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1 **Membrane fouling, chemical cleaning and separation performance assessment**
2 **of a chlorine-resistant nanofiltration membrane for water recycling**
3 **applications**

4
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8 Moe Ma Ma Tin ¹, Anioke George ¹, Osamu Nakagoe ¹, Shuji Tanabe ¹,
9 Hitoshi Kodamatani ², Long D. Nghiem ³, Takahiro Fujioka ^{1,*}

10 ¹ *Department of Advanced Engineering, Graduate School of Engineering,*
11 *Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan*

12 ² *Division of Earth and Environmental Science, Graduate School of Science and Engineering,*
13 *Kagoshima University, 1-21-35 Korimoto, Kagoshima 890-0065, Japan*

14 ³ *Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental*
15 *Engineering, The University of Wollongong, NSW 2522, Australia*

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17 *Corresponding author: Takahiro Fujioka, Email: tfujioka@nagasaki-u.ac.jp, Ph +81 095 819 2695

18 **Abstract**

19 The effectiveness of hypochlorite cleaning for fouling mitigation of a prototype chlorine-
20 resistant nanofiltration (NF) membrane was assessed for direct filtration of a secondary treated
21 effluent. The chlorine resistance and separation performance of the prototype NF membrane
22 were also compared to commercial NF and reverse osmosis membranes. The prototype chlorine
23 resistant NF membrane did not show any changes in permeability and conductivity rejection
24 after exposing a NaOCl solution for up to 5×10^4 ppm-h. By contrast, a considerable deterioration
25 in rejection was observed for the other two commercial membranes. Direct filtration of a
26 secondary treated effluent by the prototype NF membrane resulted in a progressive permeability
27 reduction by up to 25% after 10 h of filtration. The membrane permeability was fully restored by
28 hypochlorite cleaning with a 2,000 ppm NaOCl solution for 1 h. Effective permeability recovery
29 by hypochlorite cleaning was demonstrated with multiple hypochlorite cleaning cycles.
30 Membrane fouling and hypochlorite cleaning were also simulated using solutions containing a
31 model foulant (sodium alginate, humic acids or bovine serum albumin). Among them, an
32 insufficient permeability recovery was observed for membrane fouling caused by humic acids.
33 Further research is recommended to develop an improved hypochlorite cleaning protocol to
34 control various membrane fouling.

35 **Keywords:** hypochlorite cleaning; chlorine-resistant nanofiltration membrane; membrane
36 fouling; water recycling; *N*-nitrosamines.

37 **1. Introduction**

38 Water purification using nanofiltration (NF) membrane has been widely applied for drinking
39 water, wastewater, and industrial wastewater treatment applications over the past decades [1, 2].
40 NF membrane, which is classified as an intermediate between ultrafiltration and reverse osmosis
41 (RO) membranes, is capable of rejecting multivalent ions and dissolved organic molecules
42 including many trace organic chemicals [3-7]. Most commercially available NF membranes
43 comprise of a composite polyamide (PA) ultrathin skin layer on top of a microporous
44 polysulfone supporting layer. In response to worsening water scarcity, rapid population growth,
45 industrialization and worsening droughts due to climate change, water purification using NF
46 membranes has attracted increasing interests for water reuse.

47 A major challenge to all membrane-based water treatment systems is membrane fouling.
48 Membrane fouling is inevitable and is caused by the deposition of impurities (foulants) on the
49 membrane surface, resulting in a drop in permeability and changes in separation performance [8-
50 10]. To date, most water recycling systems using high pressure membranes (i.e. NF and RO)
51 have deployed a pretreatment with microfiltration (MF) or ultrafiltration (UF) as a pretreatment
52 step for fouling mitigation [11]. The additional pretreatment processes increase capital and
53 operating costs in water reuse, thus, the elimination of these pretreatment processes could
54 provide an advantage on reducing the water recycling cost and make water reuse more feasible.

55 Without pretreatment, NF filtration operation is likely to face accelerated membrane fouling but
56 can be counteracted by frequent and effective chemical cleaning. In conventional NF operation,
57 chemical cleaning is periodically conducted by filling up the feed side of the membrane with

58 solutions containing caustic (e.g. NaOH) or acidic (e.g. HCl) chemicals and recirculating the
59 solutions [12]. The downside of frequent chemical cleanings is the disruption to the continuous
60 operation of the membrane skid, because typical chemical cleaning requires a cleaning period of
61 up to 8 h [13]. In addition to these conventional chemicals, membrane cleaning with a chlorine-
62 containing solution (e.g. hypochlorite) has attracted attention in recent years due to its
63 inexpensive and affordable supplies of sodium hypochlorite and its high ability in fouling
64 mitigation [14, 15]. Major mechanisms of hypochlorite cleaning are to disinfect the membrane
65 and to oxidize the functional groups of organic foulants to ketone, aldehyde and carboxylic
66 groups. The presence of these functional groups increases the hydrophilicity and charges of their
67 parent compounds, reducing the adhesion and attraction of fouling substances to the membranes
68 [16]. In fact, many MF- or UF-based water reclamation systems can be frequently cleaned using
69 a hypochlorite solution [17]. However, hypochlorite cleaning cannot be applied to conventional
70 NF and RO membranes because their PA active skin layer is readily degraded by chlorine [18-
71 20].

72 Exposing PA-based NF membranes to chlorine can lead to the degradation of amide bonds (-CO-
73 NH-) of the PA structure [21]. Extended contact with chlorine ultimately causes the deterioration
74 in separation performance [22-24]. To avoid the degradation issue, significant research work has
75 devoted to the development of chlorine-resistant PA membranes [25-29]. For example, Shintani
76 et al. [30] developed a chlorine-resistant PA NF membrane and reported that the immersion of
77 the NF membrane in a sodium hypochlorite solution (200 ppm) over 70 days did not change the
78 separation performance. However, no previous studies have demonstrated the effectiveness of

79 hypochlorite cleaning in fouling mitigation of a chlorine-resistant membrane for direct filtration
80 of secondary treated wastewater.

81 This study aimed to assess the effectiveness of hypochlorite cleaning for fouling mitigation of a
82 prototype chlorine-resistant NF membrane. The chlorine resistance and separation performance
83 of the prototype NF membrane were also compared to commercial NF and RO membranes.
84 Separation performance of the NF membrane was evaluated using inorganic salts and uncharged
85 trace organic contaminants (i.e., *N*-nitrosamines) of significant concern in water recycling
86 applications. A secondary treated effluent was used to simulate the elimination of pretreatment in
87 NF filtration. Solutions containing a model foulant (sodium alginate, humic acids or bovine
88 serum albumin) were also used to identify organic substances in wastewater that are persistent
89 against hypochlorite cleaning.

