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Long-term pilot plant study using direct chlorination for biofouling control of a chlorine-resistant polyamide reverse osmosis membrane

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ABSTRACT

The inhibition of biofilm formation on a chlorine-resistant polyamide reverse osmosis membrane using direct chlorination in a long-term pilot plant study at a constant permeate flux operation was investigated. Stable salt rejection of the chlorine-resistant membrane during continuous chlorination was achieved at least until 120,000 mg•h/L, whereas decreasing salt rejection was observed in the conventional polyamide membrane. Pilot plant studies with intermittent chlorination for one module under conditions determined by laboratory-scale experiments (10 mg/L free chlorine for 10 min every 12 h) showed a successful operation of the chlorine-treated module, exhibiting relatively stable inlet and differential pressure. The untreated module exhibited significant performance decline, attributed to biofilm formation observed from parallel laboratory experiments fed with the same feed water as the pilot plant. Cleaning with citric acid and NaOH solutions revealed lesser inorganic deposits from the untreated module and deposits originating from non-biofilm organic matters in the feed water were not contributory to fouling as demonstrated by the stable performance of the chlorine-treated module, confirming that the performance decline observed in the untreated module was due to biofouling. This study revealed the immense potential of direct chlorination in biofouling prevention of chlorine-resistant polyamide membranes without endangering membranes to degradation.

Keywords: Biofouling; Chlorine-resistant membranes; Direct chlorination; Polyamide; Reverse osmosis membrane

1. Introduction

At present, reverse osmosis (RO) is the leading global desalination technology [1,2] due to substantial improvements and innovations toward reducing the costs of desalinated water compared with other water resources [3]. Currently, an approximate capacity of 10 million m^3/d is desalinated by RO technology, wherein half of the capacity is installed in the Middle East and other desert regions, and the remaining half is in the United States, Europe, and Japan [4]. One critical issue to the desalination industry is membrane fouling, which is the accumulation of unwanted substances on the membrane surface. The major types of fouling in RO membranes are due to inorganic precipitation of sparingly soluble salts

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or scaling, organic fouling, particulate and colloidal fouling, and microbiological fouling or biofouling. While scaling and organic fouling increases the hydraulic resistance to permeate flux, colloidal fouling and biofilms decrease the permeate flux through cake-enhanced and biofilm-enhanced osmotic pressure [5–8]. Generally, the first three types of fouling can be prevented or controlled by reducing the concentration of the foulant in the feed water. For biofouling, which is a consequence of the adhesion and accumulation of microorganisms, followed by formation and growth of biofilm on the membrane surface resulting in the decline of membrane performance, reduction of microorganisms in the water phase is particularly hard to control since microorganisms, even in very low numbers, can multiply and grow [9].

Biofouling control usually employs a variety of methods, involving one or a combination of strategies such as enhanced pretreatment, improved system hygiene, preventive and/or periodic membrane cleaning, and chemical dosing of biocides or disinfectants [10]. Most commonly used disinfectants include free chlorine, chlorine dioxide, chloramines, ozone, potassium permanganate and ultraviolet radiation [11–13]. Free chlorine, one of the most widely used disinfectants, injected at the head of a pretreatment process in the form of chlorine gas (Cl_2) or sodium hypochlorite (NaOCl) is considered to be the standard practice [14,15]. Chlorine application is mainly classified as intermittent chlorine injection and continuous chlorine injection. Continuous chlorination is done through the addition of chlorine continuously at the intake point and a free residual chlorine concentration of 0.5–1.0 mg/L is maintained throughout the whole pretreatment line for disinfection of microorganisms [14,16,17]. During intermittent chlorination, chlorine is periodically applied off-line in the pretreatment section and then the feed water is sent to drain prior to reaching the membranes [14]. For both injection systems, dechlorination must be performed upstream prior to the RO stage because the residual chlorine in the feed water can cause irreversible damage to the RO membranes [16,18], particularly on polyamide thin-film composite membranes.

Polyamide thin-film composite (TFC) membranes have emerged as the premier technology for pure water production through desalination [19] because of their chemical and physical stability, strong resistance to bacterial degradation, applicability to a wider range of pH (3–11), and high salt rejections [14,20]. However, the amide linkage in the membranes is susceptible to chlorine, where the mechanism is believed to be the formation of an N-chlorinated amide in a reversible and instantaneous reaction by an initial attack of free chlorine to the amide nitrogen, and then an irreversible, ring chlorination reaction via Orton rearrangement [21,22]. It has also been shown that in the presence of metal ions typically found in RO source waters, there is enhanced membrane degradation during hypochlorite treatment of the polyamide membrane [23]. It has also been reported that degradation of the polyamide composite membrane occurs almost immediately upon 200 and 1,000 ppm h of exposure to free chlorine, which corresponds to 200–1,000 h of exposure to 1 mg/L free chlorine and can result in significant reduction in salt rejection [24]. In recent years, various novel materials have been investigated as supplements or even replacements of current TFC membranes [25]. Some studies involved improving the anti-biofouling properties of RO membranes [26–28]. Huge efforts have also been directed into developing chlorine-resistant polyamide membranes [26,29–34] or improving both chlorine-resistance and anti-biofouling properties [35,36]. Brand-new RO membrane materials with excellent permeation, salt rejection, chlorine tolerance, and biofouling resistance are also being explored [37]. However, despite having attained these improvements on traditional polyamide RO membranes, problems due to fouling and membrane degradation in the presence of chlorine are still prevailing and developing new RO membranes are at its infancy and would need further investigation before commercialization [25].

