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1 **Hybrid forward osmosis-reverse osmosis for wastewater reuse and seawater**
2 **desalination: Understanding the optimal feed solution to minimise fouling**

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25 **Abstract**

26 To enhance the seawater desalination energy efficiency forward osmosis – reverse osmosis (FO-RO)
27 hybrid system has recently been developed. In this process, the FO “pre-treatment” step is designed to
28 dilute the seawater (SW) with reclaimed wastewater (WW) before the desalination step, thereby
29 reducing the energy demand for the SWRO process. However, membrane fouling is a major issue that
30 needs to be addressed. Proper selection of suitable WWs is necessary before proceeding with large-
31 scale FO-RO desalination plants. In this study, long-term experiments were carried out, using state-of-
32 the-art FO membrane with real WW solutions. A combination of water flux modelling and membrane
33 characterisation were used to fouling to process performance. Initial water fluxes as high as $22.5 \text{ L.m}^{-2}.\text{h}^{-1}$
34 were observed when using biologically treated secondary effluent. It was also found that secondary
35 effluents cause negligible flux decline. On the other hand, biologically treated wastewater and raw
36 wastewater caused mild and severe flux decline respectively (25% and 50% of flux decline after 80 hrs,
37 compared to no-fouling conditions). Ammonia leakage to the diluted seawater was also measured,
38 concluding that, if biologically treated wastewater is used as feed, the final NH_4^+ concentration in the
39 draw is likely to be negligible.

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46 **Keywords:** Forward osmosis; membrane fouling; osmotic dilution; seawater; wastewater.

47 1 Introduction

48 Ensuring availability and sustainable management of water and sanitation for all was one of the 17
49 Sustainable Development Goals put forward by the United Nations for the 2030 Agenda [1]. The lack
50 of access to clean water is a significant health concern in developing countries, as more than 2 billion
51 people live without proper sanitation, and millions die from waterborne diseases every year [2]. At the
52 beginning of the millennium, about 27% of the world population already lived in water-stressed regions,
53 and this number is expected to keep rising as these regions are now experiencing population growth and
54 industrialisation [3]. Moreover, one of the several consequences of climate change is putting an
55 additional strain on water resources all over the world. In 2014, the 5th assessment report of the
56 international panel on climate change warned against the possible adverse impacts of increased
57 greenhouse gases emissions on renewable freshwater availability and safety, especially in presently dry
58 regions [4]. Shannon et al. [5] highlighted several paramount research areas where further work is
59 needed to ensure more efficient and sustainable use of water resources. Among them are the reclamation
60 of impaired water and desalination.

61 With more than 97% of the world's water being seawater or brackish water, desalination technologies
62 have been seen as a way to drastically increase the water supply thereby getting closer to meeting the
63 future water demand. The first desalination plants have been opened in the middle of the twentieth
64 century and relied on thermal processes to treat the saline feeds and produce fresh water. Since then,
65 membrane processes have proven to be less energy-intensive, and seawater reverse osmosis (SWRO)
66 is now used in most desalination plants [6]. Reverse osmosis (RO) is the most widespread water-
67 purifying technique. It applies hydraulic pressure to overcome the osmotic pressure of a solution,
68 thereby allowing water from a saline or contaminated feed stream (e.g., seawater, brackish water,
69 wastewater) to cross a semi-permeable membrane while rejecting ions and other contaminants. The
70 produce water costs of current RO designs in SWRO plants lies between 0.5-1 USD m⁻³ [7]. However,
71 the SWRO energy consumption is not expected to improve as we are near the limit set by
72 thermodynamics [8]. Making use of impaired water sources could be a way to reduce the produced
73 water cost [7]. However, if wastewater is sent directly through an RO process, irreversible fouling of
74 the RO membrane is expected to occur [9].

75 In alignment with the principles of circular economy, reclamation means viewing wastewater (WW) as
76 a possible valuable resource and not as pure waste that needs to be disposed of. It is, however,
77 paramount to find non energy intensive technologies. This is to reduce, or at least not increase, the
78 already high WW treatment cost due to e.g. pumping, aeration and biosolids treatment. If this is
79 achieved, the treated effluents can even be made available for re-use, e.g. irrigation, toilet flushing,
80 cooling towers, etc. [10].

81 Because of its lower irreversible fouling propensity, forward osmosis (FO) was recently investigated as
82 SWRO pre-treatment to make use of impaired water sources (e.g., wastewater primary or secondary
83 effluent) to reduce the fresh water production cost [7]. In the FO pre-treatment step, seawater is used as
84 a draw solution (DS) to extract water from an impaired water source. Water transport is created as the
85 osmotic pressure of seawater (i.e., 25-30 bars) is much higher than the one of sewage wastewater (i.e.,
86 0.3-1 bar). Afterwards, the diluted seawater is sent through the SWRO filtration to produce fresh water.
87 This pre-treatment step lowers the SWRO operating pressure, as it reduces the osmotic pressure of
88 seawater, thereby moderating the energy demand of the desalination step. As aforementioned, due to
89 the absence of hydraulic pressure, the FO process was found to be less prone to irreversible fouling
90 [11]. This application that is particularly interesting is the use of reclaimed WW [12], as it will also
91 produce concentrated dewatered waste that can be reused for nutrients recovery or disposed of.

92 Several researchers have investigated the performance and feasibility of the FO-RO hybrid system, both
93 at lab-scale and pilot-scale, using different types of FO membranes [13-16]. However, at this stage, this
94 process is still not ready for large-scale implementation, primarily because of the issue of membrane
95 fouling. Fouling, which is the deposition of different components (organic, inorganic, or living matter)
96 on the membrane, is a recurrent problem when working with challenging stream such as wastewater
97 [17]. Despite the lower fouling propensity of FO compared to SWRO, when high fouling potential
98 solutions are used, i.e. raw WW, this issue persists. Strategies need to be systematically developed to
99 lessen the impact of this phenomenon as it decreases the water flux and affects the product water quality
100 while damaging the membrane, hence increasing the operational and capital costs. Although raw WW
101 is cheap and readily available, removals of membrane fouling promoters are still necessary before the
102 FO filtration. As pre-treatment operations will inevitably increase the overall cost, a trade-off needs to
103 be found between membrane fouling and an acceptable number of pre-treatment steps. Understanding
104 the degree of raw WW pre-treatment is necessary to minimise the process cost and therefore to select
105 the best feed for this application is crucial to ensure optimal process operation.

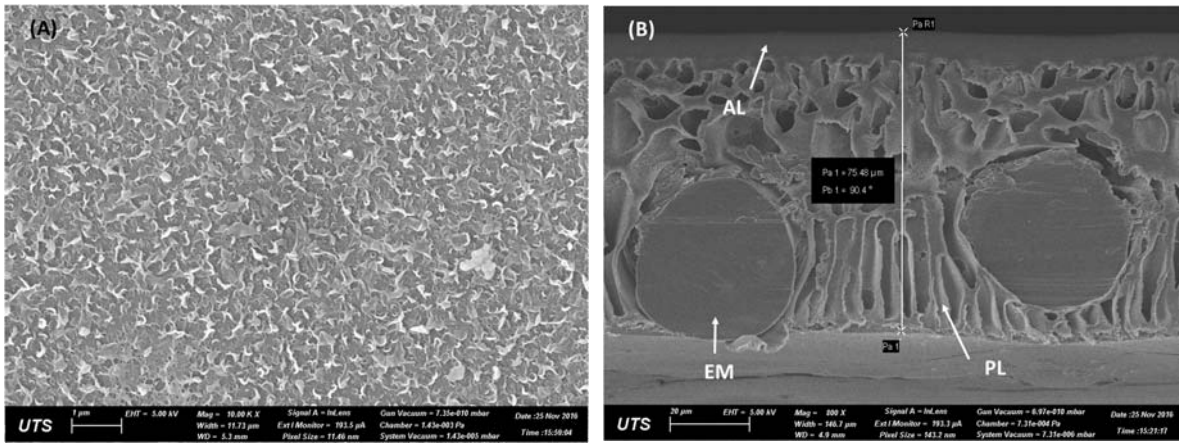
106 With these premises, the primary objectives of this study were the following: (i) To assess the fouling
107 behaviour on newly developed thin film composite (TFC) FO membranes using real wastewater and
108 seawater solutions. (ii) To evaluate the influence of pre-treatment of wastewater solutions on the fouling
109 potential and the quality of the product seawater. (iii) To understand the nitrogen leakage to the seawater
110 draw solution.