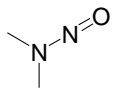
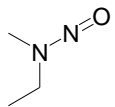
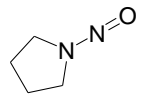
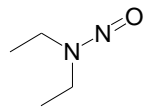
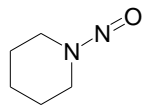
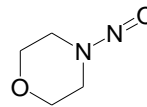
90 **2. Materials and methods**

91 **2.1 Chemicals**

92 Analytical grade NaCl, NaHCO₃ and CaCl₂ were purchased from Wako Pure Chemical
93 Industries (Tokyo, Japan) and used as background electrolyte. Analytical grade sodium
94 hypochlorite solution (10% available chlorine) was purchased from Sigma-Aldrich (St Louis,
95 MO, USA). Six analytical grade *N*-nitrosamines were purchased from Ultra scientific
96 (Kingstown, RI, USA). They include *N*-nitrosodimethylamine (NDMA), *N*-
97 nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodiethylamine
98 (NDEA), *N*-nitrosopiperidine (NPIP) and *N*-nitrosomorpholine (NMOR) (**Table 1**). A stock
99 solution was prepared at 1.0 mg/mL of each *N*-nitrosamine in pure methanol. Analytical grade

100 luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) was supplied from Wako Pure Chemical
 101 Industries (Tokyo, Japan). Three model foulants used here include sodium alginate (SA), bovine
 102 serum albumin (BSA), humic acids (HA). Sodium alginate and humic acid were supplied by
 103 Sigma-Aldrich (St Louis, MO, USA). BSA was purchased from Wako Pure Chemical Industries
 104 (Tokyo, Japan). Secondary treated effluent was collected after activated sludge treatment but
 105 prior to post chlorination at a municipal wastewater treatment plant in Japan. The obtained
 106 secondary treated effluent was used directly without any pretreatment to promote membrane
 107 fouling during filtration experiments.

108 **Table 1.** Selected *N*-nitrosamine physicochemical properties.

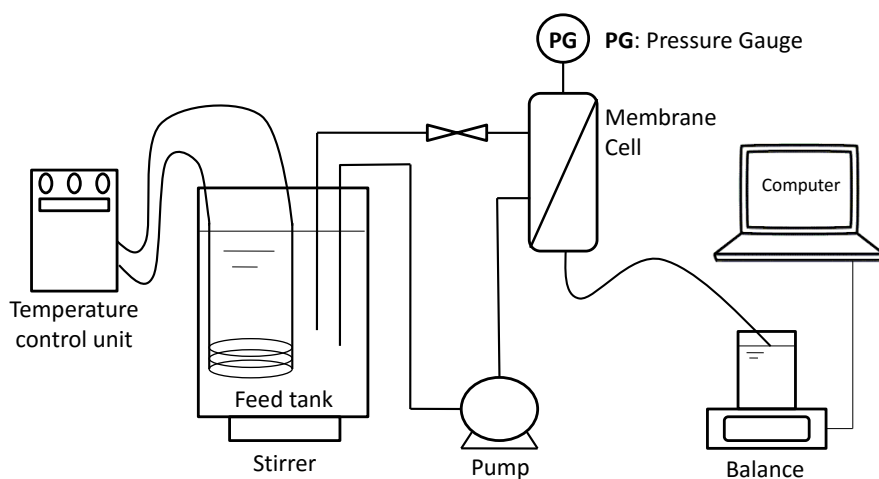
Compound	NDMA	NMEA	NPYR	NDEA	NPIP	NMOR
Structure						
Molecular formula	C ₂ H ₆ N ₂ O	C ₃ H ₈ N ₂ O	C ₄ H ₈ N ₂ O	C ₄ H ₁₀ N ₂ O	C ₅ H ₁₀ N ₂ O	C ₄ H ₈ N ₂ O ₂
Molecular weight [g/mol]	74.05	88.06	100.06	102.08	114.08	116.06
Low <i>D</i> at pH 8 ^a	0.04	0.40	0.44	0.52	0.44	-0.18

109 ^a Chemicalize (<http://www.chemicalize.org>).

110 2.2 Membranes and filtration system

111 Prototype chlorine-resistant NF membrane was supplied as flat sheet samples by Nitto Denko
 112 (Osaka, Japan). Two other commercial flat sheet membranes – namely DK NF membrane (GE,
 113 USA) and ESPA2 RO membrane (Hydranautics, USA) – were also used. The DK NF and
 114 ESPA2 membranes have been widely used for water recycling applications [31, 32]. A bench-

115 scale cross-flow filtration system was used (**Fig. 1**). The system comprised of a stainless-steel
116 membrane cell with an effective surface diameter of 2.2 cm, an effective surface area of 3.80
117 cm², a channel height of 0.44 cm, a pressure gauge, a 2 L feed tank and a high-pressure pump
118 (KP-12, FLOM, Tokyo, Japan). Feed solution in the feed tank was stirred throughout each
119 experiment. Feed solution temperature was controlled at 20.0 ± 0.1 °C by a temperature control
120 unit (CCA-1112, Tokyo Rikakikai, Tokyo, Japan) which was equipped with a stainless steel heat
121 exchange coil. Permeate flow was monitored using a digital balance (FX-300i, A&D, Tokyo,
122 Japan) that was connected to a computer for data logging.



123

124 **Fig. 1** – Schematic diagram of the bench-scale cross-flow filtration system.

125 **2.3 Experimental protocols**

126 **2.3.1 Chlorine exposure**

127 Prior to the chlorine exposure experiments, membrane coupons were gently rinsed and soaked in
128 Milli-Q water overnight. To simulate a long-term exposure of the membrane to chlorine, NaOCl
129 solutions were prepared in pure water to obtain a concentration of either 1,000 ppm (as NaOCl at
130 pH 11.0) or 100,000 ppm (as NaOCl at pH 11.0). Each membrane sample was immersed in a 50

131 mL NaOCl solution in a Pyrex glass beaker covered with aluminum foils and placed in a water
132 bath at 20.0 ± 0.1 °C for a specified duration. As soon as the chlorine exposure experiments
133 ended, the membranes were rinsed with a copious amount of deionized water and were stored in
134 the dark at 4 °C. Permeability of each membranes was evaluated at the permeate flux of 20
135 L/m²h Milli-Q water. Conductivity rejection of the membranes was evaluated using a 20 mM
136 NaCl solution at the permeate flux of 20 L/m²h. Throughout the tests, a cross-flow velocity of
137 the feed solution was maintained at 0.52 cm/s. Feed and permeate samples were collected after at
138 least 1 h operation for conductivity evaluation. Conductivity rejection was determined by
139 measuring conductivity of the feed and permeate solutions.