Because the majority of recent studies focus on the development and improvement of chlorine-resistant polyamide membranes, biofouling control can now be achieved even with prolonged chlorine exposure without a decline in salt rejection, resulting in lesser maintenance and operational costs of RO processes [38]. During chlorination, it is very important that the free chlorine is maintained at a concentration that will kill all microorganisms because bacterial regrowth occurs when free chlorine drops below the detection limit [39]. Thus, continuous chlorination is considered the industry standard. However, direct chlorination with intermittent chlorine injection was also reported to be effective in preventing the increase in differential pressure and stabilized the quality and quantity of the produced water during seawater filtration in pilot plants and actual RO desalination plants installed with cellulose triacetate membranes [40]. Optimized conditions during direct chlorine treatment of secondary effluent water through intermittent application were also shown to be successful in controlling biofilm formation on polyamide RO membranes, with the dose and frequency used within limits of allowed exposure conditions for commercial RO membranes and their expected membrane lifetimes [41]. This means that direct chlorination is now a viable option in preventing biofouling on chlorine-resistant membranes, offering the advantage of reducing biofilm formation along with a simplification of the conventional pretreatment scheme since dechlorination need not be done. It is, therefore, important to investigate the use of direct chlorination (whether continuous or intermittent injection) for biofouling control on chlorine-resistant membranes beyond the laboratory-scale cross-flow tests. The results of this study not only confirm the importance of developing and using chlorine-resistant membranes in a larger scale, but also give huge implications to the potential decrease in operational costs associated with membrane cleaning, replacement, and related energy consumption since during the separation process, biofouling is controlled through optimized chlorination conditions without employing the dechlorination step. To the best of the authors' knowledge, this is the first application of direct chlorination without the dechlorination step in a long-term pilot plant study using a chlorine-resistant polyamide RO membrane for the treatment of effluent water.

The primary goal of this study is to evaluate the inhibition of biofilm formation of a recently developed chlorine-resistant polyamide membrane [26] using direct chlorination in long-term pilot plant experiments. The effect of direct chlorination on membrane degradation of the chlorine-resistant polyamide membrane was first examined by comparing its salt rejection to a conventional polyamide RO membrane using continuous chlorine injection during pilot plant experiments. Then, in order to determine optimum dose and frequency that would be applicable during pilot plant experiments, the conditions for intermittent direct chlorination were investigated under laboratory-scale tests using conventional polyamide RO membranes. Finally, the resulting optimum chlorination conditions from laboratory experiments were applied in the pilot plant study to evaluate biofouling control using direct chlorination in untreated and treated membrane modules installed with the chlorine-resistant polyamide RO membrane.

2. Materials and experimental methods

2.1. Materials

Commercially available polyamide RO membrane (NTR759HR, Nitto Denko Co., Osaka, Japan) and newly developed chlorine-resistant RO membrane (CRX prototype, Nitto Denko Co., Osaka, Japan) using a chlorine-resistant polyamide reported by Shintani et al., [29] were used in this study. Spiral wound membrane modules (NTR 759-S4, Nitto Denko Co., Osaka, Japan) were used for the pilot plant experiments. Polypropylene spacers were also used (Nitto Denko Co., Osaka, Japan) for laboratory-scale cross-flow experiments.

Secondary effluent water before chlorination, used as growth medium for biofilm formation on RO membranes, was taken from Higashi-Hiroshima Wastewater Treatment Plant (WTP), a facility for domestic wastewater treatment (Higashi-Hiroshima, Japan). The Higashi-Hiroshima WTP was operated by conventional activated sludge treatment.

Bacillus subtilis was purchased from JCM 2499 Riken BioResource Center (Ibaraki, Japan). Glucose ($C_6H_{12}O_6$), sodium chloride (NaCl) and sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$), and Ca, Cu, Fe, Mn standard solutions were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Sodium hypochlorite (NaOCl) (approximately 10% available chlorine) was purchased from Sigma-Aldrich Corp. (St. Louis, Missouri, Unites States). DPD (N,N-diethyl-p-phenylenediamine) used for free chlorine analysis was purchased from Hanna Instruments, Inc. (Chiba, Japan). All other reagents of analytical grade were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan) and Kanto Chemical Co. Inc. (Tokyo, Japan). Pure water was prepared using a Milli-Q Reference Ultrapure Water Purification System (Merck Millipore Corp., Darmstadt, Germany). Phosphate buffer solution (pH 8) was prepared from $NaH_2PO_4{\cdot}2H_2O$ and NaOH.

2.2. Pilot plant description

The pilot plant was used to evaluate the chlorine resistance of NTR759HR and the chlorine-resistant membranes by conducting parallel experiments (section 2.3). After this investigation, the same pilot plant was used in carrying out parallel experiments to evaluate biofouling control by direct chlorination using the chlorine-resistant membranes (section 2.4.2). A schematic diagram of the pilot plant cross-flow filtration set-up used in this study is illustrated in Fig. 1. The set-up was equipped with a 4-inch RO membrane vessel, a feed pump (PMD-1563B2P, Sanso Electric Co., Ltd., Hyogo, Japan), a pressure pump (25EVML1864.0, Ebara Co., Ltd., Tokyo, Japan), and cartridge filter (1 μm). The membrane element was placed inside the RO membrane vessel, and then the apparatus was operated by running feed water with stirring at a flow rate of 15 L/min and a fixed permeate flux of 2.4 L/min. The effective filtration area of the operating membrane was 7 m^2. The flow rate, operating pressure, pH, and water temperature of the feed water, concentrate, and permeate were monitored every 1 min, and electric conductivities of the feed water and permeate were measured once a day.

Treated wastewater, which comes from laboratory glassware washing in Hiroshima University (1,200 m^3/d water treated by coagulation, sedimentation, sand filtration, and activated carbon filtration), was used as feed water for the pilot plant. The treated wastewater was then filtered through a cartridge filter (1 μm, Micropore, PFR-010W-1TO, Organo Co., Ltd., Tokyo, Japan) using a pump (P7276.75, Ebara Co., Ltd., Tokyo, Japan), and was then transferred to the feed tank of the apparatus. Table 1 shows a summary of the water quality of the feed water.

