2017

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

Moe Tin
Nagasaki University

George Anioke
Nagasaki University

Osamu Nakagoe
Nagasaki University

Shuji Tanabe
Nagasaki University

Hitoshi Kodamatani
Kagoshima University

See next page for additional authors

Publication Details
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 10^4 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.

Disciplines
Engineering | Science and Technology Studies

Publication Details

Authors
Moe Tin, George Anioke, Osamu Nakagoe, Shuji Tanabe, Hitoshi Kodamatani, Long D. Nghiem, and Takahiro Fujioka

This journal article is available at Research Online: http://ro.uow.edu.au/eispapers1/580
Membrane fouling, chemical cleaning and separation performance assessment of a chlorine-resistant nanofiltration membrane for water recycling applications

Revised manuscript submitted to

*Separation and Purification Technology*

June 2017

Moe Ma Ma Tin 1, Anioke George 1, Osamu Nakagoe 1, Shuji Tanabe 1, Hitoshi Kodamatani 2, Long D. Nghiem 3, Takahiro Fujioka 1,*

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

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

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

*Corresponding author: Takahiro Fujioka, Email: tfujioka@nagasaki-u.ac.jp, Ph +81 095 819 2695
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 $5 \times 10^4$ 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 2,000 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.

Keywords: hypochlorite cleaning; chlorine-resistant nanofiltration membrane; membrane fouling; water recycling; N-nitrosamines.
1. Introduction

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

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

Without pretreatment, NF filtration operation is likely to face accelerated membrane fouling but can be counteracted by frequent and effective chemical cleaning. In conventional NF operation, chemical cleaning is periodically conducted by filling up the feed side of the membrane with
solutions containing caustic (e.g. NaOH) or acidic (e.g. HCl) chemicals and recirculating the solutions [12]. The downside of frequent chemical cleanings is the disruption to the continuous operation of the membrane skid, because typical chemical cleaning requires a cleaning period of up to 8 h [13]. In addition to these conventional chemicals, membrane cleaning with a chlorine-containing solution (e.g. hypochlorite) has attracted attention in recent years due to its inexpensive and affordable supplies of sodium hypochlorite and its high ability in fouling mitigation [14, 15]. Major mechanisms of hypochlorite cleaning are to disinfect the membrane and to oxidize the functional groups of organic foulants to ketone, aldehyde and carboxylic groups. The presence of these functional groups increases the hydrophilicity and charges of their parent compounds, reducing the adhesion and attraction of fouling substances to the membranes [16]. In fact, many MF- or UF-based water reclamation systems can be frequently cleaned using a hypochlorite solution [17]. However, hypochlorite cleaning cannot be applied to conventional NF and RO membranes because their PA active skin layer is readily degraded by chlorine [18-20].

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

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

2. Materials and methods

2.1 Chemicals

Analytical grade NaCl, NaHCO₃ and CaCl₂ were purchased from Wako Pure Chemical Industries (Tokyo, Japan) and used as background electrolyte. Analytical grade sodium hypochlorite solution (10% available chlorine) was purchased from Sigma-Aldrich (St Louis, MO, USA). Six analytical grade N-nitrosamines were purchased from Ultra scientific (Kingstown, RI, USA). They include N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPRY), N-nitrosodiethylamine (NDEA), N-nitrosopiperidine (NPIP) and N-nitrosomorpholine (NMOR) (Table 1). A stock solution was prepared at 1.0 mg/mL of each N-nitrosamine in pure methanol. Analytical grade
luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) was supplied from Wako Pure Chemical Industries (Tokyo, Japan). Three model foulants used here include sodium alginate (SA), bovine serum albumin (BSA), humic acids (HA). Sodium alginate and humic acid were supplied by Sigma-Aldrich (St Louis, MO, USA). BSA was purchased from Wako Pure Chemical Industries (Tokyo, Japan). Secondary treated effluent was collected after activated sludge treatment but prior to post chlorination at a municipal wastewater treatment plant in Japan. The obtained secondary treated effluent was used directly without any pretreatment to promote membrane fouling during filtration experiments.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>NDMA</th>
<th>NMEA</th>
<th>NPYR</th>
<th>NDEA</th>
<th>NPIP</th>
<th>NMOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>N-N-O</td>
<td>N-N-O</td>
<td>N-N-O</td>
<td>N-N-O</td>
<td>N-N-O</td>
<td>N-N-O</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C$_2$H$_6$N$_2$O</td>
<td>C$_3$H$_8$N$_2$O</td>
<td>C$_4$H$_8$N$_2$O</td>
<td>C$<em>4$H$</em>{10}$N$_2$O</td>
<td>C$<em>5$H$</em>{10}$N$_2$O</td>
<td>C$_4$H$_8$N$_2$O$_2$</td>
</tr>
<tr>
<td>Molecular weight [g/mol]</td>
<td>74.05</td>
<td>88.06</td>
<td>100.06</td>
<td>102.08</td>
<td>114.08</td>
<td>116.06</td>
</tr>
<tr>
<td>Low $D$ at pH 8$^a$</td>
<td>0.04</td>
<td>0.40</td>
<td>0.44</td>
<td>0.52</td>
<td>0.44</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

$^a$Chemicalize (http://www.chemicalize.org).