140 **2.3.2 Separation performance**

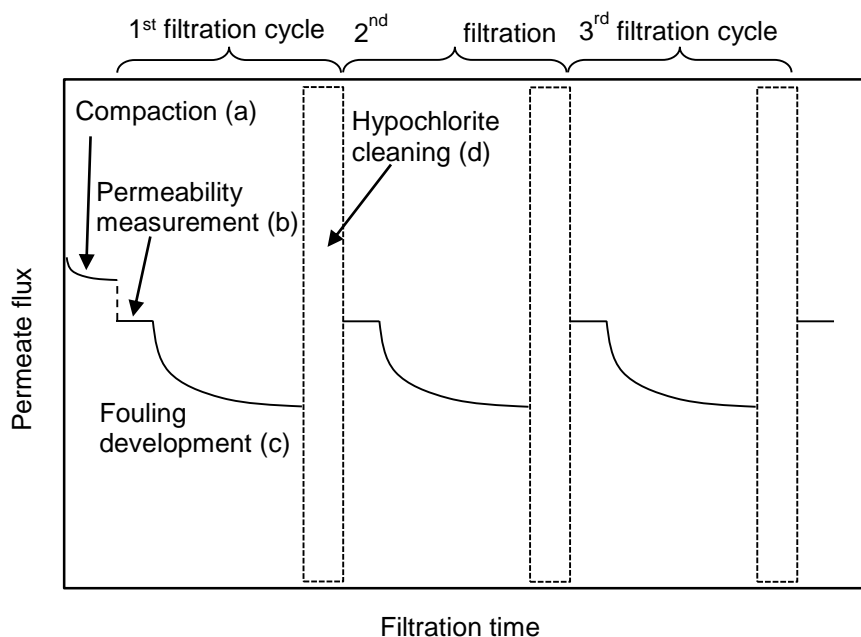
141 Separation performance of the three selected membranes was evaluated by measuring the
142 rejection of cations (Na⁺ and Ca²⁺) and uncharged organic solutes (*N*-nitrosamines). The
143 membrane sample was first compacted by operating system with Milli-Q water at 1 MPa for 1 h.
144 Background electrolytes were then added at a concentration of 20 mM NaCl, 1 mM NaHCO₃, 1
145 mM CaCl₂ in Milli-Q water. *N*-nitrosamines were also introduced into the feed to obtain 1,000
146 ng/L of each *N*-nitrosamine. This high *N*-nitrosamine was necessary to ensure measurable
147 concentrations in the permeate for an accurate rejection assessment. A previous study [33] has
148 shown that *N*-nitrosamine concentration does not influence their separation by polyamide RO
149 membrane. The pH of secondary treated effluent is usually in the range of 6.5 to 8.0 [34]. Since
150 the solution pH does not significantly affect *N*-nitrosamine rejection [33], the feed solution was
151 adjusted to pH 8 in this study. The filtration system was operated at a constant flux of 20 L/m²h,
152 and a cross-flow velocity of the feed solution was maintained at 0.52 cm/s. The concentrate and

153 permeate were recirculated into the feed tank to avoid any increase in the concentrations of
154 chemicals in [the feed](#). After at least 1 h of filtration, feed and permeate samples were collected in
155 amber vials.

156 **2.3.3 Hypochlorite cleaning**

157 The effectiveness of hypochlorite cleaning on fouling mitigation was evaluated with the
158 prototype chlorine-resistant NF membrane using three filtration cycles of fouling and cleaning
159 (**Fig. 2**). The membrane sample was first compacted using Milli-Q water at 1 MPa for 1 h (**Fig.**
160 **2a**). The Milli-Q water was then replaced with an NF-treated wastewater for the measurement of
161 permeate flux in treated wastewater without the effects of foulants. The NF-treated wastewater
162 was prepared by filtering the secondary treated effluent by an NF membrane (ESNA1-LF2,
163 Hydranautics, USA), which has a capacity of removing foulants but has a negligible capacity of
164 removing ions. With the wastewater treated with the ESNA1-LF2 NF membrane, permeability of
165 the membrane was measured at 1 MPa (**Fig. 2b**). Thereafter, the NF-treated wastewater was
166 replaced with the secondary treated effluent for fouling development. The filtration system was
167 operated at a constant feed pressure of 1.0 MPa for 10 h (**Fig. 2c**). Feed cross-flow velocity and
168 feed temperature in the feed tank were maintained at 0.52 cm/s and 20.0 ± 0.1 °C, respectively.
169 After 10 h filtration, membrane cleaning was performed with a NaOCl solution (2,000 ppm as
170 NaOCl and pH 11.0) (**Fig. 2d**). Cleaning started with flushing the membrane with Milli-Q water.
171 Hypochlorite cleaning comprised of three steps: (1) recirculation with the NaOCl solution at a
172 cross-flow velocity of 0.52 cm/s for 15 min, (2) settling for 30 min and (3) another recirculation
173 with the chlorine solution at a cross-flow velocity of 0.52 cm/s for 15 min. These cleaning steps
174 were performed without providing a pressure on the membrane cell. After the filtration system

175 was thoroughly rinsed with Milli-Q water, two more filtration cycles comprising of (b)
176 permeability measurement, (c) fouling development and (d) chlorine cleaning were conducted
177 and only permeability measurement was performed in the 4th filtration cycle (**Fig. 2**). Same
178 experimental procedure described above was applied to the evaluation of chlorine-based
179 chemical cleaning for model foulants (HA, SA and BSA). The model foulant solutions contained
180 background electrolytes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂) and 100 mg/L of one of
181 the model foulants in Milli-Q water.



182

183

Fig. 2 – Conceptual diagram of the NF filtration cycles.