111

112 **2 Materials and Methods**

113 **2.1 FO membrane**

114 Thin film composite (TFC) flat-sheet membranes (Toray Industries, Korea) were employed in this
115 study. The thin active layer is made of polyamide and is attached to a polysulfone support layer in which
116 a woven mesh was embedded for better mechanical strength. SEM images of the membrane are shown
117 in Figure 1. The TFC FO membranes used in this study were about 75 μm thick with a highly porous
118 support layer and a thin active layer with tight pores.



119
120 **Figure 1: a) Active layer surface (x 30,000). b) side-view of the membrane (800x). The thin active layer (AL) is resting**
121 **on top of the porous support layer (PL) (EM: embedded mesh)**

122 **2.2 Bench-scale FO system**

123 An acrylic FO cell with an active membrane area of 20.02 cm^2 was connected to two variable-speed
124 gear pumps (Cole Palmer, VT, USA), and the solutions were stored in two 5 L plastic tanks. Figure S1
125 displayed the schematic representation of the system. The pump flow velocity was set to 400 mL/min
126 (8.5 cm/s) for all experiments, and the solutions were pumped through the membrane cell in counter-
127 current mode. FO experiments were conducted in batch mode, with constant recycling of the feed and
128 draw solutions to their respective tank. The active layer of the FO membrane faced the FS (FO mode).
129 The weight of the draw tank was continuously monitored using a digital 15 kg scale (Adam Equipment
130 PGL-15001 Precision Balance 15 kg x 0.1 g) and was used to calculate the variation of water flux
131 throughout the experiments. A temperature control system connected to a water bath was used to keep
132 both solutions at 25°C. Conductivity, total dissolved solids (TDS) and pH were monitored using an
133 HQ30D portable multi-meter (Hach, CO, USA). The reverse salt flux J_s (RSF, $\text{g}/\text{m}^2/\text{h}$) was calculated
134 based on the conductivity measured continuously in the feed solution as:

135
$$J_s = \frac{\lambda * \Delta(C_F * V_F)}{(A * \Delta t)} \quad (1)$$

136 Where λ (cm/S/L) is a conductivity calibration factor. This was obtained by linear regression of the
137 conductivity of NaCl solutions as a function of its concentration (i.e. conductivity = $(1/\lambda) * \text{mass}$
138 concentration of NaCl), C_F is the conductivity of the feed solution, V_F is the volume of the feed solution.
139 The specific reverse salt flux (SRSF, g/L) was calculated as follows:

$$140 \quad \text{SRSF} = \frac{J_S}{J_W} \quad (2)$$

141 **2.3 Feed and draw solutions**

142 Real seawater was collected from the faculty of science at the University of Technology, Sydney (UTS).
143 Johns Water Exchange provided the seawater to the university after its collection in Rose Bay, Sydney.
144 The seawater was pre-treated directly at UTS with a five μm filtration bag and a UV filter sterilizer.
145 These pre-treatment steps were necessary to reduce the risk of fouling and biofouling within the support
146 layer. Real wastewater was collected from the wastewater treatment plant in Central Park, Sydney. In
147 this plant, the wastewater undergoes different treatment steps as shown in Figure S2. In this Figure, the
148 FS sampling locations were also outlined. In fact, solutions were collected at various points to assess
149 the impact of pre-treatment of the feed solutions:

- 150 1. **Primary effluent (i.e. solution 4, Primary Eff.)**. The raw municipal WW was pre-treated in two
151 different ways to remove large particles that could instantly damage the membrane. The first is
152 a simple settling (for two days) and the second is coagulation-flocculation (10 g/L of FeCl_3 was
153 used as a coagulant).
- 154 2. **Mixed liquor before ultrafiltration (i.e. solution 3, also referred to as Mixed Liq)**. This consists
155 of the recirculated mixed liquor together with the activated sludge. For the same reason of **the**
156 **primary effluent**, the **mixed liquor** was either filtered using 1.2 μm paper filters or left to settle
157 down during two days. After settling down, the supernatant was collected using a peristaltic
158 pump.
- 159 3. **Secondary effluent i.e., mixed liquor after ultrafiltration (i.e. solution 2, Secondary Eff.)**. This
160 solution was used directly without any additional treatment.

161
162 Synthetic seawater was prepared by dissolving 0.6 M of sodium chloride (i.e. NaCl, 35 g/L) in deionized
163 (DI) water. This is the approximate concentration in real seawater in Sydney. For the real seawater, its
164 composition is displayed in table 2.

165 All solutions were stored in the fridge and the dark before use. Wastewater and seawater solutions were
166 used within a week after sampling.

167 **2.4 Experimental protocol**

168 2.4.1 Determination of membrane parameters

169 Three key membrane parameters were determined to model the FO water flux: the pure water
 170 permeability coefficient A ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$), the salt permeability coefficient B ($\text{Lm}^{-2}\text{h}^{-1}$) and the
 171 membrane structural parameter S (μm). The A and B parameters represent the transport of water and
 172 salts through the membrane, while S indicates the solute transport in the support layer. The membrane
 173 parameters were determined using the methodology described by Tiraferri et al. [18]. Four consecutive
 174 FO experiments were run for 1 hour with DI water as feed solution. Initial volumes were set to 2 L. The
 175 DSs were prepared with different concentrations of NaCl (0.5 M, 1 M, 1.5 M and 2 M).

176 2.4.2 Short-term experiments using synthetic seawater and real wastewater

177 Seven baseline experiments were conducted with different real wastewater feed solutions (Table 1). 0.6
 178 M NaCl solution was used as a DS for 6 of the tests, and real seawater was used in only one experiment
 179 to check that the behaviour of seawater was similar to the one of the synthetic solution. Real seawater
 180 was not used for the baseline experiments because one of the goals was to carry out mineral and organic
 181 analyses on the final draw solution, to see the nutrients leakage, and real seawater would have made it
 182 difficult given its inevitable variability of the initial composition of real seawater. All experiments were
 183 conducted for 8 hours with 2 L of FS and DS. The relative flux decline was plotted to assess the impact
 184 of the wastewater composition.

185 **Table 1. Long and short-term experiments conducted. For the short-term experiments each 2 L of FS and DS was**
 186 **used, while 4 L of FS was used for the long-term one.**

Experimental Period	Feed Solution (FS)	Draw Solution (DS)
Short-term experiment (8 hr)	DI water	0.6 M NaCl
	DI water	Real Seawater
	Secondary effluent (Secondary Eff.)	0.6 M NaCl
	Mixed liquor after filtration 1.2 microns (Mixed Liq.f)	0.6 M NaCl
	Mixed liquor after settling (Mixed Liq.s)	0.6 M NaCl
	Raw WW after coagulation-flocculation (Primary Eff.cf)	0.6 M NaCl
	Raw Wastewater after settling (Primary Eff.s)	0.6 M NaCl
Long-term experiment (80 hr)	Secondary effluent (Secondary Eff.)	Real Seawater
	Mixed liquor after settling (Mixed Liq)	Real Seawater
	Raw WW after coagulation-flocculation (Primary Eff.)	Real Seawater

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189 2.4.3 Long-term experiments using real seawater and wastewater

190 Three long-term experiments were conducted, with the duration of 80 hours, to investigate the long-
191 term flux decline and fouling behaviour of wastewater in actual conditions. The initial volume of the
192 FS was set to 4 L. An initial amount of 2 L of real seawater was used as a draw solution for all the
193 experiments. Table 1 displayed the different FS and DS used for the experiments. At the end of each
194 experiment, the membrane was collected for further analyses of the fouling layer and determination of
195 the primary fouling precursors in real solutions.

