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

Abstract

The effectiveness of hypochlorite cleaning for fouling mitigation of a prototype chlorine-resistant nanofiltration (NF) membrane was assessed for direct filtration of a secondary treated effluent. The chlorine resistance and separation performance of the prototype NF membrane were also compared to commercial NF and reverse osmosis membranes. The prototype chlorine resistant NF membrane did not show any changes in permeability and conductivity rejection after exposing a NaOCl solution for up to 5 x 10⁴ ppm-h. By contrast, a considerable deterioration in rejection was observed for the other two commercial membranes. Direct filtration of a secondary treated effluent by the prototype NF membrane resulted in a progressive permeability reduction by up to 25% after 10 h of filtration. The membrane permeability was fully restored by hypochlorite cleaning with a 2000 ppm NaOCl solution for 1 h. Effective permeability recovery by hypochlorite cleaning was demonstrated with multiple hypochlorite cleaning cycles. Membrane fouling and hypochlorite cleaning were also simulated using solutions containing a model foulant (sodium alginate, humic acids or bovine serum albumin). Among them, an insufficient permeability recovery was observed for membrane fouling caused by humic acids. Further research is recommended to develop an improved hypochlorite cleaning protocol to control various membrane fouling.

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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**

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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.

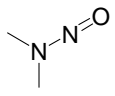
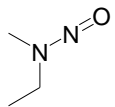
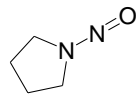
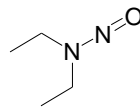
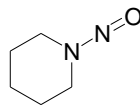
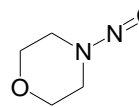
90 **2. Materials and methods**

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.

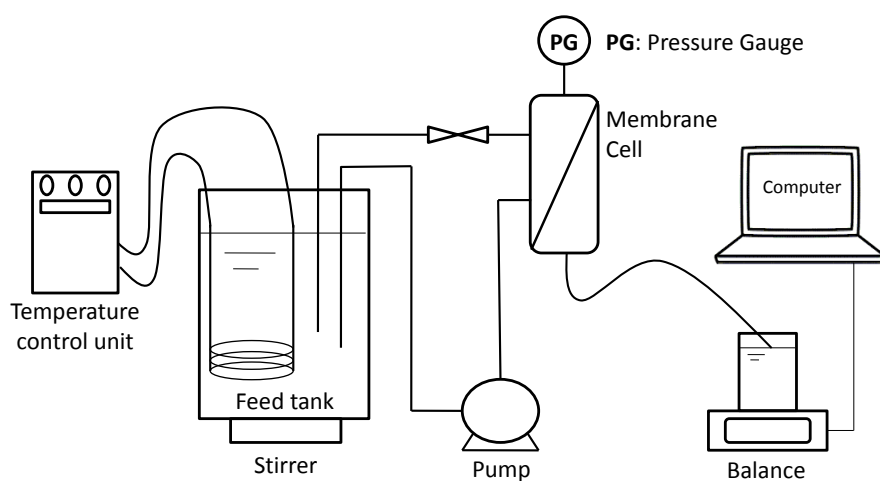
Compound	NDMA	NMEA	NPYR	NDEA	NPIP	NMOR
Structure						
Molecular formula	C ₂ H ₆ N ₂ O	C ₃ H ₈ N ₂ O	C ₄ H ₈ N ₂ O	C ₄ H ₁₀ N ₂ O	C ₅ H ₁₀ N ₂ O	C ₄ H ₈ N ₂ O ₂
Molecular weight [g/mol]	74.05	88.06	100.06	102.08	114.08	116.06
Low <i>D</i> at pH 8 ^a	0.04	0.40	0.44	0.52	0.44	-0.18