2.3. Chlorine resistance of membranes

Chlorine resistances of a conventional polyamide RO membrane (NTR759HR) and the chlorine-resistant membrane (CRX prototype) using direct chlorination were evaluated from May to November 2015 by installing the membranes into two separate membrane modules. The modules were continuously treated with 10 mg/L of NaOCl solution during this period, no dechlorination step employed. The residual free chlorine concentration on the conventional polyamide membrane module was 9.7 ± 1.7 mg/L (May 18 until July 28). While on the chlorine-resistant membrane module, the residual free chlorine concentration

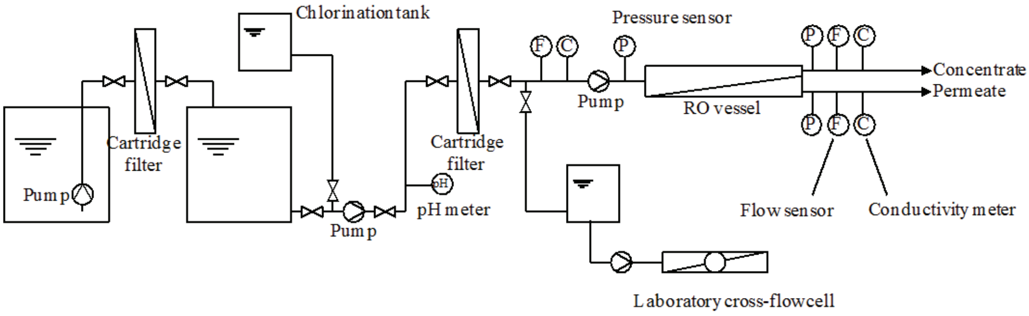

Fig. 1. Schematic diagram of the cross-flow RO filtration set-up in the pilot plant.

Table 1
Water quality of the feed water for the pilot plant

Water quality parameter	Concentration, mg/L
Dissolved organic carbon, DOC	<0.86
Dissolved nitrogen, DN	<0.97
Fluoride ion, F^-	<0.09
Chloride ion, Cl^-	<28.9
Nitrate, NO_3^-	<3.3
Sulfate, SO_4^{2-}	<9.64
Phosphate, PO_4^{3-}	Below detection limit
Ammonium ion, NH_4^+	Below detection limit
Sodium ion, Na^+	<20.6
Potassium ion, K^+	<2.32
Magnesium ion, Mg^{2+}	<1.37
Calcium ion, Ca^{2+}	<11.5

was 10.1 ± 1.6 mg/L (May 18 until October 7). To evaluate the performance of the chlorine-resistant membrane at higher CT (concentration–time) values, continuous treatment with 100 mg/L NaOCl solution was done for a month (October 7 until November 9). The residual free chlorine for this period was 104.1 ± 16.3 mg/L. CT value was calculated as the product of average free chlorine concentration (mg/L) and exposure time (h) for 1 d. The free chlorine concentration of the concentrate was measured and adjusted twice or three times a day to maintain the free chlorine concentration during the treatment. However, pH and water temperature were not adjusted.

For the evaluation of membrane degradation associated with the chlorination, corrected salt rejection of the chlorine-resistant membrane and conventional polyamide membrane treated with a continuous injection of NaOCl solution were evaluated against CT. The salt rejection of the membrane expressed in percentage (%) was calculated from the conductivities using Eq. (1), which were determined by measuring the conductivity with an electrical conductivity meter (7759-A100, Tech Morioka, Co., Ltd., Yamagata, Japan). The corrected salt rejection was calculated from the salt rejection at the nth time (S_n) and the initial salt rejection (S_1) using Eq. (2).

$$\text{Salt rejection}(\%) = \left(1 - \frac{\text{Permeate conductivity}}{\text{Feed conductivity}}\right) \times 100 \quad (1)$$

$$\text{Corrected salt rejection} = \frac{S_1 - (S_1 - S_n)}{S_1} \quad (2)$$

2.4. Evaluation of biofouling inhibition by direct chlorination

2.4.1. Determination of optimum intermittent chlorination conditions by laboratory-scale soaking experiments

Laboratory soaking experiments using the conventional polyamide NTR759HR membranes were first performed to determine the conditions for optimum direct chlorination that will be used in the pilot plant. Secondary effluent water obtained from the Higashi-Hiroshima Wastewater Treatment Plant was filtered through a glass fiber filter (1.0 μm pore size, GF/B, Whatman, Kent, UK). The filtered secondary effluent water added with 1 mM of glucose and 3 to 6 × 10^7 cfu/mL *B. subtilis* to enhance biofilm formation on the membranes was used as a soaking solution for all laboratory-scale experiments. The method of preparation of the bacterial stock of *B. subtilis* can be found in a previous paper [42]. The NTR759HR membrane, received as a flat sheet, was first cut into 2 × 2 cm pieces using sterile scissors, and the pieces were washed thoroughly with pure water before immersing them in the soaking solution. Biofilm was allowed to form on the membranes by leaving the container in the dark at 37°C with shaking at 45 rpm for 12 h. For control experiments, membranes were soaked in filtered secondary effluent water without free chlorine. Intermittent direct chlorination was done every 12 h by soaking the membranes in filtered secondary effluent water added with hypochlorite solution (soaking solution). The soaking solution was replaced with a fresh soaking solution every 12 h. To determine the optimum residual free chlorine concentration, the filtered secondary effluent water was added with hypochlorite, within 1–10 mg/L residual free chlorine concentration. In order to determine optimum treatment time, the membranes were soaked for 1–50 min in the filtered secondary effluent water added with hypochlorite. For all determinations, the free chlorine concentration under study was maintained throughout the treatment. The biofilm formation (12 h) and chlorination were done for a total of four times for three membranes per condition under study. For this investigation, biofilm formation, expressed as fluorescence intensity (FI), was evaluated against the CT value. Biofilm on the membrane was quantified using FI analysis (section 2.5.1) at the end of the 4th treatment. CT value, in this case, was calculated as the product of free chlorine concentration and the treatment time for one-time soaking. In summary, laboratory-scale conditions for the optimization of direct intermittent chlorination were 1, 3, 5, and 10 mg/L of residual free chlorine, 1–50 min of treatment, and intermittent treatment every 12 h.