196 2.5 Modelling the water flux of the FO experiments

197 To better understand the impact of fouling using different types of wastewater streams and how the
198 water flux (J_w) deviates from the theoretical one. Water flux was modelled via the classical solution-
199 diffusion model coupled with the diffusion-convection transport in the membrane support layer [19].
200 Membrane pure water permeability (A), NaCl salt permeability coefficients (i.e., B_{NaCl}) and structural
201 parameters S were obtained as above described. The results are shown in Table 4. The effect of the
202 internal concentration polarization (ICP), on the porous support layer of the FO membrane, was taken
203 into account in the equation used. Since all the experiments have been carried out in FO mode (i.e.,
204 active layer (AL) facing the feed solution (FS)), equation (3) was used to predict the water flux [19, 20].

$$205 J_w = \sigma K_m \ln \left(\frac{A\pi_D + B_s}{A\pi_F + J_w + B_s} \right) \quad (\text{AL-facing FS}) \quad (3)$$

206 In this equation, σ is the reflection coefficient, assumed as unity (complete rejection of the solute), K_m
207 is the mass transfer coefficient of NaCl, given as salt diffusivity divided by S . The bulk osmotic
208 pressures of the draw and feed are displayed as π_D and π_F are the DS and FS bulk osmotic pressure
209 respectively.

210 2.6 Analytical methods

211 Several analyses were carried out on the solutions before, during and after the FO filtration. Cation and
212 anion concentrations were respectively measured using a 4100 MP-AES (Agilent Technologies, VI,
213 Australia) and a 790 Personal IC (Metrohm, Switzerland). Spectroquant® Cell Test kits and Reagent
214 Test kits (Merck Millipore, Germany) were also used to measure the concentrations of anions and
215 cations (Cl^- , PO_4^{3-} , NO_3^- and NH_4^+), and for the determination of total phosphorus, total nitrogen, and
216 COD values. A 2100P Portable Turbidimeter (Hach, CO, USA) was used to determine the turbidity
217 values of wastewater samples. Dissolved organic carbon (DOC) values were measured using a multi
218 N/C® 3100 TOC Analyzer (Analytik Jena, Germany). Prior to the TOC analysis, samples were filtered
219 using a 0.45 μm filter to obtain the DOC values. Total suspended solids (TSS) values were calculated
220 upon filtration of the solution with a 0.45 μm ceramic filter, drying off the clogged filter in a 104°C

221 oven and measurement of the weight increase of the filter. The osmotic pressure of the solutions was
222 computed using OLI Stream Analyser 3.2 (OLI System Inc., Morris Plains, NJ, US). The detailed
223 organic matter characterisation of the real wastewater was performed using liquid chromatography-
224 organic carbon detection or LC-OCD (DOC-Labor, Germany) as per the procedure described elsewhere
225 [21].

226 **2.7 Membrane analysis**

227 Following the long-term experiments, the three fouled membranes were collected and dried off in an
228 oven at 50°C. The surface of the active layer was measured by scanning electron microscopy (SEM)
229 using a SUPRA 55-VP instrument (Zeiss, Germany). Before the SEM analyses, the membrane samples
230 were coated with a palladium-gold layer using an EM ACE 600 coater (Leica, Germany). The elements
231 composing the fouling layer on the membrane were determined by electron - dispersive X - Ray (EDX).
232 The cake layer was also analysed by Fourier transform infrared (FTIR) Spectroscopy using the
233 IRAffinity-1 from Shimadzu (Japan).

234

235 **3 Results and Discussion**

236 **3.1 Feed and draw solution characterisation**

237 After conducting all the chemical analysis on the different types of real WW used as FS, a full
238 characterization was obtained. Table 2 shows the initial composition of the real WW and SW samples
239 utilised for the experiments. It can be seen that, while Table 3 displays its LC-OCD fractionation.
240 Additionally, in Table S1 the turbidity values before and after the pre-treatments are shown. From the
241 LC-OCD fractionation data, it can be seen that there is a much higher concentration of low molecular
242 weight neutrals organic compounds (LMW neutrals) in the primary effluent compared to the mixed
243 liquor. This is expected as, when the primary effluent is mixed with the biomass in the aerobic reactor,
244 the carbon source in the WW is first absorbed and then gradually degraded by the heterotrophic bacteria
245 community.

246 In terms of filtration, these compounds are likely to have higher fouling propensity compared to larger
247 molecular weight one. In fact, they could stick on the rough membrane promoting the attachment of
248 other organic or inorganic compounds.

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Table 2 Composition of the real seawater and wastewater solutions used in all the experiments. Feed and draw samples were collected at the beginning and the end of each experiments. * The osmotic pressure was calculated via OLI Stream Analyser 3.2 (OLI System Inc., Morris Plains, NJ, US).

		SEAWATER	Mixed liquor	Secondary effluent	Primary effluent
		(Rose Bay. Sydney)	(Central Park. Sydney)	(Central Park. Sydney)	(Central Park. Sydney)
pH	[-]	7.9	7.38	7.5	7.9
COD	[mg/L O ₂]	[-]	27	23	212
TDS	[mg/L]	33100	357	336	646
Turbidity	[NTU]	0.31	1.3	0.39	63.6
Osmotic Pressure*	[bar]	27.16	0.38	0.335	0.57
Na⁺	[mg/L]	10800	122.5	113	142.4
Ca²⁺	[mg/L]	790	33.5	20.63	16.5
Mg²⁺	[mg/L]	1460	8	5.56	9.25
SO₄²⁻	[mg/L]	2600	38	45.06	38
TP	[mg/L]	0.51	7	3	22.4
NO₃⁻	[mg/L]	6.6	12.8	23.3	0.89
NH₄⁺	[mg/L]	7.97	8.62	2.44	84.3

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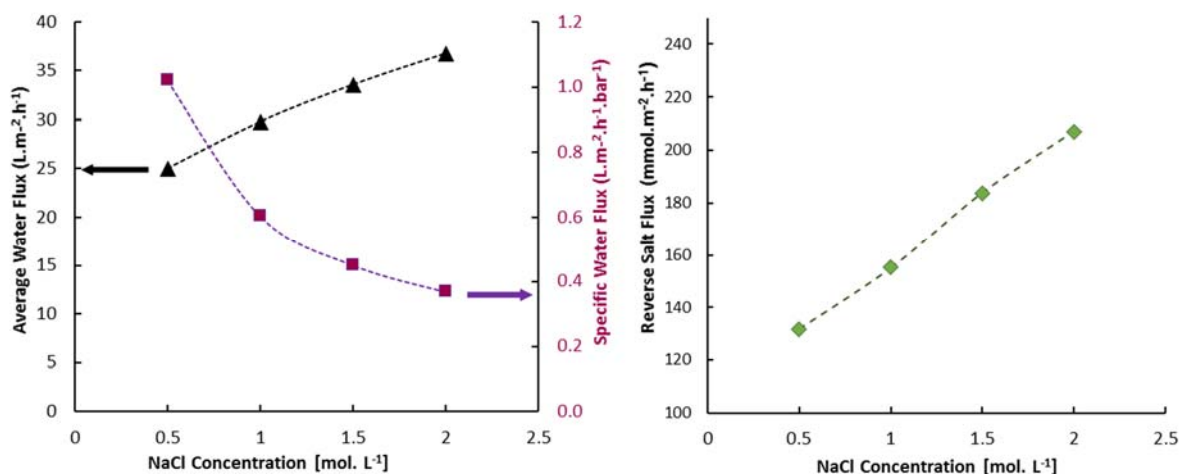
Table 3. LC-OCD fractionation results of different wastewaters used in the experiments where: LMW = low-molecular weight; n.q. = not quantifiable (< 1 µg/L; signal-to-noise ratio); “Biopolymers” = polysaccharides, proteins, aminosugars; “Building blocks” = breakdown products of humics; “Neutrals” = include mono-oligosaccharides, alcohols, aldehydes, ketones; “Acids” = summary value for monoprotic organic acids < 350 Da.

