantly for this application, high salt content within the pre-  
255 concentrated wastewater can have adverse effects on subsequent anaerobic treatment  
256 processes (Ansari et al., 2015).

257 A promising approach to mitigate salinity build-up in FO pre-concentrated wastewater  
258 involves the use of ionic organic draw solutes. When sodium chloride was used as the draw  
259 solution, the conductivity of wastewater significantly increased as water recovery increased  
260 (Figure 2A). On the other hand, ionic organic draw solutes such as sodium acetate and  
261 EDTA-2Na presented a significantly lower conductivity compared to sodium chloride,  
262 demonstrating mitigation of salinity accumulation to a high degree. A similar result was  
263 expected by Bowden et al. (2012) when using organic ionic draw solutes in an aerobic  
264 osmotic membrane bioreactor. Because each experiment pre-concentrated wastewater to 90%  
265 water recovery, the main contributor to the variance in salinity was the reverse draw solute  
266 flux. As shown in Figure 2B, the extent of salt accumulation was inversely related to the  
267 magnitude of reverse solute flux selectivity (RSFS) for each draw solution. Both sodium  
268 acetate and EDTA-2Na exhibited a larger RSFS compared to sodium chloride, indicating that  
269 a smaller amount of solute diffused through the membrane for a constant permeate volume.  
270 Thus, adopting ionic organic draw solutions could achieve a pre-concentrated solution with a  
271 lower salinity, without compromising the achievable organic content in pre-concentrated  
272 wastewater.

## 273 [FIGURE 2]

274 The lower reverse solute flux behavior of sodium acetate and EDTA-2Na can be explained by  
275 the mobility of the draw solute molecule. Both draw solutes have a lower diffusivity  
276 compared to sodium chloride, as acetate and EDTA ions are significantly larger than chloride  
277 (Ansari et al., 2015). Thus, solute diffusion from the draw solution to the feed solution is  
278 restricted. This has implications for the attainable water flux for each draw solution (Section  
279 3.2.3). Binary ion analysis for sodium acetate showed a similar performance to sodium

280 chloride, whereby both the cation and anion diffused into the feed solution at a similar rate  
281 (Figure 3A). In contrast, binary ion analysis for EDTA-2Na revealed the potential decoupling  
282 of sodium and EDTA diffusion rates (Figure 3B). In other words, sodium tended to diffuse  
283 through the FO membrane at a faster rate than EDTA. This is likely due to the large size and  
284 high negative charge of EDTA, minimising EDTA diffusion through the membrane (Hau et  
285 al., 2014). Nonetheless, despite the identified decoupling of the EDTA-2Na draw solute,  
286 compared to sodium chloride and sodium acetate, the reverse salt flux with respect to only  
287 sodium was still insignificant. The combination of EDTA with solutes other than sodium has  
288 also shown potential to minimise reverse solute flux and would greatly benefit the FO pre-  
289 concentration process (Nguyen et al., 2015).

### 290 [FIGURE 3]

#### 291 3.2.2 COD content of pre-concentrated wastewater

292 In addition to mitigating salinity build-up, ionic organic draw solutes enhance COD when  
293 pre-concentrating low strength wastewater. At 90% water recovery, both sodium acetate and  
294 EDTA-2Na displayed higher COD concentrations compared to sodium chloride (Figure 4A).  
295 This may be due to the reverse solute flux of the ionic organic draw solutes, enhancing the  
296 COD concentration of the low strength wastewater. Although reverse solute flux is generally  
297 viewed as a hindrance for the FO process, in the case of ionic organic draw solutes, the  
298 mechanism could be beneficial for subsequent anaerobic treatment. For example, unlike  
299 sodium chloride which inhibits methane production during anaerobic treatment, the presence  
300 of sodium acetate and EDTA-2Na in pre-concentrated wastewater can benefit methane  
301 production (Ansari et al., 2015). By adopting ionic organic draw solutes when treating low  
302 strength wastewater, opportunities exist to operate at a favourably lower water recovery,  
303 whilst attaining the desired COD range and allowable salinity level. On the other hand, for  
304 moderate strength wastewater, the contribution of reverse solute flux to COD concentration  
305 was negligible (Figure 4B). The higher initial COD of the wastewater may have masked the  
306 contribution by reverse solute flux, and was possibly the reason why all three draw solutes  
307 displayed similar COD concentration performance.