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**

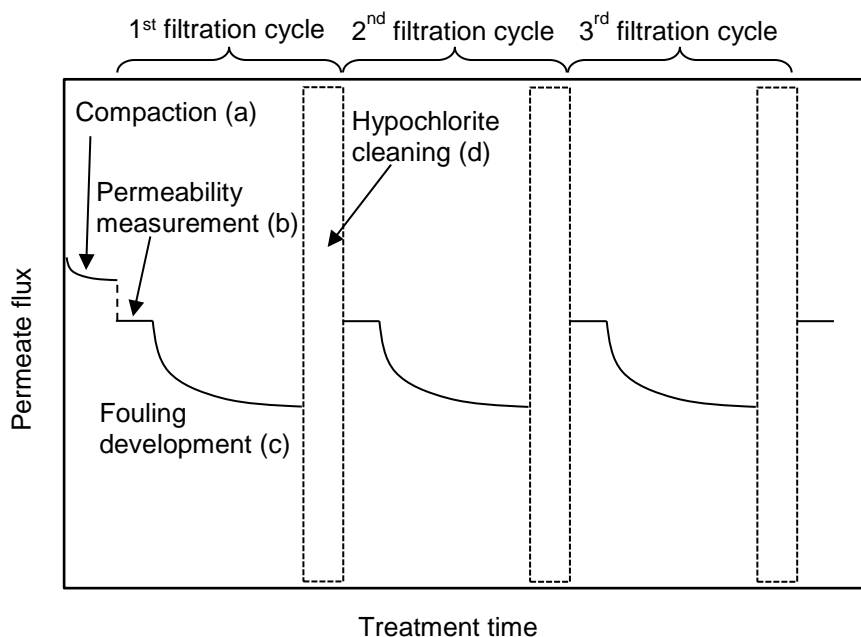
141 Separation performance of the three selected membranes was evaluated by measuring the
142 rejection of cations (Na⁺ and Ca²⁺) and uncharged organic solutes (*N*-nitrosamines). The
143 membrane sample was first compacted by operating system with Milli-Q water at 1 MPa for 1 h.
144 Background electrolytes 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 Ca^{2+} 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 KH_2PO_4 and 1.5 g/L $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$. Samples were pre-treated using a 0.45 μm filter paper and
196 a sample volume of 1.0 mL was injected.