		Approximate molecular weights (g/mol):					
		>> 20,000	~1000	~300-500	< 350	< 350	
		DOC	Biopolymers	Humic substances	Building blocks	LMW neutrals	LMW acids
Secondary effluent	mgC/L	9.660	0.119	5.434	0.582	2.025	n.q.
	% DOC	100%	1.2%	56.2%	6.0%	21.0%	--
Mixed liquor	mgC/L	11.177	0.458	5.907	0.622	2.654	n.q.
	% DOC	100%	4.1%	52.8%	5.6%	23.7%	--
Primary effluent	mgC/L	42.646	4.248	9.083	1.944	16.995	1.790
	% DOC	100%	10.0%	21.3%	4.6%	39.9%	4.2%

261

262 3.2 Membrane parameters

263 The water flux and reverse salt flux values for different concentrations of NaCl as DS are shown in
264 Figure 2. The reverse salt flux increases proportionally with the draw solution concentration. However,
265 as a consequence of the concentration polarization effect, the water flux increase was not linear with
266 the increase in osmotic pressure difference as shown by the trend of specific water flux (specific water
267 flux = $J_w/\Delta\pi$).



268

269 **Figure 2. Baseline experiments to determine the membrane parameters (A, B, S) according to Tiraferri et al. [18].**
 270 **Water flux and Reverse salt flux have been monitored for four different concentrations of NaCl draw solution (i.e. 0.5,**
 271 **1, 1.5 and 2 M) with DI water as FS. The experiments were run for 2 hours.**

272

273 Membrane parameters were determined by using these data as input in the Tiraferri et al. algorithm
 274 making sure to have an $R^2 > 0.9$. The results and are presented in Table 4. As expected, the A value is
 275 high compared to values found in the literature for CTA membranes (typically between 1 and 2
 276 LMH/bar [18]). Higher water permeability of TFC compared with CTA can be explained by the
 277 enhanced hydrophilicity of the TFC active layer and the fact that the porous layer is thinner, more
 278 porous and less tortuous. Higher porosity and less tortuosity decrease the S parameter, which in turns
 279 reduces the internal concentration polarisation effect. Compared to other commercial TFC membranes
 280 [22, 23], Toray membranes have also slightly higher water and salt permeability coefficients. Finally,
 281 the B/A ratio of the Toray membranes (Table S2) is relatively low compared to other commercial CTA
 282 and TFC membranes, which indicates a good selectivity [23, 24].

283

284 **Table 4. Membrane parameters of the Toray TFC membrane, determined with the methodology developed by**
 285 **Tiraferri et al. [18]**

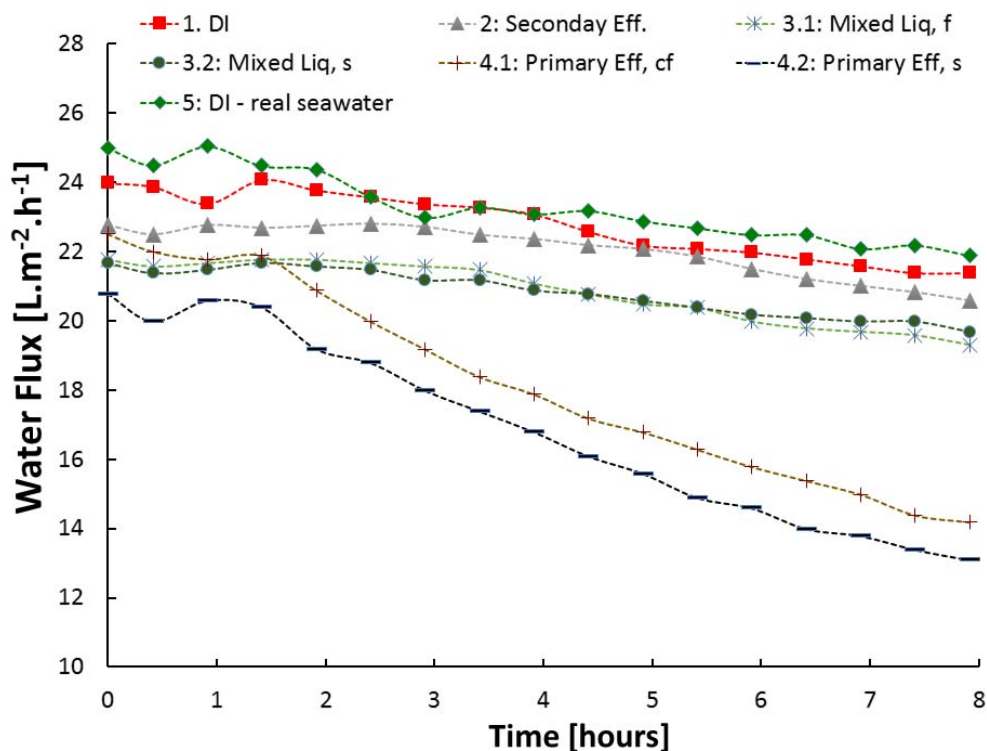
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Parameter	Value	Unit
A	6.47	LMH/bar
B	1.74	LMH
S	409	Mm
K	0.276	s/ μ m

287 3.3 Impact of wastewater quality on the process performance and the type of fouling

288 3.3.1 Short-term experiments

289 The water flux decline trends when using different qualities of wastewater were shown in Figure 3. The
290 initial water flux varies because of the increasing TDS amount of wastewater and the subsequent rise
291 of osmotic pressure. Because of the configuration of the experimental set-up, the DS is diluted, and the
292 FS concentrated during the experiments. The DS dilution causes the flux to decline due to the reduction
293 of the process driving force.



294

295 Figure 3. Water Flux for seven different feed-draw solutions couples. Operating parameters: Draw solutions = NaCl
296 (except 1. Real Seawater); Feed solutions = Real Wastewater (Secondary effluent, mixed liquor pre-treated or not,
297 primary effluent pre-treated or not); Operating time = 8 hours.

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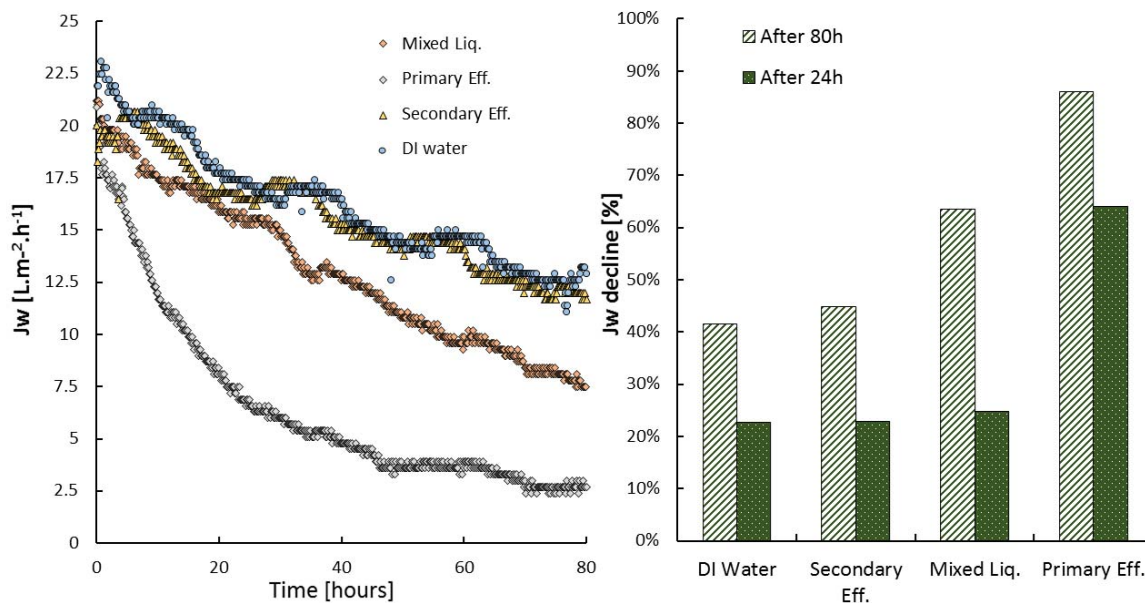
299 Based on the experimental results it can be seen that, when **secondary effluent** or **mixed liquor** are used,
300 no severe flux decline was observed. In fact, the water flux trends are similar for DI, **Secondary Eff.**
301 **and Mixed Liq.** Low membrane fouling using biologically treated WW was also found by Cath. et al.
302 with CTA membranes and secondary effluents [14]. However, when primary effluents (i.e. Primary
303 Eff.) is used, severe flux decline was observed. It can be noticed that the type of pre-treatment carried
304 out on activated sludge (3.1 and 3.2), and raw wastewater (4.1 and 4.2) did not impact the short-term
305 water flux decline. Therefore, it can be argued that an initial biological treatment of the WW is deemed
306 necessary if FO wants to be used as a dewatering method for WW. To conclude, different wastewaters

