Controlling Biofouling and Disinfection By-Product Formation During Reverse Osmosis Treatment for Seawater Desalination

Takahiro Fujioka,[1,*] My Thi Tra Ngo,[1] Sandrine Boivin,[1]

Kengo Kawahara,[2] Akihiro Takeda,[2] Yuki Nakamura,[2] Hiro Yoshikawa,[2]

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

[2]*R&D Center, Organo Corporation, 4-4-1 Nishionuma Minamiku, Sagamihara 252-0332, Japan*

* Corresponding author: Takahiro Fujioka, Email: tfujioka@nagasaki-u.ac.jp, Ph +81 95 819 2695

Abstract

Controlling membrane fouling and disinfection by-products (DBPs) is an ongoing challenge in achieving sustainable membrane-based seawater desalination. This study assessed the efficacy of a new disinfectant, stabilized hypobromite, for controlling biofouling and DBP formation during reverse osmosis (RO) membrane treatment of seawater. Accelerated chemical exposure tests revealed that stabilized hypobromite did not degrade a commercial polyamide RO membrane; thus, unlike other powerful oxidants, it is able to remain as a residual chemical on membrane surfaces. In our experiments, stabilized hypobromite also effectively inactivated bacteria in seawater and reduced potential organic foulants (e.g., humic acid-like and protein-like substances). Disinfection at a stabilized hypobromite dose of 5 mg/L resulted in the formation of trihalomethanes (THMs), haloacetic acids (HAAs), and bromate at 55, 29, and <10 μg/L, respectively. Chlorine treatment resulted in higher formations of THMs, HAAs, and bromate (80, 74, and 50 μg/L, respectively), indicating stabilized hypobromite is superior to chlorine in this respect. Pilot-scale validation demonstrated that pre-disinfection with stabilized hypobromite enabled the RO membrane treatment to operate for half a year without significant fouling. The findings in this study indicate the great potential of stabilized hypobromite for controlling DBP formation and biofouling in seawater desalination.

Keywords: THMs; HAAs; DBPs; biofouling; disinfection

1 Introduction

Seawater desalination is a powerful strategy for augmenting the drinking water supply in many coastal regions with severe droughts or arid climates. These classical seawater desalination technologies include thermal treatment processes, such as multistage flash and multi-effect distillation. In recent years, many newly developed desalination plants have employed a powerful desalination technology, that is, reverse osmosis (RO) membrane treatment [1]. RO membrane treatment can readily achieve the removal of over 99% of salts with an energy consumption lower than the classical thermal processes [2]. As the biofouling of RO membrane treatment during long-term operation leads to an increase in the required operating pressure and consequently energy consumption, a pre-disinfection process using conventional chlorination is often employed prior to the treatment [3]. Typical seawater treatment trains thus consist of a pretreatment to remove suspended and dissolved constituents, RO membrane treatment, and a post-disinfection process. Two examples of the pretreatment are media filtration and low-pressure membrane filtration (such as microfiltration or ultrafiltration).

Despite the adoption of a pretreatment, biofouling control is still a major challenge in seawater desalination [4]. Chlorine, a strong oxidant and disinfectant, can readily degrade polyamide RO membranes, resulting in the deterioration of RO membranes during salt separation. Thus, residual chlorine is quenched prior to the RO process, and bacterial growth on the membrane surface may occur [5]. Viable bacteria in the disinfected water can attach themselves onto the membrane surface and form a biofilm as a result of their rapid multiplication and a continuous inflow of nutrients [6]. Pre-disinfection using chlorine or other stronger disinfectants, such as ozone, can also induce excess biofouling, as their oxidation reaction may make organics in the water biologically degradable (i.e., they are

45 converted into a food source). The occurrence of biofouling can be mitigated by maintaining
46 residual biocides at the membrane surface [7]. Chloramine, a weak disinfectant typically used
47 in RO-based wastewater recycling, has been found to deteriorate the performance of
48 polyamide RO membranes when it was used in seawater [8, 9]. One of the potential biocides
49 that can be continuously applied during the continuous pre-disinfection stage of RO processes
50 is stabilized hypobromite, which has been suggested as an alternative to conventional
51 chloramine in water recycling applications [10]. Hypobromite (BrO^-) is a strong but unstable
52 disinfectant [11]; thus, hypobromite ions are stabilized in stabilized hypobromite with
53 sulfamic acid at a high pH. However, the efficacy of the new disinfectant (i.e., stabilized
54 hypobromite) for biofouling mitigation in seawater applications still remains unclear, and
55 changes in membrane properties (e.g., the removal of salts or boron) caused by the new
56 disinfectant are of great concern for the viability of its long-term performance [12].