184 **2.4 Analytical techniques**

185 High performance liquid chromatography photochemical reaction chemiluminescence (HPLC-
186 PR-CL) was used to determine *N*-nitrosamine concentrations in solution. The volume of the
187 injection sample was in the range of 200 μ L. This analytical technique has been described in

188 details elsewhere [35, 36]. Concentrations of Na⁺ and Ca²⁺ ions were determined using an ion
189 chromatography-conductivity detection system equipped with IC Pak C M/D column (Waters,
190 MA, USA). Solution pH and conductivity were measured by a pH meter (Navi F-53, Horiba,
191 Kyoto, Japan) and a conductivity meter (LAQUAact ES-71, Horiba, Kyoto, Japan), respectively.

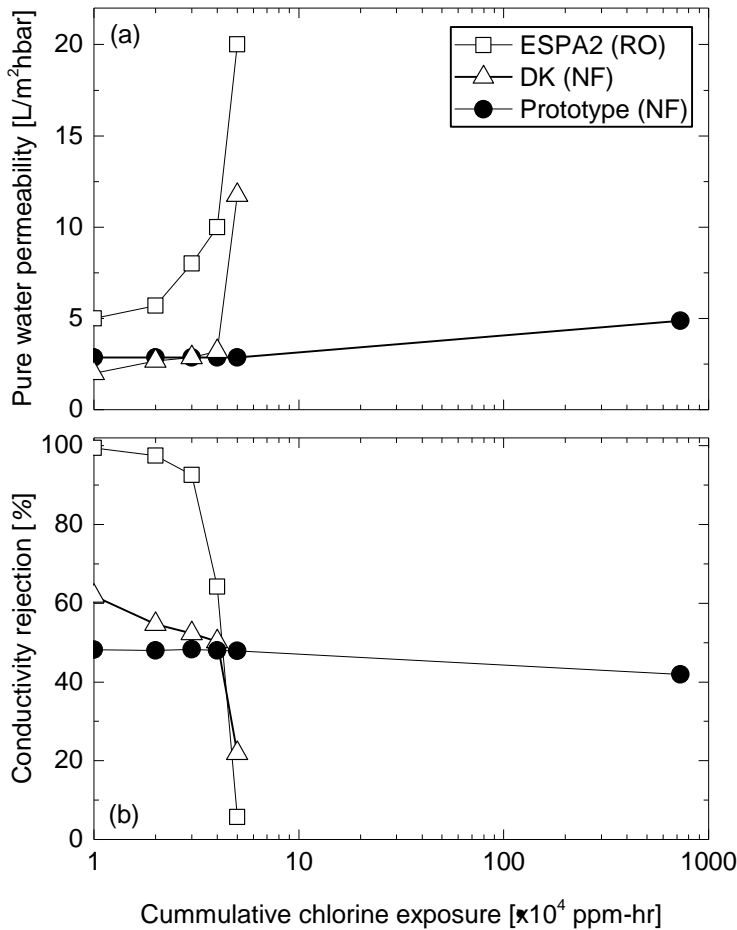
192 Organics in the secondary treated effluent were characterised by a liquid chromatography-
193 organic carbon detection (LC-OCD) system (DOC-LABOR, Karlsruhe, Germany) [37, 38]. The
194 analysis was performed at 1.1 mL/min flow rate with a mobile phase of phosphate buffer, 2.5 g/L
195 KH₂PO₄ and 1.5g/L Na₂HPO₄·2H₂O. Samples were pre-treated using a 0.45 µm filter paper and
196 a sample volume of 1.0 mL was injected.

197 **3. Results and discussion**

198 **3.1 Chlorine exposure**

199 Stability in the performance of the prototype NF membrane against chlorine exposure was
200 evaluated and compared to that of the other two commercial membranes. When prototype NF
201 membrane was exposed to a 1,000 ppm NaOCl solution for up to 50 h (= 5×10⁴ ppm-h), the
202 permeability remained constant at 2.9 L/m²hbar (**Fig. 3a**). In addition, the prototype membrane
203 revealed a stable rejection of 48.0% for up to 5×10⁴ ppm-h (**Fig. 3b**). The results suggested that
204 the prototype NF membrane can be used without any discernible damage on separation
205 performance for chlorine exposure of up to 5×10⁴ ppm-h. The exposure of prototype NF
206 membrane to NaOCl solution was further extended to 73 h with a very high concentration of
207 NaOCl solution (100,000 ppm as NaOCl) to accelerate membrane degradation. The cumulative
208 chlorine exposure of 7.3×10⁶ ppm-h equates to 1,825 day (= 5 year) operation, when the

209 membrane is assumed to undergo hypochlorite cleaning with a 2,000 ppm NaOCl solution for 1
210 h twice a day. As a result, permeability of the prototype NF membrane increased from 2.9 to 4.9
211 L/m²hbar and conductivity rejection (i.e., salt rejection) decreased from 48.0 to 42.0%. The
212 results indicate a small but nevertheless discernible degradation of the prototype NF membrane
213 after an extended period of chlorine exposure (equivalent to 7.3×10⁶ ppm-h). Despite of the
214 slight change in separation performance the results here demonstrated that the prototype NF
215 membrane can be considered as a chlorine-resistant NF membrane.



216

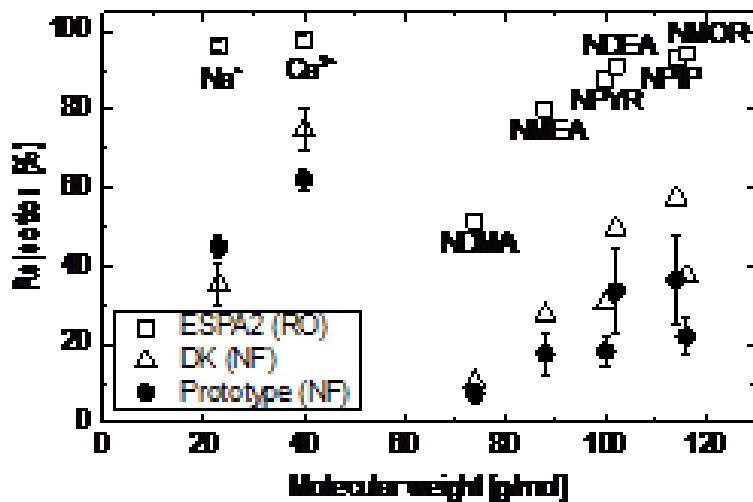
217 **Fig. 3** – Changes in (a) permeability and (b) conductivity rejection as a function of chlorine
218 exposure. Chlorine exposure was performed at a NaOCl concentration of 1,000 ppm (at up to
219 5×10^4 ppm-h) or 100,000 ppm (at 7.3×10^6 ppm-h) at pH 11.0. Pure water permeability was
220 measured at the permeate flux of 20 L/m²h. Conductivity rejection was measured at a NaCl
221 concentration of 20 mM, permeate flux of 20 L/m²h and feed temperature of 20 °C.