2.2 Membranes and filtration system

Prototype chlorine-resistant NF membrane was supplied as flat sheet samples by Nitto Denko (Osaka, Japan). Two other commercial flat sheet membranes – namely DK NF membrane (GE, USA) and ESPA2 RO membrane (Hydranautics, USA) – were also used. The DK NF and ESPA2 membranes have been widely used for water recycling applications [31, 32]. A bench-
scale cross-flow filtration system was used (Fig. 1). The system comprised of a stainless-steel membrane cell with an effective surface diameter of 2.2 cm, an effective surface area of 3.80 cm², a channel height of 0.44 cm, a pressure gauge, a 2 L feed tank and a high-pressure pump (KP-12, FLOM, Tokyo, Japan). Feed solution in the feed tank was stirred throughout each experiment. Feed solution temperature was controlled at 20.0 ± 0.1 °C by a temperature control unit (CCA-1112, Tokyo Rikakikai, Tokyo, Japan) which was equipped with a stainless steel heat exchange coil. Permeate flow was monitored using a digital balance (FX-300i, A&D, Tokyo, Japan) that was connected to a computer for data logging.

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

2.3 Experimental protocols

2.3.1 Chlorine exposure

Prior to the chlorine exposure experiments, membrane coupons were gently rinsed and soaked in Milli-Q water overnight. To simulate a long-term exposure of the membrane to chlorine, NaOCl solutions were prepared in pure water to obtain a concentration of either 1,000 ppm (as NaOCl at pH 11.0) or 100,000 ppm (as NaOCl at pH 11.0). Each membrane sample was immersed in a 50
mL NaOCl solution in a Pyrex glass beaker covered with aluminum foils and placed in a water bath at 20.0 ± 0.1 °C for a specified duration. As soon as the chlorine exposure experiments ended, the membranes were rinsed with a copious amount of deionized water and were stored in the dark at 4 °C. Permeability of each membranes was evaluated at the permeate flux of 20 L/m²h Milli-Q water. Conductivity rejection of the membranes was evaluated using a 20 mM NaCl solution at the permeate flux of 20 L/m²h. Throughout the tests, a cross-flow velocity of the feed solution was maintained at 0.52 cm/s. Feed and permeate samples were collected after at least 1 h operation for conductivity evaluation. Conductivity rejection was determined by measuring conductivity of the feed and permeate solutions.

2.3.2 Separation performance

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

2.3.3 Hypochlorite cleaning

The effectiveness of hypochlorite cleaning on fouling mitigation was evaluated with the prototype chlorine-resistant NF membrane using three filtration cycles of fouling and cleaning (Fig. 2). The membrane sample was first compacted using Milli-Q water at 1 MPa for 1 h (Fig. 2a). The Milli-Q water was then replaced with an NF-treated wastewater for the measurement of permeate flux in treated wastewater without the effects of foulants. The NF-treated wastewater was prepared by filtering the secondary treated effluent by an NF membrane (ESNA1-LF2, Hydranautics, USA), which has a capacity of removing foulants but has a negligible capacity of removing ions. With the wastewater treated with the ESNA1-LF2 NF membrane, permeability of the membrane was measured at 1 MPa (Fig. 2b). Thereafter, the NF-treated wastewater was replaced with the secondary treated effluent for fouling development. The filtration system was operated at a constant feed pressure of 1.0 MPa for 10 h (Fig. 2c). Feed cross-flow velocity and feed temperature in the feed tank were maintained at 0.52 cm/s and 20.0 ± 0.1 °C, respectively. After 10 h filtration, membrane cleaning was performed with a NaOCl solution (2,000 ppm as NaOCl and pH 11.0) (Fig. 2d). Cleaning started with flushing the membrane with Milli-Q water. Hypochlorite cleaning comprised of three steps: (1) recirculation with the NaOCl solution at a cross-flow velocity of 0.52 cm/s for 15 min, (2) settling for 30 min and (3) another recirculation with the chlorine solution at a cross-flow velocity of 0.52 cm/s for 15 min. These cleaning steps were performed without providing a pressure on the membrane cell. After the filtration system
was thoroughly rinsed with Milli-Q water, two more filtration cycles comprising of (b) permeability measurement, (c) fouling development and (d) chlorine cleaning were conducted and only permeability measurement was performed in the 4th filtration cycle (Fig. 2). Same experimental procedure described above was applied to the evaluation of chlorine-based chemical cleaning for model foulants (HA, SA and BSA). The model foulant solutions contained background electrolytes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂) and 100 mg/L of one of the model foulants in Milli-Q water.