### 308 [FIGURE 4]

309 *3.2.3 Effect of draw solute on water flux decline*

310 During the batch wastewater pre-concentration experiments, the choice of draw solute did not  
311 significantly affect water flux decline even at high water recovery values (Figure 5). This  
312 suggests that both membrane fouling and salinity accumulation did not significantly  
313 contribute to water flux decline under these conditions (i.e. small processing volume and 90%  
314 water recovery cycle). As discussed in Section 3.3, continuous operation did result in more  
315 severe membrane fouling. For these batch experiments, the osmotic pressure of the pre-  
316 concentrated wastewater was significantly lower than the draw solution throughout the  
317 experiment. Flux decline was likely caused by the sparse accumulation of foulants on the  
318 membrane surface, as the implemented hydrodynamic conditions (i.e. increased cross-flow  
319 velocity) prevented excessive build-up of foulant materials.

320 **[FIGURE 5]**

321 Although the draw solution did not affect water flux decline, the initial water flux was  
322 significantly governed by the draw solution. Sodium chloride and sodium acetate gave  
323 similar initial water fluxes (5.5 and 5.4 L/m<sup>2</sup>h, respectively) at the same osmotic pressure (i.e.  
324 60 bar), whilst the initial water flux of EDTA-2Na was significantly lower (3.3 L/m<sup>2</sup>h).  
325 EDTA-2Na exhibited the lowest water flux, owing to the negative effects of internal  
326 concentration polarisation (McCutcheon and Elimelech, 2006). This has limitations regarding  
327 the scale-up of FO systems using EDTA based draw solutions, since a large membrane area  
328 would be required. Nonetheless, since FO is an osmotically driven process, other operational  
329 costs would not be significantly impacted.

330 *3.2.4 Effect of draw solute on pre-concentrated wastewater pH*

331 For all three draw solutions, the wastewater pH gradually increased during the pre-  
332 concentration process (Figure 6). This is a result of the net diffusion of hydrogen ions from  
333 the feed to the draw solution. Hydrogen ion diffusion occurs in order to maintain solution  
334 electroneutrality, as a result of reverse solute flux (Hancock and Cath, 2009; Xie et al.,  
335 2014b). When EDTA-2Na was used, the wastewater pH tended to increase at a fractionally  
336 slower rate compared with the other two draw solutions, and may be due to the significantly  
337 lower reverse solute flux rate of EDTA-2Na. Additionally, despite the lower reverse solute  
338 flux of sodium acetate compared to sodium chloride, the basic nature of highly concentrated

339 sodium acetate solution may have contributed to the observed high wastewater pH. Results  
340 indicate that independent of the selected draw solution, FO pre-concentrated wastewater will  
341 have a high pH (approximately pH 8) and thus may need adjustment prior to feeding into an  
342 anaerobic reactor.

343 **[FIGURE 6]**

### 344 3.3 *Membrane fouling*

345 Sustained wastewater pre-concentration inevitably leads to membrane fouling. As shown in  
346 Figure 7, when a cross-flow velocity of 9 cm/s was applied, severe membrane fouling was  
347 evident by a rapid water flux decline. Importantly, a water recovery of only 70% could be  
348 achieved as the water flux had reduced to below 1 L/m<sup>2</sup>h.

349 We increased the cross flow velocity as a hydraulic fouling control method during the  
350 continuous flow experiment. The difference in water flux decline patterns between the two  
351 cross-flow velocities (i.e. 9 cm/s and 17 cm/s) was significant (Figure 7). When the cross-  
352 flow velocity was approximately doubled, water flux decline was considerably lower, and the  
353 target water recovery of 90% could be achieved in one cycle. Increasing the cross-flow  
354 velocity provides additional shear force, which hinders the accumulation of foulants on the  
355 membrane surface (Boo et al., 2013). For the higher cross flow velocity, the water flux  
356 decline was minimal up to a water recovery of 70%. From this point onwards, water flux  
357 declined more rapidly, most likely due to the increased solids content of the pre-concentrated  
358 wastewater at high water recoveries. Despite the flux declining by approximately half at a  
359 water recovery of 90%, the increased cross-flow velocity was shown to effectively reduce the  
360 rate of water flux decline for the complex pre-concentrated wastewater solution. High cross-  
361 flow velocity flushing regimes can be further optimised to lower the energy consumption of  
362 this membrane fouling control strategy. However, this aspect is beyond the scope of our  
363 current study.