222 In contrast, the permeability of the other commercial membranes increased over time and
223 revealed a sharp increase after 40 h exposure (= 4×10^4 ppm-h), which caused an increase in
224 permeability over four times – from 5.0 to 20.0 L/m²hbar for ESPA2 RO membrane and from
225 2.0 to 11.8 L/m²hbar for DK NF membrane (**Fig. 3a**). Likewise, the considerable change was
226 also observed for conductivity rejection. Conductivity rejection by the ESPA2 RO membrane
227 remained at >90% until chlorine exposure of 3×10^4 ppm-h, thereafter it dropped down to 5.7% at
228 5×10^4 ppm-h (**Fig. 3b**). The DK NF membrane revealed a similar but less deterioration in
229 conductivity rejection from 61.8 to 21.9 % from 0 to 5×10^4 ppm-h. The considerable increase in
230 the permeability of the commercial membranes after chlorine exposure is the indication of the
231 degraded membrane by chlorine attack [23].

232 **3.2 Separation performance**

233 The separation performance of low molecular weight chemicals by the three selected membranes
234 was evaluated using inorganic chemicals (Na⁺ and Ca²⁺) and six uncharged organic chemicals
235 (*N*-nitrosamines). The prototype and DK NF membranes revealed similar but low rejections of
236 *N*-nitrosamines all below 60%, which were by far lower than those by ESPA2 RO membrane
237 (50–94%) (**Fig. 4**). The low separation of the NF membranes were comparable to other
238 commercial NF membranes (e.g. NF270 and NF90, Dow/Filmtec) that were reported in a
239 previous study [39]. In contrast, the rejections of sodium ions and calcium ions by the prototype

240 NF membrane were relatively high (45% and 62%, respectively) (**Fig. 4**). This was also observed
 241 for DK NF membrane (35% for sodium ions and 75% for calcium ions, respectively). Because
 242 sodium and calcium ions are strongly hydrated at the tested pH, their hydrated ion size can lead
 243 to the enhanced rejections. In addition, the rejection of charged ions can also be enhanced by the
 244 electrostatic interactions that occur between the ions and membrane [40]. The separation
 245 performance of the prototype NF membrane was greater than that of DK NF membrane for
 246 sodium ions, but vice versa for calcium ions. A previous study [6] has also observed variable
 247 rejections depending on ionic constituent among NF membranes, while the cause still remains
 248 unclear and this could be scope for future study. The results here indicate that the prototype
 249 chlorine-resistant NF membrane is comparable to commercial NF membranes in terms of the
 250 separation performance for Na⁺ and Ca²⁺ ions and low molecular weight organics.

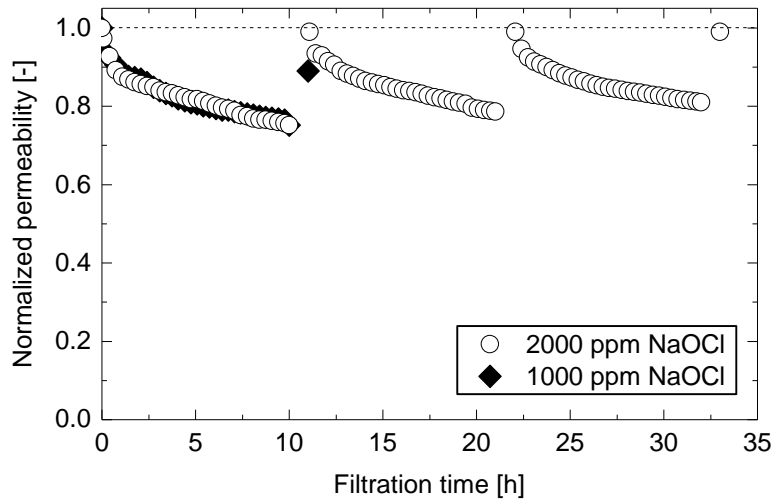


251
 252 **Fig. 4** – Separation performance of the three selected membranes (20 mM NaCl, 1 mM NaHCO₃,
 253 1 mM CaCl₂, 1 μg/L of each *N*-nitrosamine, permeate flux = 20 L/m²h, feed temperature = 20 °C
 254 and feed pH = 8). Values reported here are the average and standard deviation of duplicate
 255 samples.

256 **3.3 Membrane chemical cleaning**

257 **3.3.1 Secondary treated effluent**

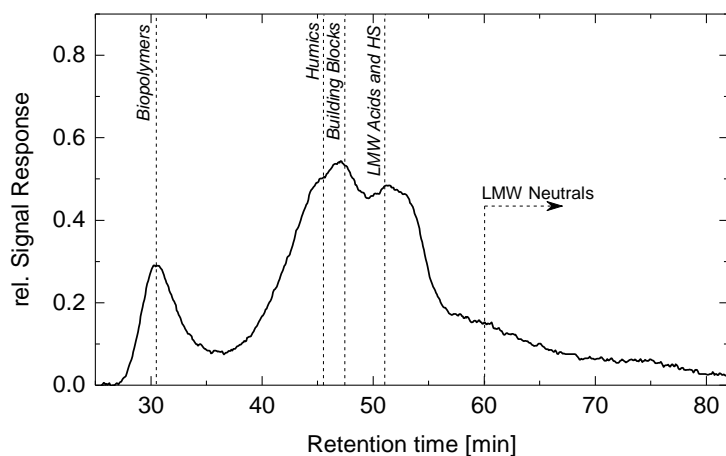
258 The effectiveness of hypochlorite cleaning on fouling mitigation of the prototype chlorine-
259 resistant NF membrane was evaluated using a secondary treated effluent. The direct filtration of
260 the secondary treated effluent resulted in a progressive decrease in the permeability of the
261 prototype NF membrane by 25% over 10 h of filtration at the first filtration cycle (**Fig. 5**).
262 Hypochlorite cleaning using a 1,000 ppm NaOCl solution (pH 11.0) did not sufficiently remove
263 foulants, leading to only 89% of the initial permeability at the beginning of the 2nd filtration
264 cycle. In contrast, hypochlorite cleaning using a 2,000 ppm NaOCl solution (pH 11.0) recovered
265 the permeability to 99%. Of a particular note, the rate of membrane fouling appears to slow
266 down after repetitive cleaning cycling using a 2,000 ppm NaOCl solution. Compared to the first
267 cycle, fouling was less significant during the 2nd (from 11 to 22 h) and 3rd (from 23 to 34 h)
268 filtration cycle, corresponding to 21 and 22% decrease in permeability, respectively. The results
269 here indicate that hypochlorite cleaning using a 2,000 ppm NaOCl solution (pH 11.0) for 1 h was
270 sufficient to clean the prototype NF membrane fouled with the secondary treated effluent.