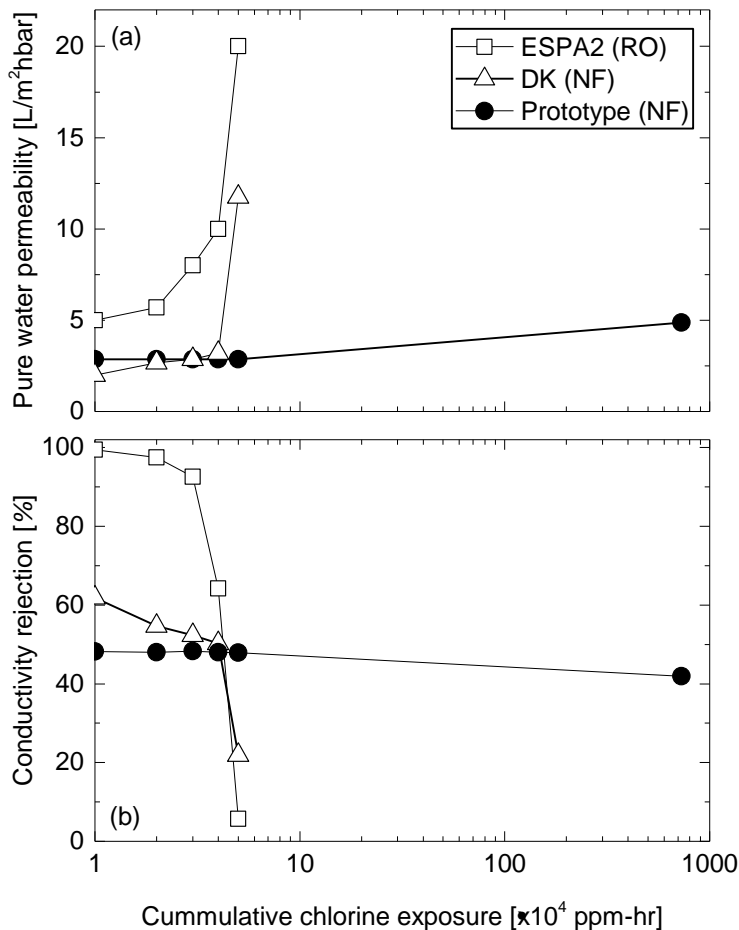
197 **3. Results and discussion**

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 ($= 5 \times 10^4$ ppm-h), the
202 permeability remained constant at 2.9 $\text{L}/\text{m}^2\text{hbar}$ (**Fig. 3a**). In addition, the prototype membrane
203 revealed a stable rejection of 48.0% for up to 5×10^4 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 5×10^4 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 7.3×10^6 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 7.3×10^6 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 In contrast, the permeability of the other commercial membranes increased over time and
217 revealed a sharp increase after 40 h exposure ($= 4 \times 10^4$ ppm-h), which caused an increase in
218 permeability over four times – from 5.0 to 20.0 L/m²hbar for ESPA2 RO membrane and from
219 2.0 to 11.8 L/m²hbar for DK NF membrane (**Fig. 3a**). Likewise, the considerable change was
220 also observed for conductivity rejection. Conductivity rejection by the ESPA2 RO membrane
221 remained at >90% until chlorine exposure of 3×10^4 ppm-h, thereafter it dropped down to 5.7% at
222 5×10^4 ppm-h (**Fig. 3b**). The DK NF membrane revealed a similar but less deterioration in
223 conductivity rejection from 61.8 to 21.9 % from 0 to 5×10^4 ppm-h. The considerable increase in
224 the permeability of the commercial membranes after chlorine exposure is the indication of the
225 degraded membrane by chlorine attack [23].



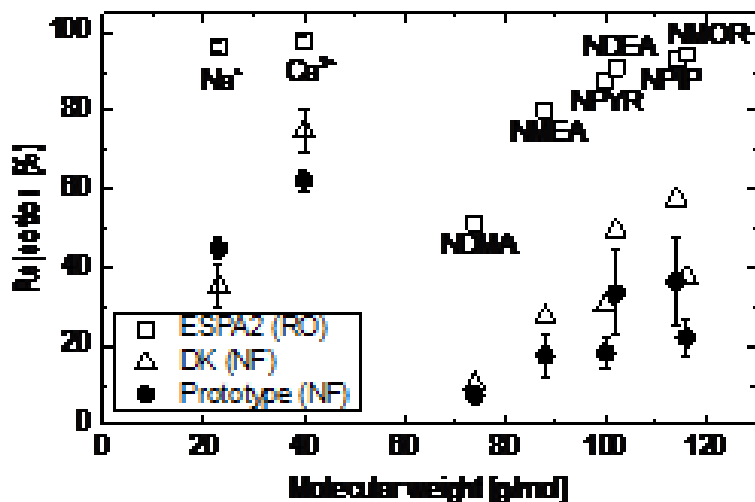
226

227 **Fig. 3** – Changes in (a) permeability and (b) conductivity rejection as a function of chlorine
 228 exposure. Chlorine exposure was performed at a NaOCl concentration of 1,000 ppm (at up to
 229 5×10^4 ppm-h) or 100,000 ppm (at 7.3×10^6 ppm-h) at pH 11.0. Pure water permeability was
 230 measured at the permeate flux of 20 $L/m^2 \cdot h$. Conductivity rejection was measured at a NaCl
 231 concentration of 20 mM, permeate flux of 20 $L/m^2 \cdot h$ and feed temperature of 20 °C.

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 Ca^{2+}) 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]. Sodium rejection by
245 the prototype NF membrane was higher than that by the DK NF membrane. However, the
246 opposite observation could be made for calcium ions (Fig. 4). A previous study [6] has also
247 observed variable rejections by different NF membranes depending on ionic composition of the
248 feed. The cause for this observation remains unclear and this could be part of a future study. The
249 results here indicate that the prototype chlorine-resistant NF membrane is comparable to
250 commercial NF membranes in terms of the separation performance for Na⁺ and Ca²⁺ ions and
251 low molecular weight organics.



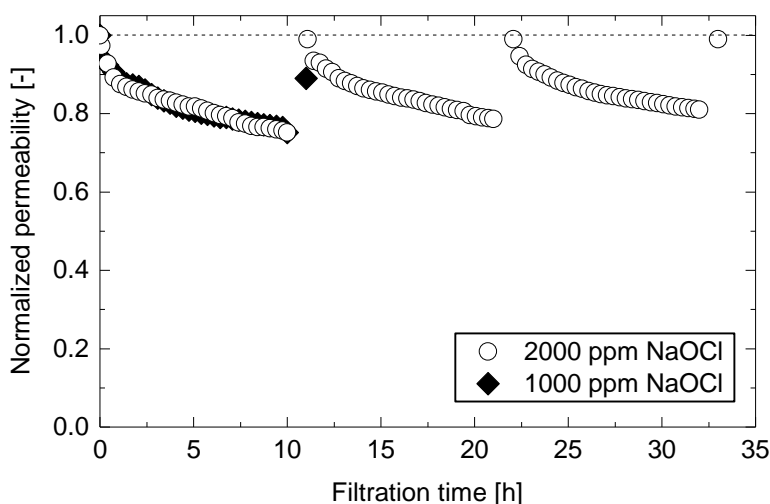
252
 253 **Fig. 4** – Separation performance of the three selected membranes (20 mM NaCl, 1 mM NaHCO₃,
 254 1 mM CaCl₂, 1 μg/L of each *N*-nitrosamine, permeate flux = 20 L/m²h, feed temperature = 20 °C
 255 and feed pH = 8). Values reported here are the average and standard deviation of duplicate
 256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