364 **[FIGURE 7]**

### 365 3.4 *Fouling reversibility and water flux sustainability*

366 Increasing the applied cross-flow velocity resulted in less flux decline during wastewater pre-  
367 concentration. However, after one cycle, water flux still declined to approximately 50% of  
368 the initial value. After membrane flushing, the initial water flux was completely restored

369 (Figure 8), demonstrating the reversibility of FO membrane fouling. Furthermore, this water  
370 flux recoverability highlights the negligible contribution of feed water salinity increase to  
371 water flux decline. The FO process inherently inhibits fouling due to the nature of the  
372 osmotic driving force. The absence of hydraulic pressure promotes a loose and highly  
373 reversible fouling layer. In addition, FO generally operates at a low water flux and therefore a  
374 lower fouling rate (Shaffer et al., 2015). For these reasons, simple membrane flushing is a  
375 highly effective cleaning strategy.

376 **[FIGURE 8]**

377 Longer-term water flux behaviour was observed by continuously operating the FO system  
378 with the pre-concentrated wastewater solution (i.e. fixed 90% water recovery) after one pre-  
379 concentration cycle. In other words, after 70 hours of operation, fresh primary effluent was  
380 fed into the FO feed solution and concentrate was withdrawn to maintain a constant 90%  
381 system water recovery. From 70 hours onwards, the water flux gradually declined due to the  
382 continuous exposure to the pre-concentrated wastewater. Interestingly, the rate of water flux  
383 decline gradually decreased and appeared to reach a steady state at approximately 150 hours.  
384 This may indicate that the fouling cake layer had reached a maximum thickness, due to the  
385 cross flow conditions. Nonetheless, membrane fouling remains a prominent hurdle for FO  
386 systems and further efforts are required to investigate the effectiveness of other fouling  
387 mitigation methods during wastewater pre-concentration.

#### 388 **4. Conclusion**

389 Pre-concentration of wastewater using FO presents a feasible approach to maximise the  
390 content of organic matter and possibly improve the digestibility of wastewater. In this study,  
391 the FO system achieved a COD concentration factor of approximately eightfold for low and  
392 moderate strength wastewater, at a water recovery of 90%. Specifically, FO allows for the  
393 pre-concentration of wastewater to the COD range (i.e. >1,000 mg/L) suitable for biogas  
394 production via anaerobic treatment, even with low strength primary effluent obtained during  
395 wet weather. Furthermore, the importance of draw solution selection is emphasised, as ionic  
396 organic draw solutes benefited the pre-concentration process in two ways. Both sodium  
397 acetate and EDTA-2Na solutes mitigated excessive salinity build-up in the pre-concentrated  
398 wastewater due to their lower reverse solute fluxes. Additionally, the ionic organic draw  
399 solutes enhanced the COD of low strength pre-concentrated wastewater, and are expected to



400 benefit the solutions digestibility in terms of biogas production compared to sodium chloride.  
401 Significant membrane fouling was observed when operating at 90% water recovery using raw  
402 wastewater during the continuous flow experiment. However, this was reversible and could  
403 be controlled by optimising the hydrodynamic conditions during the FO process. Further  
404 developments of this FO wastewater pre-concentration process are recommended, including  
405 sustainable membrane fouling mitigation strategies and techno-economic evaluation at pilot  
406 scale level.

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410 University of Wollongong is gratefully acknowledged.