271

272 **Fig. 5** – Effects of fouling on the prototype NF membrane using the secondary treated effluent
 273 and NaOCl cleaning (2,000 and 1,000 ppm). Filtration was performed at 1.0 MPa feed pressure
 274 and 20 °C feed temperature for 10 h. The initial permeate flux was 31 L/m²h. Each chemical
 275 cleaning was performed at 20±0.1 °C for 1 h.

276 The secondary treated effluent contained a variety of dissolved organic constituents as
277 characterised by LC-OCD (Fig. 3). The distribution of these organic contents was biopolymers
278 (14%), humic substances (44%), building blocks (15%) and low molecular weight (LMW)
279 neutrals (18%). Fraction of biopolymers (>20,000 Da) represents polysaccharides and proteins in
280 the secondary treated effluent, and fraction of humics (approximately 1000 Da) represents humic
281 acid-like substances [38, 41]. Corresponding model substances of these large fractions include
282 sodium alginate (i.e. polysaccharide), BSA (i.e. protein) and humic acids, and they were used as
283 model foulants in the next section. It should be noted that no appropriate model foulants were
284 found for dissolved organics with smaller fractions such as building blocks (300–500 Da) and
285 LMW neutrals (<350 Da).

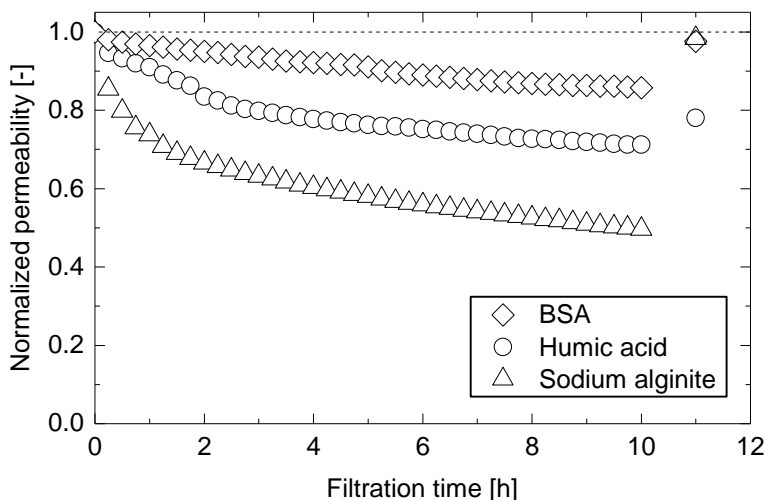


286
287 **Fig. 6 – LC-OCD chromatogram of the secondary treated effluent.**

288 3.3.2 Model foulant solutions

289 To achieve a sustainable NF process using hypochlorite cleaning, potential foulants in treated
290 wastewater that are persistent to the prototype chlorine-resistant NF membrane were investigated
291 by filtering a solution containing one of the model foulants (sodium alginate, BSA or humic

292 acid) and performing hypochlorite cleaning (2,000 ppm as NaOCl and pH = 11.4) for 1 h.
293 Sodium alginate and BSA represent biopolymers (polysaccharide and protein, respectively) in
294 treated wastewater. Humic acids represent humic-like substances in treated wastewater. The
295 substance that most reduced permeability was sodium alginate, causing a 50% reduction in
296 permeability (**Fig. 6**). However, the permeability was well restored to 98% after hypochlorite
297 cleaning. Likewise, the permeability of the prototype NF membrane fouled with BSA was also
298 sufficiently restored with hypochlorite cleaning, while filtration with the BSA solution caused
299 less membrane fouling through 10 h filtration. The results suggest that hypochlorite cleaning is
300 effective for the removal of biopolymers. The model foulant most persistent in this study was
301 humic acid (**Fig. 6**). Membrane fouling with humic acid solution caused a 29% reduction in
302 permeability and the permeability was recovered only slightly to 78% by hypochlorite cleaning.
303 The effective removal of biopolymers can be attributed to the enhanced cleavage of
304 polysaccharides and proteins into sugars and amides by hydrolysis after oxidation of these
305 substances with hypochlorite [42]. In contrast, strong complexation between humic substances
306 and calcium ions could limit flux recovery [43, 44]. These results indicate that the cleaning
307 protocol used in this study may not be sufficient for the treated wastewater with abundant humic-
308 like substances.



309
 310 **Fig. 7** – Effects of fouling on the prototype chlorine-resistant NF membrane using the model
 311 foulant solutions (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, 100 mg/L model foulant and pH
 312 = 8.0) and NaOCl cleaning. Filtration was performed at 1.0 MPa feed pressure and 20°C feed
 313 temperature. The initial permeate flux was 33 L/m²h. Each chemical cleaning was performed
 314 with a 2,000 ppm NaOCl solution (pH = 11.4) at 20 °C for 1 h.