57 The formation of disinfection by-products (DBPs) is an emerging concern with respect to the
58 application of disinfectants during seawater desalination. Small DBPs, such as
59 trihalomethanes (THMs), readily permeate through RO membranes and have an adverse
60 impact on public health via drinking water. In addition, large DBPs rejected by RO
61 membranes are discharged as brine, which may contribute to having negative consequences
62 on water environments [3]. Among the DBPs that form through conventional chlorination
63 during seawater desalination, THMs and haloacetic acids (HAAs) have gained considerable
64 attention [13]. THM and HAA concentrations in drinking water have been regulated in many
65 countries to 25–250 or 60–150 μg/L, whereas high concentrations of THMs up to 67 μg/L
66 have also been reported in the RO permeate of full-scale desalination plants [14]. Moreover,
67 chlorination has been reported to cause high THM concentrations of up to 860 μg/L and
68 HAA concentrations of up to 175 μg/L in chlorinated RO feeds [3]. Because the new
69 disinfectant suggested in this study, i.e., stabilized hypobromite, is a weaker oxidant than

chlorine, it has the potential to minimizing DBP formation [10]. However, the use of a bromide-based disinfectant raises concern with respect to the formation of bromate (BrO_3), a brominated DBP, which is more toxic than chlorinated DBPs [15].

This study assesses the efficacy of stabilized hypobromite as an alternative to chlorine for controlling membrane fouling and DBP formation during seawater desalination. The evaluations were performed by evaluating (a) the degradation of a polyamide RO membrane, (b) the reduction of potential foulants (bacteria and dissolved organics), (c) the formation of THMS, HAAs, and bromate, and (d) fouling control levels at a pilot scale.

2 Materials and methods

2.1 Chemicals

A sodium hypochlorite (NaOCl) solution (12% chlorine concentration) was purchased from Tosoh Co. (Tokyo, Japan). Stabilized hypobromite was supplied by Organo Co. (Tokyo, Japan). The stabilized hypobromite contained hypobromite ions, sulfamic acid, and sodium hydroxide. Throughout this study, the stabilized hypobromite dose is presented in units mg-Cl_2/L by a conversion of the bromine concentration in terms of chlorine. Flat sheet polyamide composite RO membrane (SWC5) samples and 4-in. RO membrane elements (SWC5-LD-4040) were obtained from Nitto/Hydranautics (Oceanside, CA, USA). It should be noted that the SWC5 RO membrane is capable of rejecting >98% of hypobromite ions.

2.2 Test protocols

2.2.1 Membrane degradation

Changes in RO membrane transport after exposure to a disinfectant agent were examined by immersing the polyamide membrane samples (membrane area = 33 cm^2) in a 500-mL

92 seawater solution containing disinfectant (stabilized hypobromite or NaOCl) or a solution
93 without any chemical addition (control). Actual seawater was obtained from the ocean and
94 was pretreated using an ultrafiltration membrane. The concentration of the chemical reagent
95 was adjusted to 800 mg-Cl_2/L in the seawater, and its concentration was maintained between
96 500 and 800 mg-Cl_2/L. At the same time, the pH of the solution was adjusted to 7.0. The
97 membrane samples were left submerged in the chemical reagent at 25°C for 96 h with a
98 continuous dose of 3 mg-Cl_2/L, which simulated the cumulative exposure over 3 years of
99 function. Thereafter, the pure water permeability of each membrane was evaluated using the
100 bench-scale RO system **(Figure S1)** in pure water and in an artificial seawater matrix (NaCl
101 = 35 g/L; boric acid = 5 mg/L; pH = 8.0 ± 0.1). The rejection of conductivity and boron by
102 each membrane was determined using the same seawater at a permeate flux of 15 L/m^2h.