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

### 2.4 Analytical techniques

High performance liquid chromatography photochemical reaction chemiluminescence (HPLC-PR-CL) was used to determine N-nitrosamine concentrations in solution. The volume of the injection sample was in the range of 200 μL. This analytical technique has been described in
Concentration of Na\(^+\) and Ca\(^{2+}\) ions were determined using an ion chromatography-conductivity detection system equipped with IC Pak C M/D column (Waters, MA, USA). Solution pH and conductivity were measured by a pH meter (Navi F-53, Horiba, Kyoto, Japan) and a conductivity meter (LAQUAact ES-71, Horiba, Kyoto, Japan), respectively.

Organics in the secondary treated effluent were characterised by a liquid chromatography-organic carbon detection (LC-OCD) system (DOC-LABOR, Karlsruhe, Germany) [37, 38]. The analysis was performed at 1.1 mL/min flow rate with a mobile phase of phosphate buffer, 2.5 g/L \(KH_2PO_4\) and 1.5 g/L \(Na_2HPO_4\cdot2H_2O\). Samples were pre-treated using a 0.45 µm filter paper and a sample volume of 1.0 mL was injected.

3. Results and discussion

3.1 Chlorine exposure

Stability in the performance of the prototype NF membrane against chlorine exposure was evaluated and compared to that of the other two commercial membranes. When prototype NF membrane was exposed to a 1,000 ppm NaOCl solution for up to 50 h (= 5×10\(^4\) ppm-h), the permeability remained constant at 2.9 L/m\(^2\)hbar (Fig. 3a). In addition, the prototype membrane revealed a stable rejection of 48.0% for up to 5×10\(^4\) ppm-h (Fig. 3b). The results suggested that the prototype NF membrane can be used without any discernible damage on separation performance for chlorine exposure of up to 5×10\(^4\) ppm-h. The exposure of prototype NF membrane to NaOCl solution was further extended to 73 h with a very high concentration of NaOCl solution (100,000 ppm as NaOCl) to accelerate membrane degradation. The cumulative chlorine exposure of 7.3×10\(^6\) ppm-h equates to 1,825 day (= 5 year) operation, when the
membrane is assumed to undergo hypochlorite cleaning with a 2,000 ppm NaOCl solution for 1 h twice a day. As a result, permeability of the prototype NF membrane increased from 2.9 to 4.9 L/m²hbar and conductivity rejection (i.e., salt rejection) decreased from 48.0 to 42.0%. The results indicate a small but nevertheless discernible degradation of the prototype NF membrane after an extended period of chlorine exposure (equivalent to 7.3×10⁶ ppm-h). Despite of the slight change in separation performance the results here demonstrated that the prototype NF membrane can be considered as a chlorine-resistant NF membrane.

In contrast, the permeability of the other commercial membranes increased over time and revealed a sharp increase after 40 h exposure (= 4×10⁴ ppm-h), which caused an increase in permeability over four times – from 5.0 to 20.0 L/m²hbar for ESPA2 RO membrane and from 2.0 to 11.8 L/m²hbar for DK NF membrane (Fig. 3a). Likewise, the considerable change was also observed for conductivity rejection. Conductivity rejection by the ESPA2 RO membrane remained at >90% until chlorine exposure of 3×10⁴ ppm-h, thereafter it dropped down to 5.7% at 5×10⁴ ppm-h (Fig. 3b). The DK NF membrane revealed a similar but less deterioration in conductivity rejection from 61.8 to 21.9 % from 0 to 5×10⁴ ppm-h. The considerable increase in the permeability of the commercial membranes after chlorine exposure is the indication of the degraded membrane by chlorine attack [23].
Fig. 3 – Changes in (a) permeability and (b) conductivity rejection as a function of chlorine exposure. Chlorine exposure was performed at a NaOCl concentration of 1,000 ppm (at up to $5 \times 10^4$ ppm-h) or 100,000 ppm (at $7.3 \times 10^6$ ppm-h) at pH 11.0. Pure water permeability was measured at the permeate flux of 20 L/m$^2$h. Conductivity rejection was measured at a NaCl concentration of 20 mM, permeate flux of 20 L/m$^2$h and feed temperature of 20 °C.