315 **4. Conclusions**

316 This study assessed the effects of hypochlorite cleaning on fouling mitigation of a prototype
 317 chlorine-resistant NF membrane for direct filtration of a secondary treated effluent. The exposure
 318 of the chlorine-resistant NF membrane to a 1,000 ppm NaOCl solution revealed that the
 319 permeability and separation performance remained stable for up to the cumulative chlorine
 320 exposure of 5×10⁴ ppm-hr. The separation performance of the prototype NF membrane for Na⁺
 321 and Ca²⁺ ions and *N*-nitrosamines was comparable to a commercial NF membrane. Filtration of
 322 the secondary treated effluent by prototype NF membrane resulted in a gradual decrease in
 323 permeability down to 75%, while hypochlorite cleaning with a 2,000 ppm NaOCl solution (pH =
 324 11.0) for 1 h restored the permeability. The recovery in permeability was demonstrated up to

325 three cycles, indicating that hypochlorite cleaning can be an effective cleaning strategy to the
326 direct filtration of secondary treated effluent. Further investigations using model foulants
327 revealed that humic substances were persistent to the prototype NF membrane and hypochlorite
328 cleaning protocol used in this study was not sufficient. To make water recycling systems using a
329 chlorine-resistant NF membrane and hypochlorite cleaning feasible, optimization techniques of
330 cleaning protocols such as NaOCl concentrations, pH and temperature are required. *In addition,*
331 *it is necessary to evaluate the formation of disinfection by-products for safe disposal of the spent*
332 *membrane cleaning solution.*

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335 **6. References**

- 336 [1] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal,
337 Nanofiltration membranes review: Recent advances and future prospects, *Desalination*,
338 356 (2015) 226-254.
- 339 [2] B. Van Der Bruggen, C. Vandecasteele, T. Van Gestel, W. Doyen, R. Leysen, A review
340 of pressure-driven membrane processes in wastewater treatment and drinking water
341 production, *Environmental Progress*, 22 (2003) 46-56.
- 342 [3] A. Maher, M. Sadeghi, A. Moheb, Heavy metal elimination from drinking water using
343 nanofiltration membrane technology and process optimization using response surface
344 methodology, *Desalination*, 352 (2014) 166-173.
- 345 [4] B.A.M. Al-Rashdi, D.J. Johnson, N. Hilal, Removal of heavy metal ions by
346 nanofiltration, *Desalination*, 315 (2013) 2-17.
- 347 [5] T. Fujioka, S.J. Khan, J.A. McDonald, L.D. Nghiem, Rejection of trace organic
348 chemicals by a nanofiltration membrane: the role of molecular properties and effects of
349 caustic cleaning, *Environmental Science: Water Research & Technology*, 1 (2015) 846-
350 854.

- 351 [6] C. Bellona, D. Heil, C. Yu, P. Fu, J.E. Drewes, The pros and cons of using nanofiltration
352 in lieu of reverse osmosis for indirect potable reuse applications, *Separation and*
353 *Purification Technology*, 85 (2012) 69-76.
- 354 [7] C. Kazner, K. Lehnberg, L. Kovalova, T. Wintgens, T. Melin, J. Hollender, W. Dott,
355 Removal of endocrine disruptors and cytostatics from effluent by nanofiltration in
356 combination with adsorption on powdered activated carbon, *Water Science and*
357 *Technology*, 58 (2008) 1699-1706.
- 358 [8] L.D. Nghiem, P.J. Coleman, C. Espendiller, Mechanisms underlying the effects of
359 membrane fouling on the nanofiltration of trace organic contaminants, *Desalination*, 250
360 (2010) 682-687.
- 361 [9] P. Xu, J.E. Drewes, T.-U. Kim, C. Bellona, G. Amy, Effect of membrane fouling on
362 transport of organic contaminants in NF/RO membrane applications, *Journal of*
363 *Membrane Science*, 279 (2006) 165-175.
- 364 [10] V. Yangali-Quintanilla, A. Sadmani, M. McConville, M. Kennedy, G. Amy, Rejection of
365 pharmaceutically active compounds and endocrine disrupting compounds by clean and
366 fouled nanofiltration membranes, *Water Research*, 43 (2009) 2349-2362.
- 367 [11] T. Wintgens, T. Melin, A. Schäfer, S. Khan, M. Muston, D. Bixio, C. Thoeye, The role of
368 membrane processes in municipal wastewater reclamation and reuse, *Desalination*, 178
369 (2005) 1-11.
- 370 [12] A. Al-Amoudi, R.W. Lovitt, Fouling strategies and the cleaning system of NF
371 membranes and factors affecting cleaning efficiency, *Journal of Membrane Science*, 303
372 (2007) 4-28.
- 373 [13] T. Fujioka, S.J. Khan, J.A. McDonald, A. Roux, Y. Poussade, J.E. Drewes, L.D. Nghiem,
374 N-nitrosamine rejection by reverse osmosis: Effects of membrane exposure to chemical
375 cleaning reagents, *Desalination*, 343 (2014) 60-66.
- 376 [14] V. Puspitasari, A. Granville, P. Le-Clech, V. Chen, Cleaning and ageing effect of sodium
377 hypochlorite on polyvinylidene fluoride (PVDF) membrane, *Separation and Purification*
378 *Technology*, 72 (2010) 301-308.
- 379 [15] N. Fujiwara, H. Matsuyama, Optimization of the intermittent chlorine injection (ICI)
380 method for seawater desalination RO plants, *Desalination*, 229 (2008) 231-244.
- 381 [16] D.L. Norwood, J.D. Johnson, R.F. Christman, J.R. Mass, M.J. Bobenrieth, Reactions of
382 chlorine with selected aromatic models of aquatic humic material, *Environmental Science*
383 *and Technology*, 14 (1980) 187-190.
- 384 [17] N. Porcelli, S. Judd, Chemical cleaning of potable water membranes: A review,
385 *Separation and Purification Technology*, 71 (2010) 137-143.