2.4.2. Biofouling by direct chlorination in the pilot plant

From January to May 2016, biofouling inhibition by direct chlorination was employed using the chlorine-resistant membranes, which were installed in the membrane modules in the pilot plant. One module was chlorine-treated (module 1) using the conditions determined previously (section 2.4.1), while another module remained untreated and served as the control (module 2, without chlorine). Without stopping the operation, a solution of NaOCl contained in a chemical tank was added to the feed solution of module 1 for 10 min every 12 h. The residual free chlorine concentration during the intermittent treatment of the chlorine-resistant membrane was 10.1 ± 1.6 mg/L. Membrane performance during the constant flux operation was evaluated from changes observed in operating pressures (inlet pressure and differential pressure [ΔP], where ΔP was calculated as the difference between feed and concentrate pressures). Permeate pressure for the pilot plant studies is zero, and thus transmembrane pressure is expected to behave similarly as the differential pressure or pressure drop. In this case, hydraulic resistance due to fouling can be assessed based on an increase in inlet pressure or an increase in the pressure drop during filtration [43].

2.4.3. Laboratory cross-flow cell description

Since it is difficult to confirm biofilm formation within the modules during pilot plant operation, two laboratory cross-flow cells were connected in parallel to the modules (Fig. 1) and were supplied with the same feed water for 2 weeks (April 8–April 22, 2016). A schematic diagram of the cross-flow test cell unit (with permeation) is shown in Fig. 2. The cross-flow test cell set-up was equipped with a custom-made cross-flow cell (Nishiyama Seisakusho Co. Ltd., Osaka, Japan) and a pump (KP-21, Flom, Tokyo, Japan) to control the flow rate of solutions at 25 mL/min. The flow cell consisted of two stainless steel plates. The bottom plate had an outlet for the permeate and an internal space for an O-ring, cut pieces of polypropylene spacers and NTR759HR polyamide RO membrane. The cover plate consisted of the pressure gauge, the feed inlet, and the concentrate outlet. Both plates were held together by screws to hold the entire cell. During assembly, a cut spacer (18 × 4.6 cm) was first placed inside the bottom plate, followed by the cut membrane (18 × 4.6 cm), then another cut spacer (17 × 3.6 cm), and lastly, the O-ring to prevent any leakage. Membrane and spacers were cut into the required dimensions with scissors and then rinsed with a copious amount of pure water before placing them inside the flow cell. The test cell was operated by running feed water with stirring at a flow rate of 25 mL/min, operating pressure of 1.5 MPa, and at 25°C for 2 weeks. The effective filtration area of the operating membrane was 77 cm^2. At the end of 2 weeks, the membranes and spacers were retrieved, and the biofilm formed on the membrane was determined through FI analysis (section 2.5.1).

2.4.4. Membrane cleaning

Instead of autopsy studies, membrane cleaning was performed on the two modules at the end of the pilot plant run to extract deposits from the modules for the determination of the type of substances that have accumulated and to evaluate the differences between the accumulated deposits from the chlorine-treated and untreated modules. Chemical cleaning solutions used were 2% (w/v) citric acid solution and aqueous NaOH solution (pH 12). Before and after applying the cleaning solution, tap water was used as feed water with a feed flow rate of 15.0 L/min and a permeate flow rate of 2.3 L/min. Chemical cleaning, on the other hand, was done by introducing and recirculating 90 L of the cleaning solution for 30 min at almost zero pressure, soaking for 1 h, and then recirculating again for 30 min at almost zero pressure. After each chemical cleaning, the spent cleaning solutions (citric acid or NaOH) from each module were collected and then analyzed for dissolved organic carbon concentration, metal ion (Ca, Fe, Cu, Mn) concentrations, and anion (F, Cl, Br, NO_2, NO_3), and cation (NH_4, Li, Na, K, Mg, Ca) concentrations. Inlet pressure and ΔP were monitored during the cleaning to evaluate the effectiveness of the membrane cleaning applied.

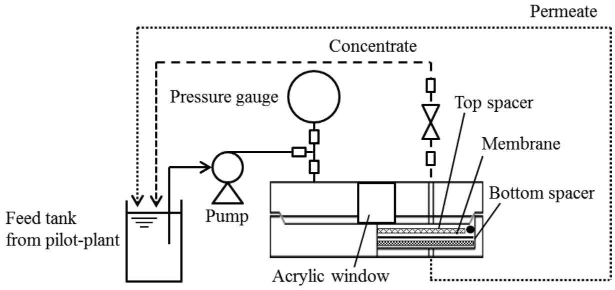

Fig. 2. Schematic diagram of the cross-flow RO laboratory test cell.

2.5. Analytical methods

2.5.1. SYTO 9 staining procedure and fluorescence intensity analysis

The green dye, SYTO 9 from the BacLightTM Bacterial Viability Kit L13152 (Invitrogen/Molecular Probes, Oregon, United States) stains both live and dead cells with a fluorescent green color. The SYTO 9 solution was prepared according to manufacturer specifications and was kept in the dark and inside the refrigerator until analysis. The membranes and spacers from the laboratory cross-flow cell set-ups were retrieved, cut into 2 × 2 cm pieces, and then biofilm formation was determined through fluorescence analysis. The 2 × 2 cm piece of the membrane (with the spacer on top) was stained with 100 μL of SYTO 9 and left in the dark for 30 min.

Stained membranes (section 2.4.1) and stained membranes and spacers (section 2.4.3) were analyzed for the amount of biofilm formed using FI analysis. The FI was determined using a microplate reader (Gemini EM, Molecular Devices Japan Co., Tokyo, Japan) with SoftMax®Pro microplate data acquisition and analysis software with excitation scan set at 485 nm and emission scan set at 545 nm. The FI values for 144 points per membrane were analyzed. The ΔFI, which indicates the amount of biofilm remaining, was calculated as the FI of the virgin membrane (with a virgin spacer on top) subtracted from the FI of the membrane (with a spacer on top) with the biofilm formed. The ΔFI value was then reported as the average of three replicate membranes and the precision was reported as the standard deviation for $n = 3$ membranes.