307 were tested on FO using model seawater as DS. The results showed a high initial J_w (22-23 LMH) using
308 the newly developed Toray TFC membrane. However, if non-biologically treated WW is used, settling
309 or coagulation-flocculation were found not sufficient to avoid quick fouling of the membrane.

310 3.3.2 Long-term experiments

311 The water fluxes exhibited by the different FS during long-term experiments with real seawater (as DS)
312 and real wastewater (as FS) are displayed in Figure 4. The initial water fluxes were 23.1, 22.1, 20.5 and
313 18.8 LMH for DI water, Secondary Eff., Mixed Liq. And Primary Eff. respectively. Again, the use of
314 secondary effluent did not induce any noticeable flux decline compared to the use of DI water. However,
315 for the mixed liquor, the flux started to be impacted by fouling after 30 hours of operation and gradually
316 decreased after that. When primary effluent was used, the water flux quickly declined at the beginning
317 of the experiments, then stabilizing to a low value after 50 hours of operation. Photographs of the
318 membranes (Figures S4 and S5) show that a uniform cake layer is rapidly built on the membrane with
319 primary effluent WW. With Secondary Eff. and Mixed Liq., a clear brown stain was visible at the outlet
320 end of the feed channel. The rest of the membrane surface was clear for Secondary Eff., but a light
321 greyish layer was visible with activated sludge. The formation of a dense cake layer explains the pattern
322 observed with primary effluent. The rapid initial flux decline is correlated to the building up of the cake
323 layer on the membrane surface. Afterwards, the plateau corresponded to a stabilization of the layer's
324 thickness which is linked to the amount of foulants in the solution and the shear force from the cross
325 flow of water.

326 A particular oscillating pattern observed for secondary effluent was also observed, and it can be
327 attributed to "self-cleaning" phenomenon. The fouling cake is detached from the membrane as soon as
328 the shear stress, caused by its thickness, is greater than its attachment to the membrane [25].



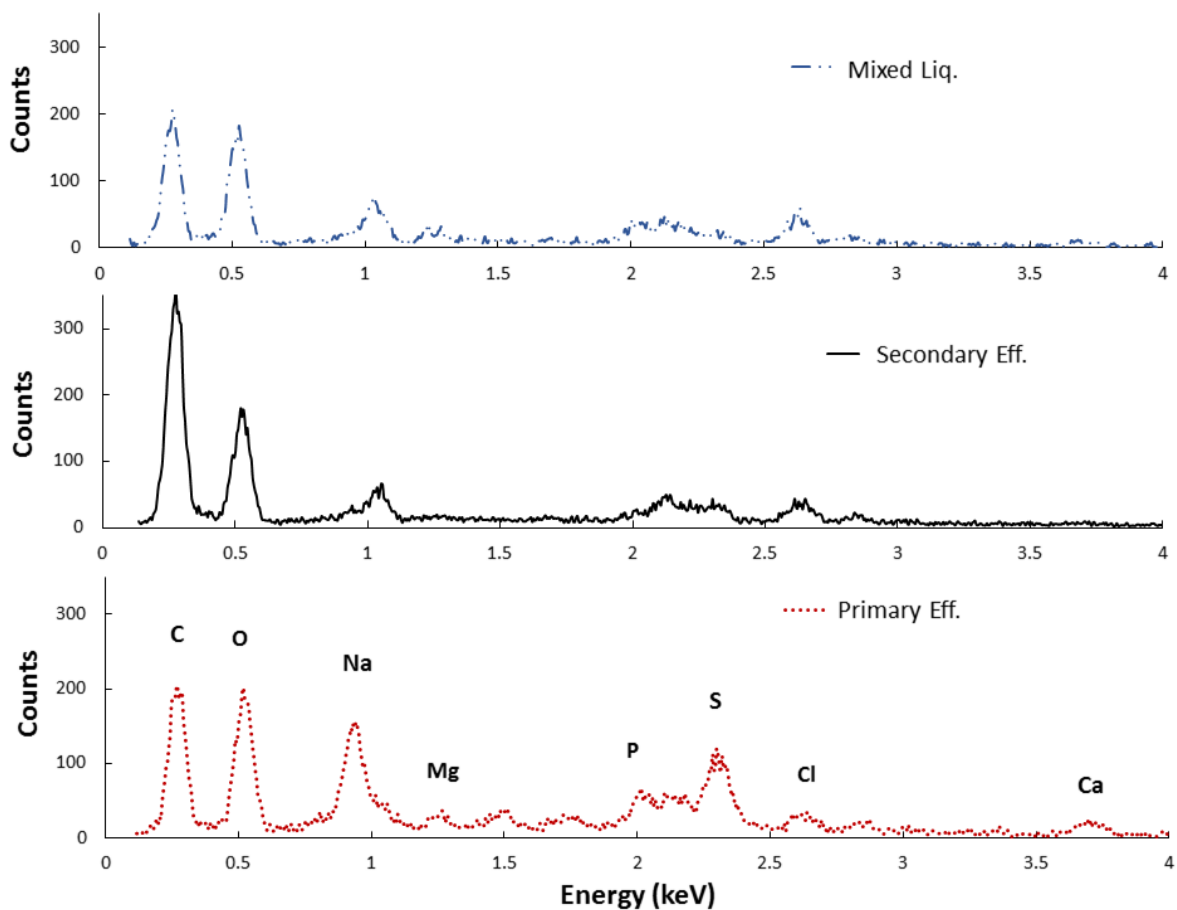
329

330 **Figure 4. Water flux as a function of water recovery for four different feed solutions (left). Water flux decline**
 331 **percentages are provided after 24 h and 80 h of operation (right). Operating parameters: Draw solution = real seawater;**
 332 **Feed solutions = DI, Secondary Eff., Mixed Liq. And Primary Eff.; Operating time = 80 hours.**

333 3.3.3 Analysis of the fouling layer

334 EDX and FTIR analyses were carried out to investigate the composition of the fouling layers. The
 335 results are gathered in both Figure 5 and Figure 6.