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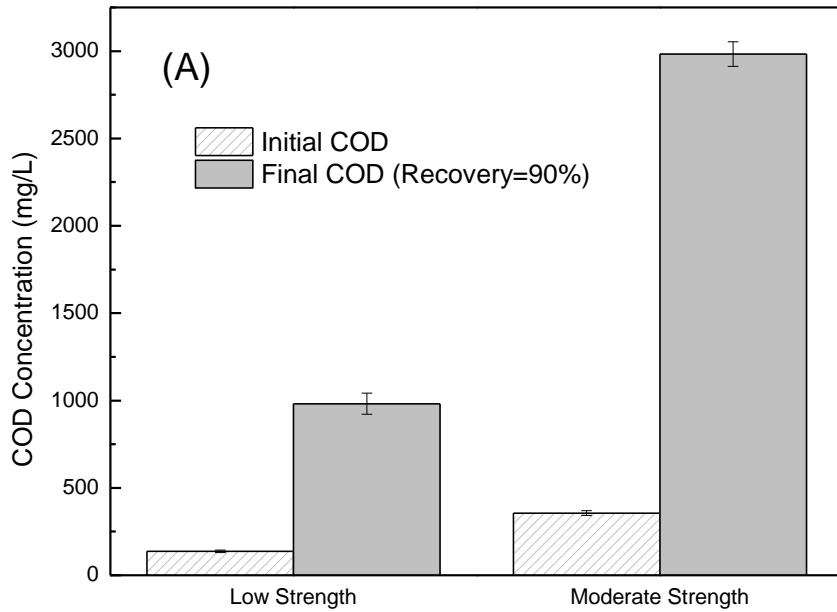
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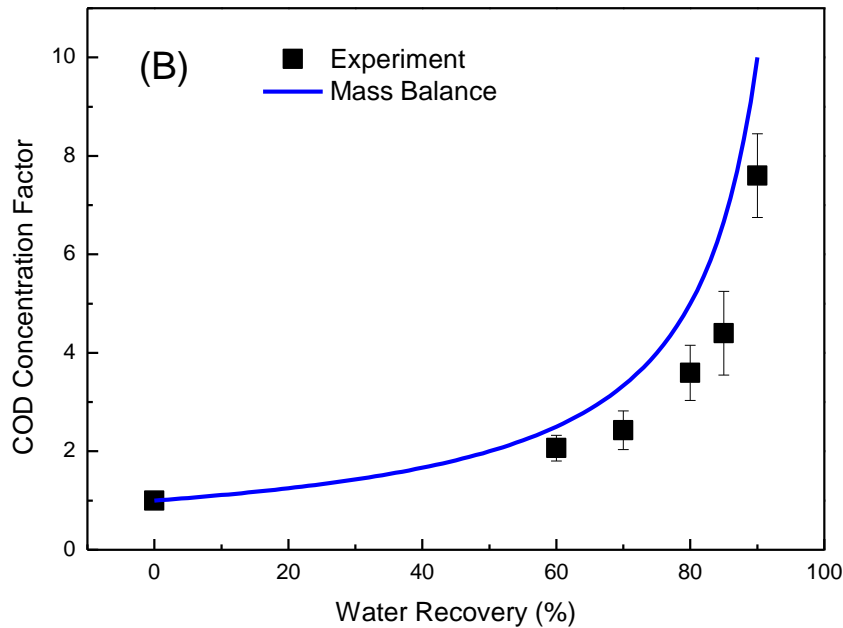
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530 **LIST of FIGURES**