2.5.2. Other analysis

For the analysis of DOC concentrations and dissolved nitrogen (DN) of the feed water quality of the pilot plant, water samples were filtered through GF/B Whatman filter. DOC and DN were measured using a total organic carbon analyzer (TOC-V CSN, Shimadzu Co., Tokyo, Japan). Inductively coupled argon plasma atomic emission spectrometry, ICP-AES (Varian 720-ES, Nakamura Sanso Corporation, Japan) equipped with argon gas (99.999% purity) used as a nebulizer, auxiliary and plasma gas at a gas pressure of 0.55 MPa, plasma flow of 15.0 L/min, auxiliary flow of 1.50 L/min, nebulizer flow of 0.85 L/min, and plasma power of 1.20 kW was used to measure Ca, Cu, Fe, and Mn with the following limits of detection: 0.576, 0.577, 0.495, and 0.155 mg/L, respectively. All anion and cation concentrations were measured using ion chromatography (Prominence HIC-SP, Shimadzu Corp., Kyoto, Japan) consisting of a manual sample injector (injection volume: 25 µL), a pump, a guard column (Shim-pack IC-GC4, 3 mm i.d., 8 mm length; Shimadzu Corp.), a separation column (Shim-pack IC-C4, 4.6 mm i.d., 150 mm length, Shimadzu Corp.), a column oven, and a conductivity detector. The mobile phase, a solution containing $(COOH)_2$ (3.0 mM), was pumped into the system with a flow rate of 1.0 mL/min. LODs in mg/L for the ions were the following: 3.49×10^{-5} (F), 4.88×10^{-5} (Cl), 7.01×10^{-5} (Br), 4.79×10^{-5} (NO_2), 4.85×10^{-5} (NO_3), 1.12×10^{-4} (PO_4), 5.87×10^{-5} (SO_4), 3.55×10^{-3} (NH_4), 1.18×10^{-3} (Li), 2.39×10^{-2} (Na), 1.36×10^{-2} (K), 1.05×10^{-2} (Mg), and 3.42×10^{-2} (Ca).

3. Results and discussion

3.1. Membrane degradation analysis of the chlorine-resistant membrane in the pilot plant

Chlorine resistances of a conventional polyamide RO membrane (NTR759HR) and the chlorine-resistant membrane (CRX Prototype) used in this study were evaluated from May to November 2015 (Fig. 3). The graph was divided into three sections, corresponding to the chlorine treatment administered during the operation: (A) treatment of both membranes with 10 mg/L free chlorine, (B) treatment stopped on conventional membrane but continued for chlorine-resistant membrane with 10 mg/L free chlorine, and (C) treatment of chlorine-resistant membrane with 100 mg/L free chlorine. Results indicate that continuous chlorination with 10 mg/L of NaOCl solution caused an early decline in salt rejection for the conventional polyamide RO membrane, that is, a 12% decline from the initial salt rejection (at around 13,000 mg•h/L), which was 55 d after the start of the operation. The operation for the conventional polyamide RO membrane was stopped at the end of July (71 d after the start of operation) with 31% decline in salt rejection at 17,000 mg•h/L CT value (Fig. 3, section A). During this treatment, the residual free chlorine concentration on the conventional polyamide membrane module was 9.7 ± 1.7 mg/L. The module with the chlorine-resistant membrane, on the other hand, was continuously treated with 10 mg/L of NaOCl solution until CT value around 35,000 mg•h/L (October) with no significant decline in salt rejection (Fig. 3, section B). During this period, the residual free chlorine concentration on the chlorine-resistant membrane module was 10.1 ± 1.6 mg/L. To evaluate the performance of the chlorine-resistant membrane at higher CT values, it was continuously treated with 100 mg/L of NaOCl solution. Results showed that the salt rejection was stable even at around 120,000 mg•h/L of CT (Fig. 3, Section C). The residual free chlorine for this period was 104.1 ± 16.3 mg/L. A slight and sharp decline in salt rejection, from 88% to 85%, after changing the NaOCl concentration from 10 to 100 mg/L, respectively, could be due to the low rejection of free chlorine and not as a result of membrane degradation. The chlorine-resistance of the chlorine-resistant membrane was expected but these stable salt rejections observed for the chlorine-resistant membrane during direct chlorination without dechlorination confirmed the applicability of direct chlorination for biofilm control without significant membrane degradation.

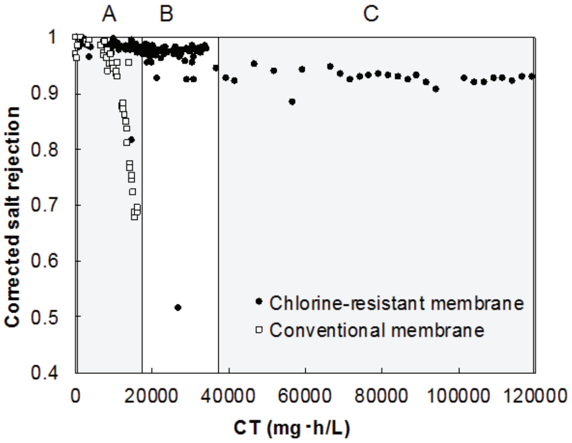

Fig. 3. Salt rejection of conventional and chlorine-resistant membrane during direct continuous chlorination (section A: 10 mg/L chlorination of both membranes, section B: 10 mg/L chlorination of chlorine-resistant membrane only, section C: 100 mg/L chlorination of chlorine-resistant membrane only).

Cellulose acetate (CA) membranes have lower salt rejection and net driving force compared with TFC membranes but are considered to be more resistant to chlorine than polyamide membranes [2]. However, membrane degradation of CA membranes had been reported at 30,000 mg•h/L and 120,000 mg•h/L CT values corresponding to 0.1% and 4.3% decline in salt rejection, respectively [44]. Although around 120,000 mg•h/L of CT without any decline in salt rejection in the chlorine-resistant membrane used in this study is not comparable with the reported 4.3% decline in CA (around 120,000 mg•h/L) due to different operating conditions as well as feed wastewater quality, the results of this study showed the advantage of the chlorine-resistant membrane over CA and conventional polyamide membranes in terms of resistance to chlorine.