103 **2.2.2 Disinfection**

104 The disinfection potentials of the stabilized hypobromite and chlorine were evaluated by
105 determining reductions in the number of bacteria using colony count as measured by
106 epifluorescence microscopy. Actual seawater was obtained from the ocean and was pretreated
107 using an ultrafiltration membrane. Each disinfectant agent (stabilized hypobromite or
108 chlorine) was added to 200-mL seawater samples stored in glass flasks at doses of 1, 3, and 5
109 mg-Cl_2/L. Each sample was placed in a temperature-controlled room (25°C) for 5 h.
110 Thereafter, the residual chemical in each sample was quenched by the addition of a sodium
111 sulfite solution.

112 **2.2.3 Formation of disinfection by-products**

113 The formation of THMs, HAAs, and bromate **(Table 1)** by stabilized hypobromite and
114 chlorine was also evaluated using a laboratory scale. For the evaluations, actual seawater was
115 obtained from the ocean and was pretreated using an ultrafiltration membrane. Each

disinfectant agent (stabilized hypobromite or chlorine) was dosed into 100-mL seawater samples stored in glass flasks at doses of 3, 5, and 10 mg-Cl_2/L. Prior to the addition of the disinfectant, the pH of the solution was adjusted via the addition of an HCl solution so that the pH of the sample solution would become approximately 7.0 after the disinfectant was added. All samples were stored in a temperature-controlled room (25°C) for 5 h, and the residual chemical was quenched via the addition of sodium sulfite solution. The formation potentials of THMs and HAAs, and bromate were examined in the seawater at a chemical dose of 5 mg-Cl_2/L for 96 h and 13.5 d, respectively. For the formation of THMs and HAAs, the residual chemical was quenched via the addition of sodium sulfite solution. It should be noted that no quenching (i.e., reducing) agent was used for bromate until the analysis, as reducing agents can decompose bromate.

Table 1 – List of disinfection by-products (DBPs) and their maximum contaminant level (MCL) concentrations in the USA

DBP	Chemical formula	MCL in CA, USA
Trihalomethanes (THMs)		80
- Chloroform	$CHCl_3$	-
- Dibromochloromethane	$CHBrCl_2$	-
- Bromodichloromethane	$CHBr_2Cl$	-
- Bromoform	$CHBr_3$	-
Haloacetic acids (HAAs)		60
- Monochloroacetic acid (MCA)	$ClCH_2COOH$	-
- Dichloroacetic acid (DCA)	$Cl_2CHCOOH$	-
- Trichloroacetic acid (TCA)	Cl_3CCOOH	-
- Monobromoacetic acid (MBA)	$BrCH_2COOH$	-
- Dibromoacetic acid (DBA)	$Br_2CHCOOH$	-
Bromate	BrO^-	10

2.2.4 Pilot-scale demonstration

The effectiveness of biofouling control using stabilized hypobromite was evaluated using a pilot-scale RO system that holds a single 4-in. RO element. In this study, media-filtered seawater was used as the RO feed **(Figure S2)**. Two SWC5 RO membrane elements with surface areas of 7.4 m^2 and nominal salt rejections of 99.6% were used. Stabilized

hypobromite was dosed prior to the RO feed reservoir at 0.2 mg-Cl_2/L. The RO system was operated at a constant flux of approximately 15 L/m^2h and a water recovery rate of 15%. The level of membrane fouling was evaluated based on the reduction in normalized permeate flux ($J_t/J_{t=0}$) and the increase in pressure drop (ΔP), which can be expressed as follows:

$$\Delta P = P_f - P_c \quad (1)$$

Here, P_f is feed pressure (kPa), and P_c is concentrate pressure (kPa). The permeate flux at time t (J_t) [L/m^2h] was corrected at 25°C with a temperature correction factor (TCF), which can be expressed as follows:

$$\mathrm{TCF} = \mathrm{Exp}\,[Ke \times (1/(273 + T) - 1/298)] \quad (2)$$

Here, T (°C) is the feed water temperature, and Ke is an empirically derived constant for a given membrane chemistry (Ke = 2206, **Figure S3**).