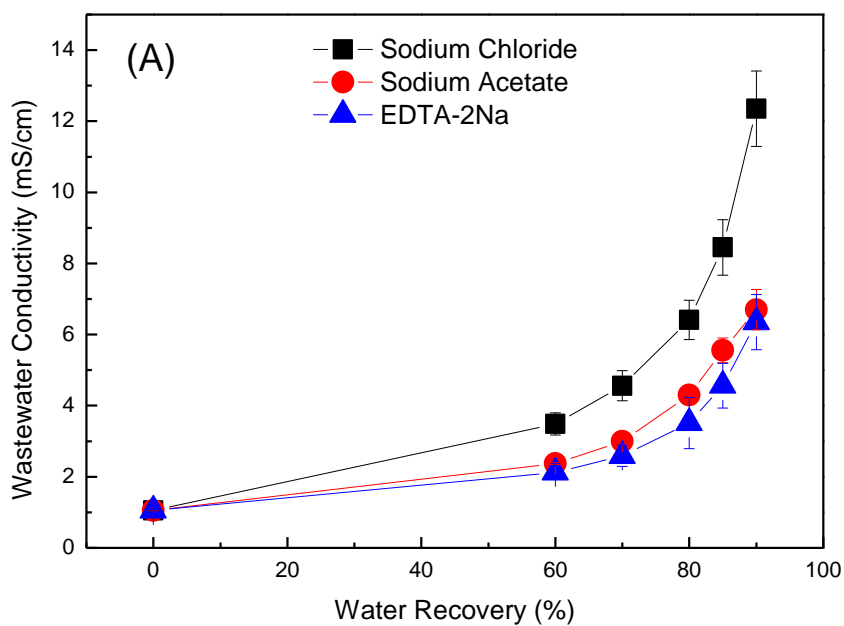


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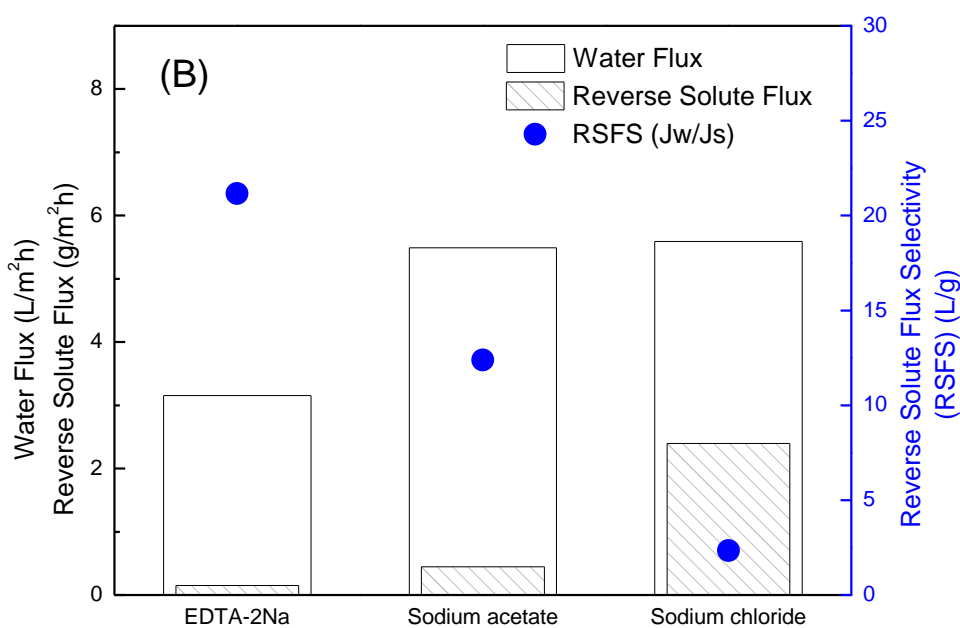


532

533 **Figure 1:** (A) Initial and final (i.e. at water recovery of 90%) COD concentrations for low  
 534 and moderate strength wastewater. Error bars represent the standard deviation of triplicate  
 535 COD sample measurements. (B) Variation of experimental and calculated wastewater COD  
 536 concentration factor during FO pre-concentration. Error bars represent the standard deviation  
 537 of triplicate COD sample measurements from duplicate experiments. The initial wastewater  
 538 COD for low and moderate strength wastewater were  $137 \pm 8$  mg/L, and  $356 \pm 13$  mg/L,  
 539 respectively. Mass balance assumes 100% COD retention in feed solution. Experimental  
 540 conditions: Primary effluent feed solution (2 L);  $\pi = 60$  bar, NaCl draw solution; cross-flow  
 541 rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of  
 542 16.7 cm/s).