3.2. Determination of optimum intermittent chlorination conditions by laboratory-scale soaking experiments

Intermittent direct chlorination at 12 h interval was first done in laboratory-scale experiments to determine optimum chlorination conditions applicable for the pilot plant studies. The behavior of biofilm formation after soaking the membranes for four times, indicated by ΔFI, against CT value per one soaking/washing is shown in Fig. 4. Results show that with 1 mg/L of free chlorine, the percent reduction of biofilm formation was only around 40% even when the soaking time was increased. Similarly, with the 3 mg/L of free chlorine concentration, biofilm removed was only 28% at 10 min of soaking time (CT = 0.5 mg•h/L), and even when CT = 2.5 mg•h/L, complete reduction of biofilm was not observed. At a CT value of more than 1.4 mg•h/L (for one washing), an almost complete biofilm reduction (99%) was observed for both 5 and 10 mg/L free chlorine concentrations at 16 and 8.5 min of soaking time, respectively. During continuous filtration, when the disinfection is incomplete, the remaining microorganisms can use the biofilm fragments and dead cells as nutrients [45,46], which create an increased risk of biofilm formation [17]. Therefore, for intermittent application, the 5 or 10 mg/L free chlorine concentration is needed for chlorination, but the 10 mg/L free chlorine would be favored because of the shorter washing time it entails. These results suggest that the intermittent direct chlorination can control biofilm formation at a reduced CT value compared with continuous chlorination and is, therefore, advantageous for disinfection of easily damaged polyamide RO membranes. These results also suggest the greater benefit of using intermittent chlorine injection at optimum conditions (biofilm control at low CT value) for disinfection of the chlorine-resistant membrane because the tendency for membrane degradation is less due to the more robust nature of this membrane. Because the optimized conditions were determined using the conventional polyamide RO membranes, it is expected that the application of such conditions for the investigations of the chlorine-resistant membrane will ensure that its membrane lifetime would be longer compared with easily damaged polyamide membranes, guaranteeing that a longer duration of study can be done for the pilot plant experiments.

3.3. Evaluation of biofilm formation inhibition by intermittent chlorination in the pilot plant

The inhibition of biofilm formation on the chlorine-resistant membranes by intermittent chlorination in a pilot plant was evaluated by carrying out experiments using two parallel set-ups (one with chlorination, another without chlorination) using RO membrane modules. Compared with the soaking solution (secondary effluent water with glucose and microorganisms) used in the laboratory-scale experiments, the water quality of the feed water in the pilot plant had considerably lower biofilm formation potential (Table 1), suggesting that a similar CT value is acceptable for use in the pilot plant chlorination experiments. Thus, based on the optimized conditions from section 3.2, 10 min direct chlorination and 10 mg/L free chlorine concentration for every 12 h (a CT value of 1.7 mg•h/L) were used as treatment conditions for one set-up (module 1) in the pilot plant.

The pilot plant experiments were run under constant permeate flux conditions, thus inlet pressure and Δ*P* were obtained throughout the duration of the experiment to monitor membrane performance. Variations in inlet pressure and differential pressure for the two set-ups during the experimental run are shown in Figs. 5 and 6, respectively. Results indicate that the membrane module with chlorination was successfully operated with relatively stable inlet pressure and differential pressure. However, for the membrane module without chlorination, inlet pressure increased continuously throughout the run (Fig. 5) and the differential pressure jumped up after 40 d of operation (Fig. 6). This increase in the inlet and differential pressure are usually associated with hydraulic resistance [43].

3.3.1. Evaluation of deposits within the chlorine-treated and untreated modules

The differences observed in membrane performance between the two modules could be explained by fouling conditions within the modules. Instead of autopsy studies, in order to determine biofilm formation, laboratory cross-flow cells were connected in parallel to the RO modules for 2 weeks. Thus, one flow cell was being fed with the chlorine-treated water while the other was fed with the untreated water. Results showed a significantly higher ΔFI from the membrane without chlorination (176 ± 14, $p < 0.01$) compared with the membrane with chlorination (8 ± 5). This indicates that significant biofilm was formed on the membranes and

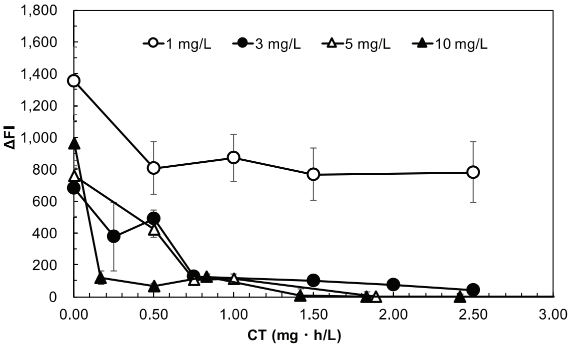

Fig. 4. Inhibition of biofilm formation during intermittent direct chlorination during laboratory soaking experiments. ΔFI = FI (fluorescence intensity units) of the membrane (with a spacer on top) with the biofilm formed – FI of the virgin membrane (with a virgin spacer on top). Error bar represents standard deviation for *n* = 3 membrane pieces (2 × 2 cm).

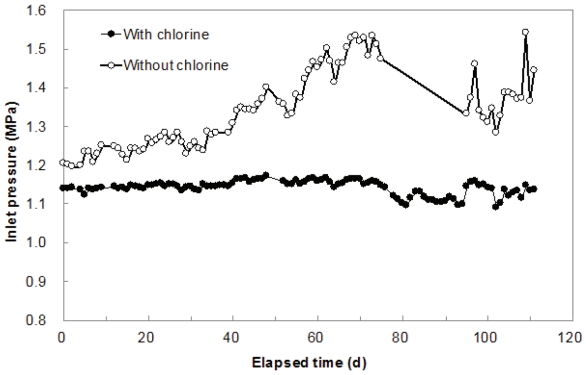

Fig. 5. Inlet pressure during pilot plant experimental run (constant flux operation).

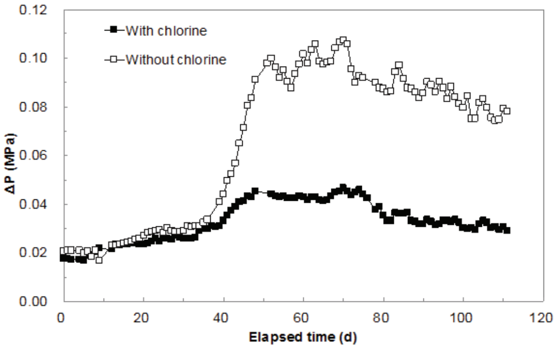

Fig. 6. Differential pressure (Δ*P*) during pilot plant experimental run (constant flux operation; Δ*P* = feed pressure – concentrate pressure).

spacers in the cross-flow cell within 2 weeks of being fed with untreated water, suggesting that there was significant biofilm within the untreated module, which has been operating for 4 months already before the laboratory cross-flow cells were connected.