257 3.3 Membrane chemical cleaning

258 3.3.1 Secondary treated effluent

259 The effectiveness of hypochlorite cleaning on fouling mitigation of the prototype chlorine-
 260 resistant NF membrane was evaluated using a secondary treated effluent. The direct filtration of
 261 the secondary treated effluent resulted in a progressive decrease in the permeability of the
 262 prototype NF membrane by 25% over 10 h of filtration at the first filtration cycle (**Fig. 5**).
 263 Hypochlorite cleaning using a 1,000 ppm NaOCl solution (pH 11.0) did not sufficiently remove
 264 foulants, leading to only 89% of the initial permeability at the beginning of the 2nd filtration
 265 cycle. In contrast, hypochlorite cleaning using a 2,000 ppm NaOCl solution (pH 11.0) recovered
 266 the permeability to 99%. Of a particular note, the rate of membrane fouling appears to slow
 267 down after repetitive cleaning cycling using a 2,000 ppm NaOCl solution. Compared to the first

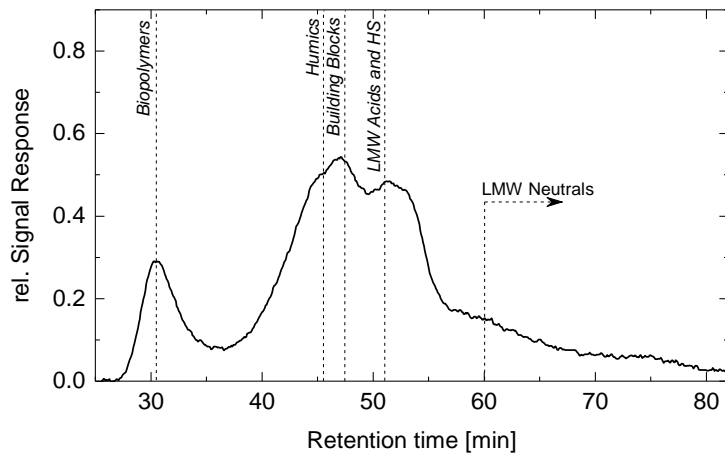
268 cycle, fouling was less significant during the 2nd (from 11 to 22 h) and 3rd (from 23 to 34 h)
269 filtration cycle, corresponding to 21 and 22% decrease in permeability, respectively. The results
270 here indicate that hypochlorite cleaning using a 2,000 ppm NaOCl solution (pH 11.0) for 1 h was
271 sufficient to clean the prototype NF membrane fouled with the secondary treated effluent.



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

277 The secondary treated effluent contained a variety of dissolved organic constituents as
278 characterised by LC-OCD (**Fig. 3**). The distribution of these organic contents was biopolymers
279 (14%), humic substances (44%), building blocks (15%) and low molecular weight (LMW)
280 neutrals (18%). Fraction of biopolymers (>20,000 Da) represents polysaccharides and proteins in
281 the secondary treated effluent, and fraction of humics (approximately 1,000 Da) represents
282 humic acid-like substances [38, 41]. Corresponding model substances of these large fractions
283 include sodium alginate (i.e. polysaccharide), BSA (i.e. protein) and humic acids, and they were

284 used as model foulants in the next section. It should be noted that no appropriate model foulants
285 were found for dissolved organics with smaller fractions such as building blocks (300–500 Da)
286 and LMW neutrals (<350 Da).