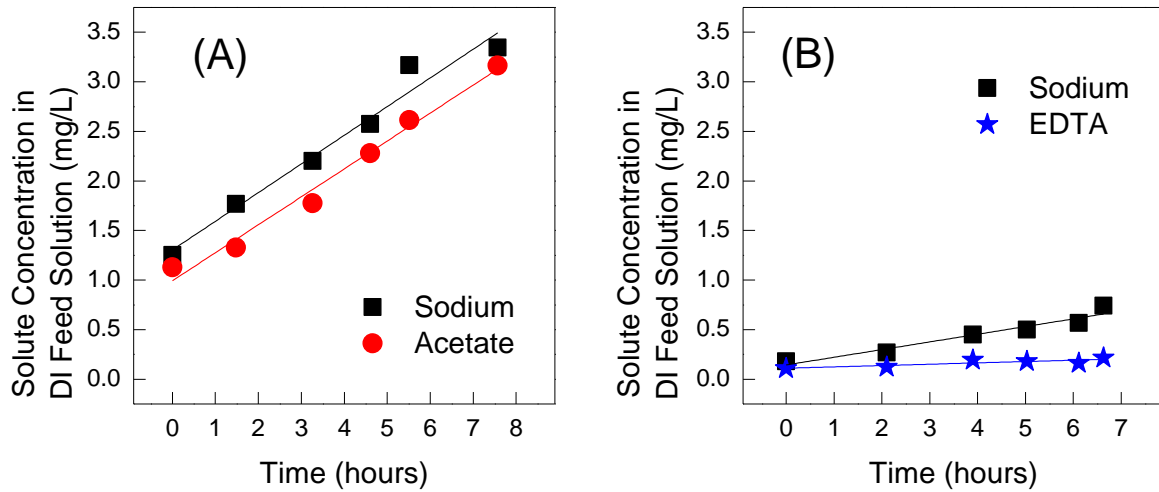


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544

545 **Figure 2:** (A) Variation of wastewater conductivity during wastewater pre-concentration for  
 546 sodium chloride, sodium acetate, and EDTA-2Na. Experimental conditions: Primary effluent  
 547 feed solution (2 L);  $\pi = 60$  bar draw solution; cross-flow rates of both feed and draw solutions  
 548 were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s). The initial wastewater  
 549 conductivity was  $1.05 \pm 0.02$  mS/cm. (B) Water flux, reverse solute flux, and RSFS of sodium  
 550 chloride, sodium acetate, and EDTA-2Na. Experimental conditions: As above, with DI water  
 551 feed solution (4 L). Error bars represent the standard deviation of measurements from  
 552 duplicate experiments.

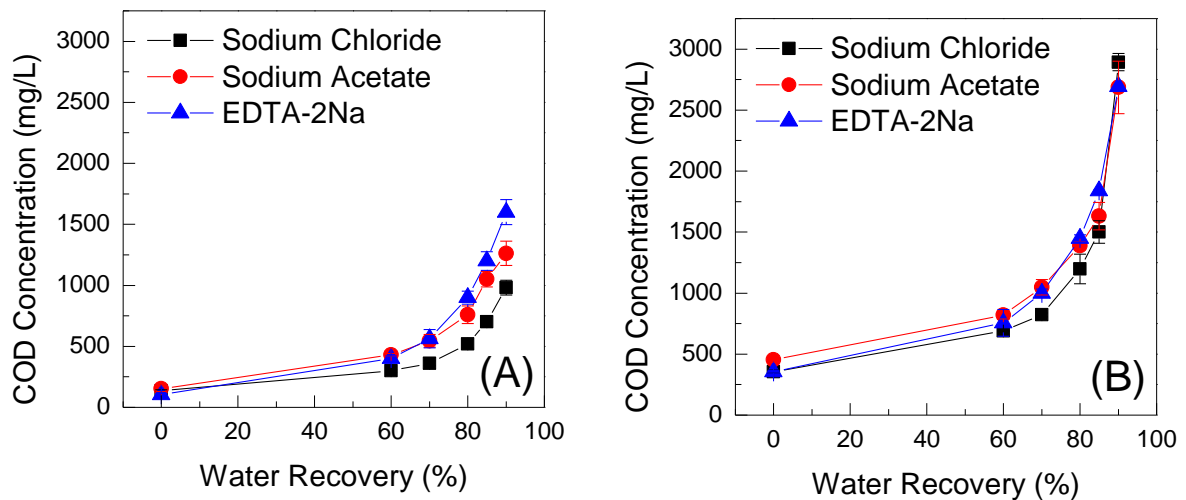


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554 **Figure 3:** Ionic organic draw solution binary ion diffusion analysis with linear regressions.  
 555 (A) Sodium acetate and (B) EDTA-2Na. Experimental conditions: As in Figure 2B.