To extract deposits and to determine inorganic and organic fouling conditions within the modules, membrane cleaning was done using citric acid and NaOH solutions. The spent citric acid and NaOH solutions were collected and analyzed to differentiate the inorganic and organic deposits between the two modules, respectively. Inorganic substances and DOC extracted from both cleaning solutions are shown in Fig. 7, where metal cation and anion concentrations (in mmol/m^2) and DOC (in mg/m^2) are given. Dissolved ions such as Na and K are very soluble and are not associated with scaling even at high concentrations. Ca and PO_4 ions were the major inorganic substances in the deposit, despite below detection limit concentrations of PO_4 ions in the feed water. Furthermore, almost stoichiometric amount of PO_4 to Ca as calcium phosphate ($Ca_3(PO_4)_2$) was extracted, suggesting that the major inorganic deposit in the modules were calcium phosphate. Dissolved salts in the feed water are concentrated 4 to 10 times depending on the system operations recovery and rejection efficiencies [47]. Because of this, sparingly soluble inorganic substances such as magnesium, calcium, carbonate, sulfate, phosphate, and silica increase causing concentration polarization at the membrane surface, leading to these substances exceeding their solubility limits and precipitating on the membrane surface as scales [48]. Compared with all other scales commonly found in the RO systems, calcium phosphate is the most insoluble of all calcium salts with a molar solubility of 2×10^{-33} [49], which could indicate that during the prolonged filtration, these ions might have accumulated and deposited in the membrane modules. Calcium phosphate has also been reported as a key scaling agent of RO membranes for wastewater treatment but its control is particularly difficult [50]. Even low doses of antiscalants have been reported to be relatively ineffective in controlling calcium phosphate deposition [49]. Since no antiscalant was added in the RO feed water in this study, the formation of calcium phosphate can be expected. Although generally high concentrations in the feed water result in major depositions on the membrane, studies with conflicting results suggest that in these cases, rather than influent concentration, other factors influence the deposition of inorganic substances. Such factors include microorganisms withdrawing these elements from the surrounding environment and using these as nutrients or extracellular polymeric substances and/or organic matter absorbing these inorganics [51,52]. Calcium phosphate deposits could either be in a crystalline form, as hydroxyapatite or fluoroapatite with varying amounts of OH$^-$, Cl$^-$, and F$^-$, or in a colloidal form [48], depending on the state in which the calcium phosphate enters the RO unit after pretreatment [49]. Mg may be similarly bound to PO_4 but its concentrations in the modules with and without chlorination were 1 and 2 mmol/m^2, respectively, and were much lower than Ca.

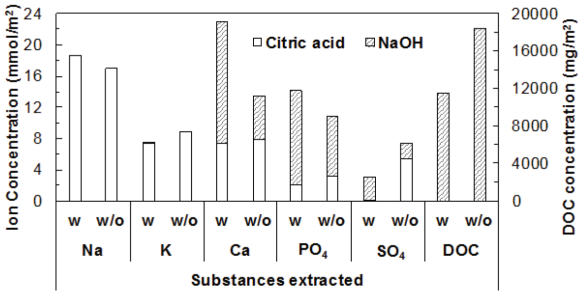

Fig. 7. Inorganic substances (>5 mmol/m^2) and DOC (mg/m^2) in citric acid and NaOH solutions for modules with chlorine (w) and without (w/o) chlorination.

The module with chlorination showed higher amounts of inorganic substances compared with the untreated module, except for SO_4 ion and in a relatively smaller degree, K ion. Among the divalent and trivalent metals detected, Ca was the only metal with more than 5 mmol/m^2 total amount extracted, which could again be attributed to its low solubility. It also accumulated in much higher amounts in the chlorine-treated module (23 mmol/m^2) than the untreated module (13 mmol/m^2). It is possible that in the chlorine-treated module, aside from disinfection of microorganisms, oxidation of halides and other anionic compounds in the feed water such as sulfite, cyanide, and nitrite by chlorine is occurring [53]. This could account for the general observation that the chlorine-treated module contained higher amounts of inorganic deposits. However, it should also be noted that the amounts of the ions in the acid wash were relatively comparable for both modules, except for SO_4 ion, and the observed increase in the amounts of extracted ions in the chlorine-treated module was due to the alkaline wash (Fig. 7). In general, alkaline solutions are recommended for biofouling and organic fouling removal, while acid solutions are more effective for removal of inorganic deposits. The slightly insoluble substances extracted in the alkali solution could, therefore, be colloidal in nature since NaOH has been shown to remove inorganic colloids [54]. There might have been less colloidal sulfates in the untreated module since most of the SO_4 scale was extracted by the acid solution.

The DOC extracted using NaOH solution for both modules is shown at the far right of Fig. 7. Since module 1 was chlorine-treated, the DOC from this module would account for non-biofilm organic matters deposited. The untreated module (module 2) contained additional organic deposits corresponding to biofilm. Results showed that the extracted DOC in the NaOH solution was higher in the untreated module ($p < 0.01$) than the DOC extracted in the chlorine-treated module, suggesting that the additional DOC in the untreated module, which was biofilm, had significantly formed in the module without chlorination. This result supports the previous observation of significant biofilm formation from the parallel laboratory cross-flow experiments.