336 The EDX analysis revealed that several elements are present in the fouling layer and that the
 337 composition of the fouling layer seems to be roughly the same independently of the feed solution. The
 338 presence of calcium and magnesium were not a surprise, as these divalent ions act as fouling promoters
 339 by forming complexes with organic molecules and biological matter. This phenomenon is known for
 340 filtration and RO processes but was also highlighted in the osmotic dilution of seawater [11, 26, 27].
 341 Phosphorous and sulphur peaks indicate that sulphate and phosphate ions are probably acting as fouling
 342 promoters, especially when primary effluent WW is used. It can also be linked to the amount of
 343 biological matter, as proteins are abundant in P and S. The C and O peaks correspond to the active layer,
 344 visible below the fouling layer. Finally, crystals on top of the fouling layer could be seen with the SEM
 345 images (Figure S3). However, they are sparse and do not cover most of the membrane surface. Instead,
 346 a uniform layer of organic fouling could be noticed from the pictures. When primary effluent was used,
 347 this layers than formed several crakes when it dried out.



348

349

Figure 5. EDX analysis of the surface of the fouling layer on the membranes.

350

The FTIR analysis confirms the regularity of the composition of the fouling layer, as the same peaks appeared for the three fouled membranes. These peaks were not visible in the pristine membrane. The associated wavenumber has typically been associated to organic matter and could correspond to the following bonds, usually found in organic foulants: O-H (3300 cm^{-1}), C=C (1630 cm^{-1}), COO^- (1550 cm^{-1}), C-O (1080 cm^{-1}) [28].

354

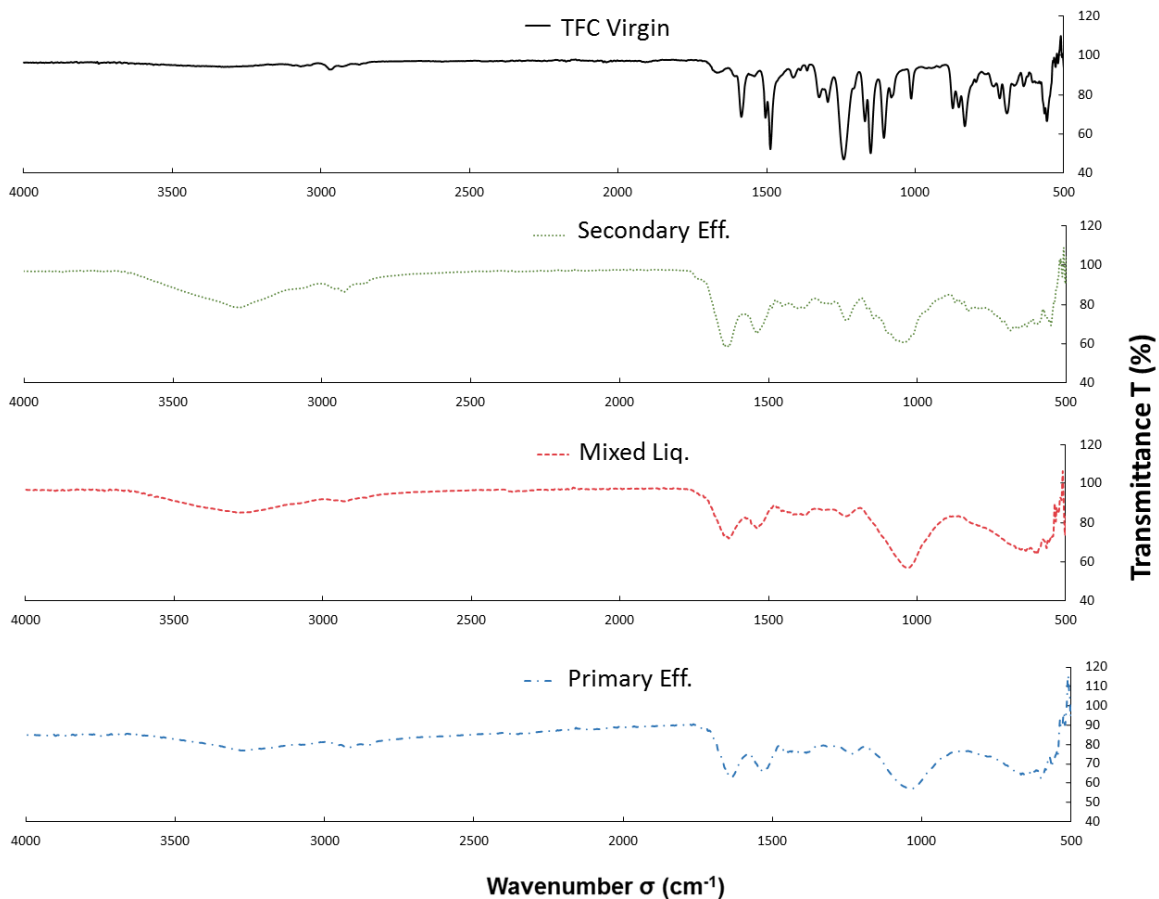


Figure 6. FTIR of fouled membranes compared to a virgin TFC membrane (in black).

355
356

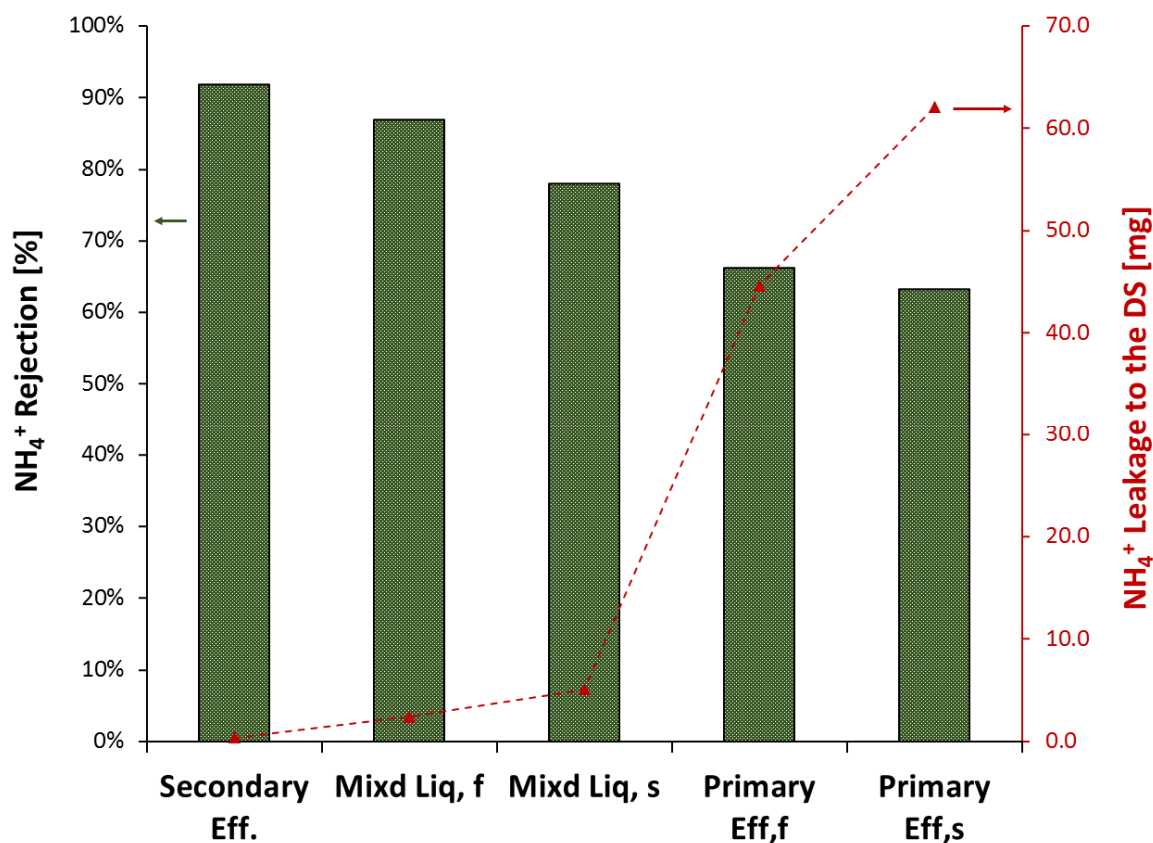
357 To sum up, as expected from the FO tests, the raw WW caused a more noticeable fouling cake on top
358 of the membrane active layer. The presence of known fouling precursors, e.g. Mg^{2+} , PO_4^{3-} , Ca^{2+} and
359 organic matter, confirmed that both organic and inorganic fouling happened. On the contrary, when
360 secondary effluent was used, the analysis of membrane coupon did not show significant evidences of
361 organic and inorganic precipitates.