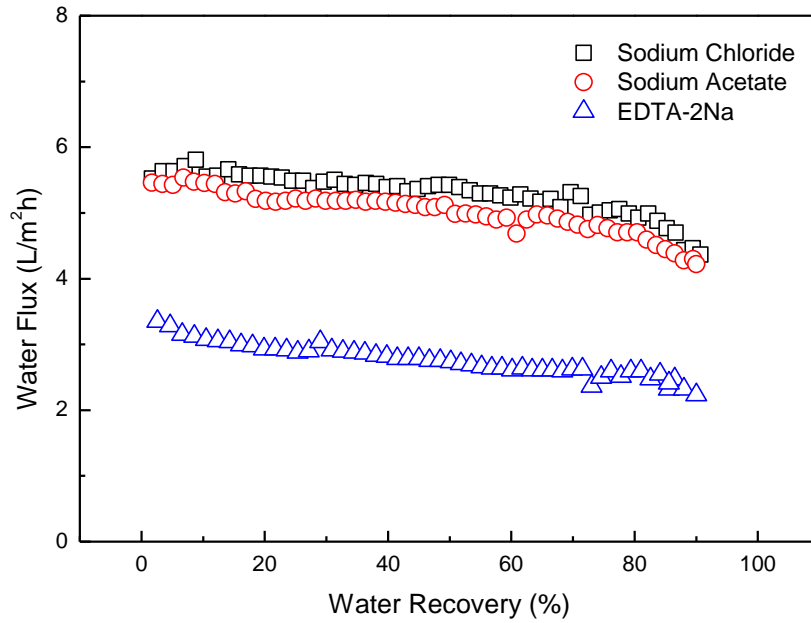
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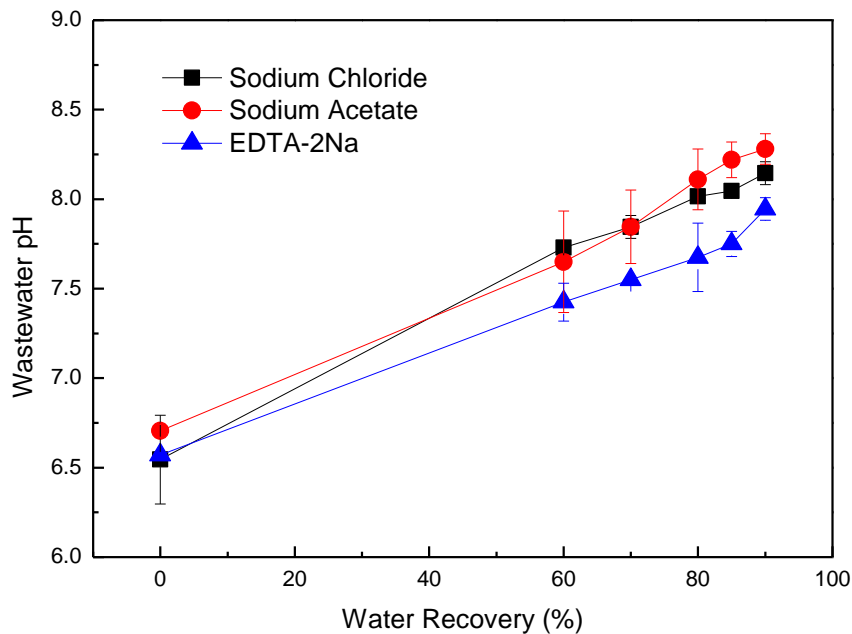
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559 **Figure 4:** Variation of COD concentration during wastewater pre-concentration for (A) low  
 560 strength and (B) moderate strength wastewater. Experimental conditions: Primary effluent  
 561 feed solution (2 L);  $\pi = 60$  bar draw solution; cross-flow rates of both feed and draw solutions  
 562 were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s). Error bars represent the  
 563 standard deviation of triplicate COD measurements.