3.3.2. Membrane performance decline in the untreated module due to biofouling

Higher amounts of inorganic deposits were extracted from the chlorine-treated module than the untreated module but there was no observed decline in membrane performance from the module with chlorination. Because lower amounts of inorganic deposit were extracted from the untreated module, the main contributory foulant that caused the increase in both inlet pressure (Fig. 5) and differential pressure (Fig. 6) in the module without chlorination could then be attributed to organic deposits (biofilm and non-biofilm organic matter). But then again, despite the observation that the chlorine-treated module still had about half of the organic deposits, there was no observed significant increase in the inlet pressure in the chlorine-treated module as shown in Fig. 5, which means that the deposits originating from non-biofilm organic matters in the feed water were not contributory to its fouling conditions. Therefore, the non-biofilm organic matter in the untreated module could not be responsible to the observed performance decline in this module without chlorination (Figs. 5 and 6), suggesting that biofilm formed was the main foulant within this module. Since it has been established earlier that ΔFI and DOC values were significantly higher in the untreated module, performance decline observed on this module without chlorination was, therefore, due to biofilm formation. In other earlier studies, membrane biofilms result in increased hydraulic resistance due to the visco-elastic properties of the biofilm [45] and to be able to maintain the same production rate, an increase in Δ*P* and inlet pressure usually arise from this hydraulic resistance [43,55]. Similarly, the biofilm would have formed on the membrane with an accompanying increase in inlet pressure from the start of the experiment (Fig. 5) and biofilm that had formed on the spacers and/or detached from the membrane surface would have clogged or hindered water passage in the membrane module resulting in an increased differential pressure after 40 d of operation (Fig. 6).

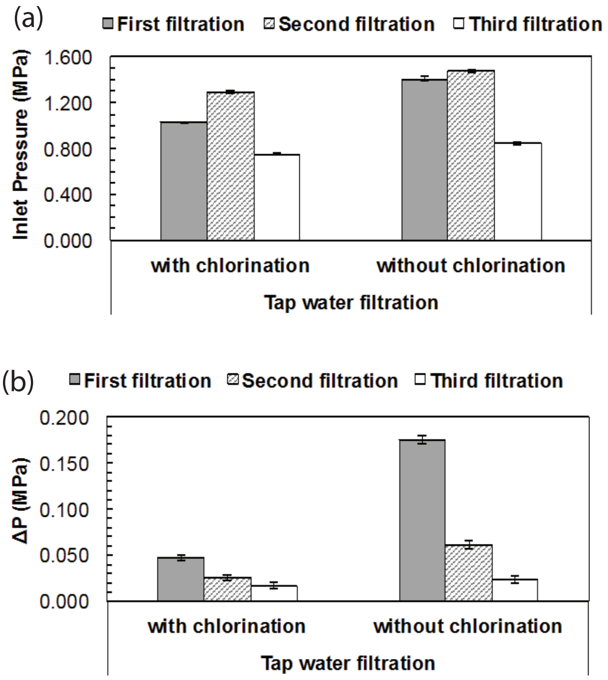

Fig. 8. (a) Inlet pressure and (b) differential pressure (Δ*P*) during tap water filtration for modules with chlorination and without chlorination during membrane cleaning (constant flux operation; Δ*P* = feed pressure – concentrate pressure; error bar represents standard deviation for 10 data points of pressure during the last stage of tap water filtration).

3.3.3. Membrane performance during membrane cleaning

Average values of (a) inlet pressure and (b) differential pressure, ΔP for 10 data points during the last stage of tap water filtration are shown in Fig. 8. The first filtration represents the tap water filtration after stopping the operation but before citric acid cleaning, meaning that foulants were still within the membrane modules. The second filtration represents tap water filtration after citric acid cleaning but before NaOH cleaning, while the third filtration represents tap water filtration after NaOH cleaning. Thus, the third tap water filtration represents the effectiveness of the membrane cleaning employed.

As shown in Fig. 8(a), for both modules, inlet pressure increased after cleaning with citric acid, with a huge jump for the chlorine-treated module, and then decreased after cleaning with NaOH. On the other hand, Δ*P* was remarkably decreased after cleaning with citric acid for both modules (Fig. 8(b)). Citric acid would have disrupted biofilm [54] and dissolved the crystalline form of calcium phosphate which was clogging and hindering water passage, resulting in the decrease in Δ*P*. However, biological and organic materials disrupted and removed from the water passage would not have been dissolved by citric acid and some amounts could have been transferred to the membrane surface resulting in the observed increase in inlet pressure particularly for the chlorine-treated module (Fig. 8(a)). After NaOH cleaning, organic materials and inorganic colloids were then dissolved and removed causing the decrease in inlet pressures to levels lower than the first filtration. As shown in the third filtration, which is the final wash, inlet pressure and differential pressure were much lower than the pressures during the first filtration, indicating removal of foulants, and effectiveness of membrane cleaning employed.

4. Conclusion

Comparison of salt rejections of the chlorine-resistant membrane and a conventional polyamide RO membrane during direct continuous chlorination confirmed the applicability of direct chlorine treatment for biofouling control without membrane degradation on the chlorine-resistant membrane. Pilot plants were then operated with intermittent chlorination for one module under conditions determined by laboratory-scale experiments (10 mg/L free chlorine concentration for 10 min every 12 h, a CT value of 1.7 mg•h/L). The membrane module with direct chlorination was successfully operated with relatively stable inlet pressure and differential pressure, whereas the untreated module showed significant performance decline as shown by the increased inlet pressure and differential pressure. Biofilm formation on the untreated module was observed from parallel cross-flow laboratory experiments fed with the same feed water as the pilot plant module without chlorination as shown by significantly higher ΔFI. Although higher amounts of inorganic deposit mainly composed of $Ca_3(PO_4)_2$ and ample amount of non-biofilm organic matters extracted from the chlorine-treated module were revealed from cleaning with citric acid and NaOH solutions, this module showed no performance decline. Since the inorganic deposits were much lower in the untreated module and that non-biofilm organic matter was not contributory to fouling in the membranes, the biofilm formed on the untreated module was then confirmed to be the cause of membrane performance decline where chlorination was not done. This long-term pilot plant study showed successful biofouling prevention of a chlorine-resistant membrane using direct chlorination, without the need of a dechlorination step and therefore gives significant implications in lessening biofouling risk alongside simplified pretreatment schemes, which means a reduction in RO operational costs. The results also reinforce the need for the development and use of the chlorine-resistant membrane for RO processes.

Conflicts of interest

The authors declared that there are no conflicts of interest.

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