362 3.4 Evaluation of the produced water quality

363 To assess the possible nutrients contamination of the diluted seawater, nitrogen, phosphorous and TOC
364 were measured in the DS. It should be noted that, in this concept, the diluted seawater is supposed to
365 pass through a second barrier, i.e. RO. The RO filtration step would further reduce the N, P and TOC
366 concentrations in the final effluent. These results refer to the tests conducted with synthetic seawater as
367 DS and primary effluent WW as FS. Synthetic seawater was used instead of real in order not to bias the
368 results since the real seawater itself has nitrogen compounds.

369 In this study, attention was focused on the rejection of NH_4^+ since, among all the nutrients, it is known
370 to be among the hardest to be rejected [29]. Other studies have already demonstrated that the rejection
371 of phosphate and COD is almost 100% [29]. The poor rejection of ammonia is to be attributed to its

372 small hydrated radii (i.e. 3.31 Å) and positive charge (being the polyamide layer negatively charged).
 373 Figure 7 shows how the rejection decreased when **primary effluent WW** was used as FS. This can be
 374 explained by the fact that the concentration of contaminants is higher in raw wastewater than in
 375 **secondary effluent**.



376
 377 **Figure 7. Rejection of NH₄⁺ after 8 h experiments having synthetic seawater as DS and different real wastewaters as**
 378 **FS (columns). The dotted line with the markers indicates the amount of NH₄⁺ that leaked through the FO membrane**
 379 **to the DS after the filtration.**

380
 381 To conclude, raw WW showed high NH₄⁺ leakage in the diluted DS, while both **secondary effluent** and
 382 mixed liquor showed final NH₄⁺ concentrations less than 2 mg/L.

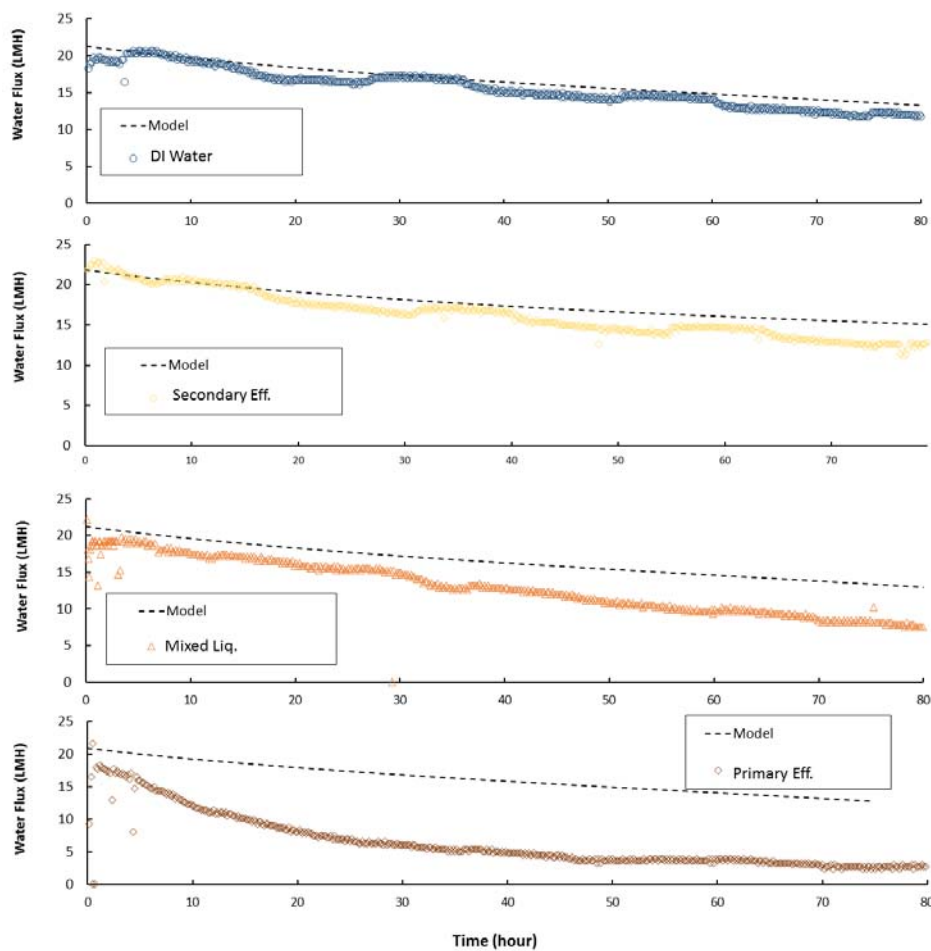
383 3.5 Modelling the system performances

384 Modelling the water fluxes with different FS was performed using Equation (3) to assess how the
 385 measured data diverge from the theoretical trend. The divergence from measured data to modelled one
 386 was used as a further indication of membrane fouling. In fact, this model does not take into account the
 387 flux decline due to membrane fouling. The model was firstly validated with DI water as FS before
 388 proceeding with WW (Figure 8). It can be seen that the predictions fit quite well the measured data. In
 389 Figure 8, the experimental water fluxes using real seawater and wastewaters results are plotted together

390 with the fluxes predicted with the model.

391 By looking at the second graph from the top in Figure 8, it can be seen that the model predicted quite
392 accurately the FO water flux when **secondary effluent** is used as FS. Only at the very end of the filtration,
393 the measured flux is slightly lower than the modelled. This is probably because in the low end of the
394 experiment the **secondary effluent** solution has been concentrated enough to create moderated fouling
395 on the membrane.

396 Fouling on the low-end of the filtration is even more noticeable when **mixed liquor** is used as FS. In
397 this case a clear divergence from the model happens after about 30 hours. Finally, when **primary effluent**
398 is used, soon after the beginning of the experiment the model over-predicted the measured data due to
399 the severe flux decline.



400

401 **Figure 8. Predicted and measured water fluxes. The model used to predict the water flux trend was developed from**
402 **Equation 3 using the membrane parameters outlined in Table 4. Excluding the top graph, all the experiments were**
403 **conducted with real seawater as DS and real wastewaters as FS.**

404 To sum up, a water flux model was developed and validated with standard experiments using DI water
405 as FS and seawater as DS. After validation, the model was applied on real wastewaters to see its
406 deviation from the measured data. As expected, **primary effluent** displayed the most visible deviation

407 even after few hours. When **mixed liquor** was used, the divergence between model and experiment
408 occurred after about 30 hours, while **secondary effluent** showed little to no discrepancies with the
409 modelled data.

410 **4 Conclusions**

411 Newly developed and commercially available TFC membranes were used to evaluate their
412 performances and fouling tendency in the FO-RO hybrid process for wastewater reclamation and
413 seawater dilution. Real wastewater and real seawater are used as feed and draw solution to get
414 meaningful results. Real seawater achieved an initial water flux of about $22.5 \text{ Lm}^{-2}\text{h}^{-1}$ when biologically
415 treated secondary effluent was used. It was also found that the secondary effluents caused negligible
416 flux decline. Also, the ammonia rejection was measured to be $> 80\%$.