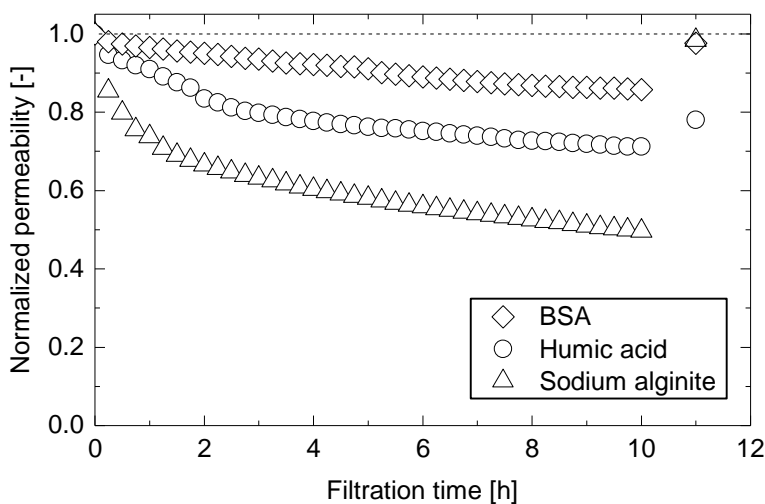


287
288 **Fig. 6** – LC-OCD chromatogram of the secondary treated effluent.

289 3.3.2 Model foulant solutions

290 To achieve a sustainable NF process using hypochlorite cleaning, potential foulants in treated
291 wastewater that are persistent to the prototype chlorine-resistant NF membrane were investigated
292 by filtering a solution containing one of the model foulants (sodium alginate, BSA or humic
293 acid) and performing hypochlorite cleaning (2,000 ppm as NaOCl and pH = 11.4) for 1 h.
294 Sodium alginate and BSA represent biopolymers (polysaccharide and protein, respectively) in
295 treated wastewater. Humic acids represent humic-like substances in treated wastewater. The
296 substance that most reduced permeability was sodium alginate, causing a 50% reduction in
297 permeability (**Fig. 6**). However, the permeability was well restored to 98% after hypochlorite
298 cleaning. Likewise, the permeability of the prototype NF membrane fouled with BSA was also
299 sufficiently restored with hypochlorite cleaning, while filtration with the BSA solution caused

300 less membrane fouling through 10 h filtration. The results suggest that hypochlorite cleaning is
 301 effective for the removal of biopolymers. The model foulant most persistent in this study was
 302 humic acid (**Fig. 6**). Membrane fouling with humic acid solution caused a 29% reduction in
 303 permeability and the permeability was recovered only slightly to 78% by hypochlorite cleaning.
 304 The effective removal of biopolymers can be attributed to the enhanced cleavage of
 305 polysaccharides and proteins into sugars and amides by hydrolysis after oxidation of these
 306 substances with hypochlorite [42]. In contrast, strong complexation between humic substances
 307 and calcium ions could limit flux recovery [43, 44]. These results indicate that the cleaning
 308 protocol used in this study may not be sufficient for the treated wastewater with abundant humic-
 309 like substances.



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

316 **4. Conclusions**

317 This study assessed the effects of hypochlorite cleaning on fouling mitigation of a prototype
318 chlorine-resistant NF membrane for direct filtration of a secondary treated effluent. The exposure
319 of the chlorine-resistant NF membrane to a 1,000 ppm NaOCl solution revealed that the
320 permeability and separation performance remained stable for up to the cumulative chlorine
321 exposure of 5×10^4 ppm-hr. The separation performance of the prototype NF membrane for Na^+
322 and Ca^{2+} ions and *N*-nitrosamines was comparable to a commercial NF membrane. Filtration of
323 the secondary treated effluent by prototype NF membrane resulted in a gradual decrease in
324 permeability down to 75%, while hypochlorite cleaning with a 2,000 ppm NaOCl solution (pH =
325 11.0) for 1 h restored the permeability. The recovery in permeability was demonstrated up to
326 three cycles, indicating that hypochlorite cleaning can be an effective cleaning strategy to the
327 direct filtration of secondary treated effluent. Further investigations using model foulants
328 revealed that humic substances were persistent to the prototype NF membrane and hypochlorite
329 cleaning protocol used in this study was not sufficient. To make water recycling systems using a
330 chlorine-resistant NF membrane and hypochlorite cleaning feasible, optimization techniques of
331 cleaning protocols such as NaOCl concentrations, pH and temperature are required. *In addition,*
332 *it is necessary to evaluate the formation of disinfection by-products for safe disposal of the spent*
333 *membrane cleaning solution.*

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336 6. References

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