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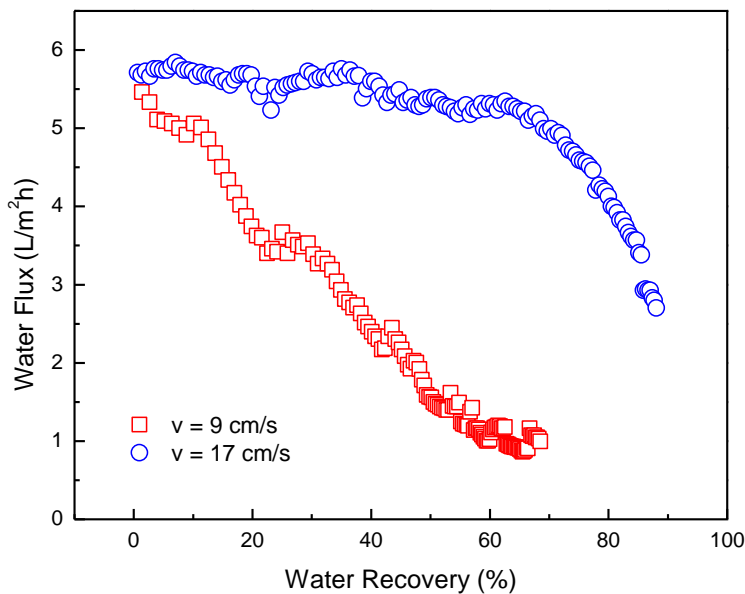
565 **Figure 5:** Water flux decline during batch wastewater pre-concentration. Experimental  
 566 conditions: Primary effluent feed solution (2 L);  $\pi = 60$  bar draw solution; cross-flow rates of  
 567 both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7  
 568 cm/s).



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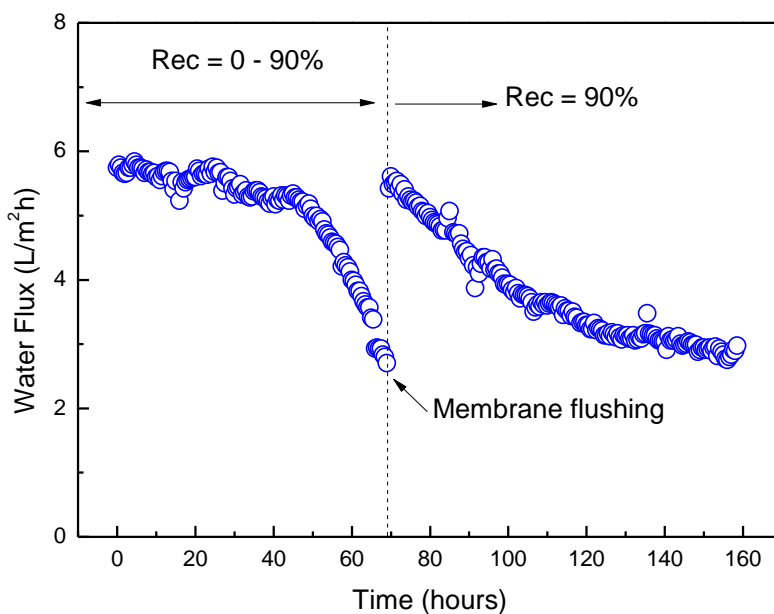
570 **Figure 6:** Variation of pre-concentrated wastewater pH during batch wastewater pre-  
 571 concentration experiments. Experimental conditions: Primary effluent feed solution (2 L);  $\pi =$   
 572 60 bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min  
 573 (corresponding to a cross-flow velocity of 16.7 cm/s). Error bars represent the standard  
 574 deviation of measurements from duplicate experiments.





575

576 **Figure 7:** Effect of applied cross flow velocity on water flux during the continuous flow  
 577 experiment. Experimental conditions: Primary effluent feed solution (5 L);  $\pi = 60$  bar, NaCl  
 578 draw solution; cross-flow rates of both feed and draw solutions were adjusted to achieve  
 579 desired cross-flow velocity.



580

581 **Figure 8:** Variation of water flux during the continuous flow experiment for one pre-  
 582 concentration cycle and at a fixed 90% water recovery (i.e. Rec=90%). Experimental  
 583 conditions: Primary effluent feed solution (5 L);  $\pi = 60$  bar, NaCl draw solution; cross-flow  
 584 rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of  
 585 16.7 cm/s).