417 On the contrary, when raw wastewater was used severe fouling and flux decline was observed. Pre-
418 treatment with sedimentation or coagulation-flocculation was not enough to ensure a good FO
419 performance during the filtration. A possible explanation is the presence of high concentrations of low
420 molecular weight organic compounds, measured with LC-OCD. These compounds are suspected to act
421 as fouling promoters thereby significantly decreasing the filtration time of the experiment. The analysis
422 of the fouling layers shows that the composition did not change significantly when using secondary
423 effluent or mixed liquor. However, when raw WW was used, a higher amount of divalent ions (e.g.
424 Ca^{2+} , Mg^{2+}) and PO_4^{3-} were found with the EDX. Modelling the water flux of the process helped validate
425 the above conclusions.

426 To conclude, if mixed liquor or secondary effluent is chosen as feed solution, commercially available
427 FO membranes were able to produce a good quality permeate, without severe fouling, even during long-
428 term filtration (> 80 hours). Given a stable FO performance, the high quality of diluted seawater will
429 likely decrease the cost of the downstream RO filtration for potable water production.

430

431

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438 **References:**

- 439 [1] UN General Assembly, Resolution 70/1, Transforming Our World: The 2030 Agenda For
440 Sustainable Development, A/RES/70/1 in, undocs.org/A/RES/70/1, 2015.
- 441 [2] M.A. Montgomery, M. Elimelech, Water and sanitation in developing countries: including health in
442 the equation, *Environ Sci Technol*, 41 (2007) 17-24.
- 443 [3] N.W. Arnell, D.P. van Vuuren, M. Isaac, The implications of climate policy for the impacts of
444 climate change on global water resources, *Global Environmental Change*, 21 (2011) 592-603.
- 445 [4] B.E. Jiménez Cisneros, T. Oki, N.W. Arnell, G. Benito, J.G. Cogley, P. Döll, T. Jiang, and S.S.
446 Mwakalila, *Freshwater Resources*, in: C.B. Field, V.R. Barros, D.J. Dokken, K.J. Mach, M.D.
447 Mastrandrea, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C. Genova, B. Girma, E.S. Kissel,
448 A.N. Levy, S. MacCracken, P.R. Mastrandrea, and L.L. White (eds.) (Ed.) *Climate Change 2014:
449 Impacts, Adaptation, and Vulnerability. Part A: Global and Sectoral Aspects. Contribution of Working
450 Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* Cambridge
451 University Press, Cambridge, United Kingdom and New York, NY, USA, 2014, pp. 229-269.
- 452 [5] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, *Science and
453 technology for water purification in the coming decades*, *Nature*, 452 (2008) 301-310.
- 454 [6] National Research Council, *Desalination: A National Perspective*, The National Academies Press,
455 Washington, DC, 2008.
- 456 [7] R. Valladares Linares, Z. Li, V. Yangali-Quintanilla, N. Ghaffour, G. Amy, T. Leiknes, J.S.
457 Vrouwenvelder, Life cycle cost of a hybrid forward osmosis - low pressure reverse osmosis system for
458 seawater desalination and wastewater recovery, *Water Research*, 88 (2016) 225-234.
- 459 [8] M. Elimelech, W.A. Phillip, *The Future of Seawater Desalination: Energy, Technology, and the
460 Environment*, *Science*, 333 (2011) 712-717.
- 461 [9] Q. Li, Z. Xu, I. Pinnau, Fouling of reverse osmosis membranes by biopolymers in wastewater
462 secondary effluent: Role of membrane surface properties and initial permeate flux, *Journal of
463 Membrane Science*, 290 (2007) 173-181.
- 464 [10] T. Asano, A.D. Levine, *Wastewater reclamation, recycling and reuse: past, present, and future*,
465 *Water Science and Technology*, 33 (1996) 1-14.
- 466 [11] V. Parida, H.Y. Ng, Forward osmosis organic fouling: Effects of organic loading, calcium and
467 membrane orientation, *Desalination*, 312 (2013) 88-98.
- 468 [12] L. Chekli, S. Phuntsho, J.E. Kim, J. Kim, J.Y. Choi, J.-S. Choi, S. Kim, J.H. Kim, S. Hong, J. Sohn,
469 H.K. Shon, A comprehensive review of hybrid forward osmosis systems: Performance, applications
470 and future prospects, *Journal of Membrane Science*, 497 (2016) 430-449.
- 471 [13] N.T. Hancock, P. Xu, M.J. Roby, J.D. Gomez, T.Y. Cath, Towards direct potable reuse with
472 forward osmosis: Technical assessment of long-term process performance at the pilot scale, *Journal of
473 Membrane Science*, 445 (2013) 34-46.
- 474 [14] T.Y. Cath, N.T. Hancock, C.D. Lundin, C. Hoppe-Jones, J.E. Drewes, A multi-barrier osmotic
475 dilution process for simultaneous desalination and purification of impaired water, *Journal of Membrane
476 Science*, 362 (2010) 417-426.
- 477 [15] V. Yangali-Quintanilla, Z. Li, R. Valladares, Q. Li, G. Amy, Indirect desalination of Red Sea water
478 with forward osmosis and low pressure reverse osmosis for water reuse, *Desalination*, 280 (2011) 160-
479 166.
- 480 [16] C. Boo, M. Elimelech, S. Hong, Fouling control in a forward osmosis process integrating seawater
481 desalination and wastewater reclamation, *J. Membr. Sci.*, 444 (2013) 148-156.
- 482 [17] Q. She, R. Wang, A.G. Fane, C.Y. Tang, Membrane fouling in osmotically driven membrane
483 processes: A review, *Journal of Membrane Science*, 499 (2016) 201-233.
- 484 [18] A. Tiraferri, N.Y. Yip, A.P. Straub, S. Romero-Vargas Castrillon, M. Elimelech, A method for the
485 simultaneous determination of transport and structural parameters of forward osmosis membranes,
486 *Journal of Membrane Science*, 444 (2013) 523-538.
- 487 [19] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration
488 polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration,
489 *Journal of Membrane Science*, 354 (2010) 123-133.
- 490 [20] J. Zhang, Q. She, V.W.C. Chang, C.Y. Tang, R.D. Webster, Mining nutrients (N, K, P) from urban

491 source-separated urine by forward osmosis dewatering, *Environmental Science and Technology*, 48
492 (2014) 3386-3394.

493 [21] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter
494 with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-
495 OND), *Water Research*, 45 (2011) 879-885.

496 [22] J. Ren, J.R. McCutcheon, A new commercial thin film composite membrane for forward osmosis,
497 *Desalination*, 343 (2014) 187-193.

498 [23] Z. Wang, J. Tang, C. Zhu, Y. Dong, Q. Wang, Z. Wu, Chemical cleaning protocols for thin film
499 composite (TFC) polyamide forward osmosis membranes used for municipal wastewater treatment,
500 *Journal of Membrane Science*, 475 (2015) 184-192.

501 [24] J. Wei, C. Qiu, C.Y. Tang, R. Wang, A.G. Fane, Synthesis and characterization of flat-sheet thin
502 film composite forward osmosis membranes, *Journal of Membrane Science*, 372 (2011) 292-302.

503 [25] F. Lotfi, L. Chekli, S. Phuntsho, S. Hong, J.Y. Choi, H.K. Shon, Understanding the possible
504 underlying mechanisms for low fouling tendency of the forward osmosis and pressure assisted osmosis
505 processes, *Desalination*, (2017).

506 [26] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO)
507 and reverse osmosis (RO), *J. Membr. Sci.*, 365 (2010) 34-39.

508 [27] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: fouling reversibility and
509 cleaning without chemical reagents, *J. Membr. Sci.*, 348 (2010) 337-345.

510 [28] C.S. Uyguner, M. Bekbolet, J. Swietlik, Natural organic matter: Definitions and characterization,
511 *Control of disinfection by-products in drinking water systems*, (2007) 253-277.

512 [29] R. Valladares Linares, Z. Li, M. Abu-Ghdaib, C.-H. Wei, G. Amy, J.S. Vrouwenvelder, Water
513 harvesting from municipal wastewater via osmotic gradient: An evaluation of process performance,
514 *Journal of Membrane Science*, 447 (2013) 50-56.

515