- 386 [18] A. Simon, L.D. Nghiem, P. Le-Clech, S.J. Khan, J.E. Drewes, Effects of membrane
387 degradation on the removal of pharmaceutically active compounds (PhACs) by NF/RO
388 filtration processes, *Journal of Membrane Science*, 340 (2009) 16-25.
- 389 [19] A. Simon, L.D. Nghiem, Effects of hypochlorite exposure on morphology and trace
390 organic contaminant rejection by NF/RO membranes, *Membrane Water Treatment*, 5
391 (2014) 235-250.
- 392 [20] Y.-N. Kwon, J.O. Leckie, Hypochlorite degradation of crosslinked polyamide
393 membranes: I. Changes in chemical/morphological properties, *Journal of Membrane
394 Science*, 283 (2006) 21-26.
- 395 [21] Y.-N. Kwon, J.O. Leckie, Hypochlorite degradation of crosslinked polyamide
396 membranes: II. Changes in hydrogen bonding behavior and performance, *Journal of
397 Membrane Science*, 282 (2006) 456-464.
- 398 [22] J. Glater, S.k. Hong, M. Elimelech, The search for a chlorine-resistant reverse osmosis
399 membrane, *Desalination*, 95 (1994) 325-345.
- 400 [23] M. Ohno, C. Manalo, L. Rossetto, T. Okuda, S. Nakai, W. Nishijima, Effect of coexisting
401 metal ions on the degradation of polyamide reverse osmosis membrane by hypochlorite
402 treatment, *Desalination*, 381 (2016) 126-134.
- 403 [24] V.T. Do, C.Y. Tang, M. Reinhard, J.O. Leckie, Degradation of Polyamide Nanofiltration
404 and Reverse Osmosis Membranes by Hypochlorite, *Environmental Science &
405 Technology*, 46 (2012) 852-859.
- 406 [25] L. Ni, J. Meng, X. Li, Y. Zhang, Surface coating on the polyamide TFC RO membrane
407 for chlorine resistance and antifouling performance improvement, *Journal of Membrane
408 Science*, 451 (2014) 205-215.
- 409 [26] Y. Gao, A.M.S. De Jubera, B.J. Mariñas, J.S. Moore, Nanofiltration membranes with
410 modified active layer using aromatic polyamide dendrimers, *Advanced Functional
411 Materials*, 23 (2013) 598-607.
- 412 [27] V.M. Kochkodan, V.K. Sharma, Graft polymerization and plasma treatment of polymer
413 membranes for fouling reduction: A review, *Journal of Environmental Science and
414 Health, Part A*, 47 (2012) 1713-1727.
- 415 [28] H. Zhao, S. Qiu, L. Wu, L. Zhang, H. Chen, C. Gao, Improving the performance of
416 polyamide reverse osmosis membrane by incorporation of modified multi-walled carbon
417 nanotubes, *Journal of Membrane Science*, 450 (2014) 249-256.
- 418 [29] T. Shintani, H. Matsuyama, N. Kurata, Development of a chlorine-resistant polyamide
419 reverse osmosis membrane, *Desalination*, 207 (2007) 340-348.

- 420 [30] T. Shintani, H. Matsuyama, N. Kurata, T. Ohara, Development of a chlorine-resistant
421 polyamide nanofiltration membrane and its field-test results, *Journal of Applied Polymer*
422 *Science*, 106 (2007) 4174-4179.
- 423 [31] T. Fujioka, S.J. Khan, Y. Poussade, J.E. Drewes, L.D. Nghiem, N-nitrosamine removal
424 by reverse osmosis for indirect potable water reuse – A critical review based on
425 observations from laboratory-, pilot- and full-scale studies, *Separation and Purification*
426 *Technology*, 98 (2012) 503-515.
- 427 [32] M.P. Lopes, C.T. Matos, V.J. Pereira, M.J. Benoliel, M.E. Valério, L.B. Bucha, A.
428 Rodrigues, A.I. Penetra, E. Ferreira, V.V. Cardoso, M.A.M. Reis, J.G. Crespo,
429 Production of drinking water using a multi-barrier approach integrating nanofiltration: A
430 pilot scale study, *Separation and Purification Technology*, 119 (2013) 112-122.
- 431 [33] T. Fujioka, L.D. Nghiem, S.J. Khan, J.A. McDonald, Y. Poussade, J.E. Drewes, Effects
432 of feed solution characteristics on the rejection of N-nitrosamines by reverse osmosis
433 membranes, *Journal of Membrane Science*, 409-410 (2012) 66-74.
- 434 [34] T. Fujioka, S.J. Khan, J.A. McDonald, A. Roux, Y. Poussade, J.E. Drewes, L.D. Nghiem,
435 N-nitrosamine rejection by reverse osmosis membranes: A full-scale study, *Water*
436 *Research*, 47 (2013) 6141-6148.
- 437 [35] T. Fujioka, H. Takeuchi, H. Tanaka, L.D. Nghiem, K.P. Ishida, H. Kodamatani, A rapid
438 and reliable technique for N-nitrosodimethylamine analysis in reclaimed water by HPLC-
439 photochemical reaction-chemiluminescence, *Chemosphere*, 161 (2016) 104-111.
- 440 [36] H. Kodamatani, S. Yamazaki, K. Saito, A. Amponsaa-Karikari, N. Kishikawa, N.
441 Kuroda, T. Tomiyasu, Y. Komatsu, Highly sensitive method for determination of N-
442 nitrosamines using high-performance liquid chromatography with online UV irradiation
443 and luminol chemiluminescence detection, *Journal of Chromatography A*, 1216 (2009)
444 92-98.
- 445 [37] R.K. Henderson, N. Subhi, A. Antony, S.J. Khan, K.R. Murphy, G.L. Leslie, V. Chen,
446 R.M. Stuetz, P. Le-Clech, Evaluation of effluent organic matter fouling in ultrafiltration
447 treatment using advanced organic characterisation techniques, *J. Membr. Sci.*, 382 (2011)
448 50-59.
- 449 [38] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-
450 humic matter with size-exclusion chromatography – organic carbon detection – organic
451 nitrogen detection (LC-OCD-OND), *Water Res.*, 45 (2011) 879-885.
- 452 [39] T. Fujioka, S.J. Khan, J.A. McDonald, L.D. Nghiem, Nanofiltration of trace organic
453 chemicals: A comparison between ceramic and polymeric membranes, *Separation and*
454 *Purification Technology*, 136 (2014) 258-264.

- 455 [40] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes
456 during NF/RO treatment - A literature review, *Water Research*, 38 (2004) 2795-2809.
- 457 [41] R.K. Henderson, R.M. Stuetz, S.J. Khan, Demonstrating ultra-filtration and reverse
458 osmosis performance using size exclusion chromatography, *Water Sci. Technol.*, 62
459 (2010) 2747-2753.
- 460 [42] W. Gao, H. Liang, J. Ma, M. Han, Z.-l. Chen, Z.-s. Han, G.-b. Li, Membrane fouling
461 control in ultrafiltration technology for drinking water production: A review,
462 *Desalination*, 272 (2011) 1-8.
- 463 [43] M. Beyer, B. Lohrengel, L.D. Nghiem, Membrane fouling and chemical cleaning in
464 water recycling applications, *Desalination*, 250 (2010) 977-981.
- 465 [44] W.S. Ang, S. Lee, M. Elimelech, Chemical and physical aspects of cleaning of organic-
466 fouled reverse osmosis membranes, *Journal of Membrane Science*, 272 (2006) 198-210.
- 467