3.2 Separation performance

The separation performance of low molecular weight chemicals by the three selected membranes was evaluated using inorganic chemicals ($\text{Na}^+$ and $\text{Ca}^{2+}$) and six uncharged organic chemicals ($N$-nitrosamines). The prototype and DK NF membranes revealed similar but low rejections of
N-nitrosamines all below 60%, which were by far lower than those by ESPA2 RO membrane (50–94%) (Fig. 4). The low separation of the NF membranes were comparable to other commercial NF membranes (e.g. NF270 and NF90, Dow/Filmtec) that were reported in a previous study [39]. In contrast, the rejections of sodium ions and calcium ions by the prototype NF membrane were relatively high (45% and 62%, respectively) (Fig. 4). This was also observed for DK NF membrane (35% for sodium ions and 75% for calcium ions, respectively). Because sodium and calcium ions are strongly hydrated at the tested pH, their hydrated ion size can lead to the enhanced rejections. In addition, the rejection of charged ions can also be enhanced by the electrostatic interactions that occur between the ions and membrane [40]. Sodium rejection by the prototype NF membrane was higher than that by the DK NF membrane. However, the opposite observation could be made for calcium ions (Fig. 4). A previous study [6] has also observed variable rejections by different NF membranes depending on ionic composition of the feed. The cause for this observation remains unclear and this could be part of a future study. The results here indicate that the prototype chlorine-resistant NF membrane is comparable to commercial NF membranes in terms of the separation performance for Na\(^+\) and Ca\(^{2+}\) ions and low molecular weight organics.
Fig. 4 – Separation performance of the three selected membranes (20 mM NaCl, 1 mM NaHCO$_3$, 1 mM CaCl$_2$, 1 µg/L of each N-nitrosamine, permeate flux = 20 L/m$^2$h, feed temperature = 20 °C and feed pH = 8). Values reported here are the average and standard deviation of duplicate samples.

3.3 Membrane chemical cleaning

3.3.1 Secondary treated effluent

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

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

The secondary treated effluent contained a variety of dissolved organic constituents as characterised by LC-OCD (Fig. 3). The distribution of these organic contents was biopolymers (14%), humic substances (44%), building blocks (15%) and low molecular weight (LMW) neutrals (18%). Fraction of biopolymers (>20,000 Da) represents polysaccharides and proteins in the secondary treated effluent, and fraction of humics (approximately 1,000 Da) represents humic acid-like substances [38, 41]. Corresponding model substances of these large fractions include sodium alginate (i.e. polysaccharide), BSA (i.e. protein) and humic acids, and they were
used as model foulants in the next section. It should be noted that no appropriate model foulants were found for dissolved organics with smaller fractions such as building blocks (300–500 Da) and LMW neutrals (<350 Da).

![LC-OCD chromatogram of the secondary treated effluent.](image)

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

### 3.3.2 Model foulant solutions

To achieve a sustainable NF process using hypochlorite cleaning, potential foulants in treated wastewater that are persistent to the prototype chlorine-resistant NF membrane were investigated by filtering a solution containing one of the model foulants (sodium alginate, BSA or humic acid) and performing hypochlorite cleaning (2,000 ppm as NaOCl and pH = 11.4) for 1 h. Sodium alginate and BSA represent biopolymers (polysaccharide and protein, respectively) in treated wastewater. Humic acids represent humic-like substances in treated wastewater. The substance that most reduced permeability was sodium alginate, causing a 50% reduction in permeability (**Fig. 6**). However, the permeability was well restored to 98% after hypochlorite cleaning. Likewise, the permeability of the prototype NF membrane fouled with BSA was also sufficiently restored with hypochlorite cleaning, while filtration with the BSA solution caused
less membrane fouling through 10 h filtration. The results suggest that hypochlorite cleaning is effective for the removal of biopolymers. The model foulant most persistent in this study was humic acid (Fig. 6). Membrane fouling with humic acid solution caused a 29% reduction in permeability and the permeability was recovered only slightly to 78% by hypochlorite cleaning. The effective removal of biopolymers can be attributed to the enhanced cleavage of polysaccharides and proteins into sugars and amides by hydrolysis after oxidation of these substances with hypochlorite [42]. In contrast, strong complexation between humic substances and calcium ions could limit flux recovery [43, 44]. These results indicate that the cleaning protocol used in this study may not be sufficient for the treated wastewater with abundant humic-like substances.

Fig. 7 – Effects of fouling on the prototype chlorine-resistant NF membrane using the model foulant solutions (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, 100 mg/L model foulant and pH = 8.0) and NaOCl cleaning. Filtration was performed at 1.0 MPa feed pressure and 20°C feed temperature. The initial permeate flux was 33 L/m²·h. Each chemical cleaning was performed with a 2,000 ppm NaOCl solution (pH = 11.4) at 20 °C for 1 h.
4. Conclusions

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

5. Acknowledgements

We thank Nitto Denko for providing NF and RO membrane samples for this investigation.
6. References