2.3 Analysis

2.3.1 Bacterial analysis

The number of viable bacteria in the treated water was determined using the heterotrophic plate count method with R2A medium (Nissui Pharmaceutical, Tokyo, Japan). Each sample (1 mL) with and without dilution was dosed into agar medium in a petri dish and incubated at 25°C. The number of bacteria was counted after 7 days and is presented in colony-forming units (CFU/mL). Intact bacterial cells were counted using a fluorescence microscope (BZ-X800, Keyence Co., Osaka, Japan). The bacteria in the 1-mL samples were stained for 15 min using a LIVE/DEAD BacLight Bacterial Viability Kit (Thermo Fisher Scientific, Waltham, MA, USA) containing SYTO®9 and propidium iodide. Thereafter, each sample was filtered using a track-etched polycarbonate microfiltration filter (0.2 μm pore size; Merck,

156 Tokyo, Japan). The number of bacteria on the filter was determined using a fluorescence
157 microscope with a green filter (excitation wavelength = 470 ± 40 nm; absorption wavelength
158 = 525 ± 50 nm) or a red filter (excitation wavelength = 545 ± 25 nm; absorption wavelength
159 = 605 ± 70 nm).

160 **2.3.2 Chemical analysis**

161 Concentrations of chlorine and stabilized hypobromite were determined using a colorimeter
162 (DR-3900, Hach Co., Loveland, CO, USA), while the concentration of organic carbon (TOC)
163 was analyzed using a TOC analyzer (Sievers 900, GE Analytical Instruments Inc., Boulder,
164 CO, USA). The size distribution of the organics was analyzed using a liquid
165 chromatography–organic carbon detection (LC–OCD) system (DOC-LABOR, Karlsruhe,
166 Germany) equipped with a chromatographic column (TSK HW 50S, Toso, Japan) [16, 17].
167 The four subfractions detected through the LC–OCD included biopolymers (molecular
168 weight (MW) of ≥20,000 Da), humics (MW of approximately 1,000 Da), building blocks
169 (MW of 300–500 Da), and low-molecular-weight (LMW) compounds (MW of <350 Da).
170 Each sample was diluted tenfold with pure water for LC–OCD analysis. The organics in the
171 seawater were characterized using excitation emission matrix (EEM) fluorescence spectra
172 measured with an RF-6000 spectrophotometer (Shimadzu Co., Kyoto, Japan). The
173 concentrations of THMs and HAAs were measured using gas chromatography–mass
174 spectrometry (GC–MS), and the detection limit for each chemical was 2 μg/L. Bromate
175 concentration was determined using liquid chromatography–mass spectrometry (LC–MS).

3 Results and discussion

3.1 Degradation of polyamide reverse osmosis membrane

The resilience of a polyamide RO membrane in making contact with stabilized hypobromite was evaluated by examining the pure water permeability of the membrane and its rejection of salts and boron after accelerated exposure tests **(Figure 1)**. Chlorine exposure resulted in a considerable increase in pure water permeability from 3.0 to 35.5 L/m^{2}hbar. Moreover, the rejection both of conductivity (a surrogate indicator of salts) and boron dramatically decreased from 99.4% to 24.0% and 76.3% to 0.0%, respectively. These deterioration effects caused by chlorine are consistent with those measured in previous studies [18, 19], indicating that chlorine degrades the cross-linked polyamide separation layer through hydrolysis and deteriorates the separation performance of the membrane. In contrast to chlorine, stabilized hypobromite exposure caused only a slight reduction in pure water permeability from 3.0 to 1.8 L/m^{2}hbar. However, the rejection of both conductivity and boron dramatically increased from 99.4% to 99.8% and 76.3% to 87.9%, respectively, for stabilized hypobromite. Altogether, the results from the three RO membranes (control, chlorine, and stabilized hypobromite) revealed a trade-off between pure water permeability and rejection of salts and boron.

The enhanced separation performance and reduced permeability after stabilized hypobromite exposure indicate that the polyamide active skin layer of the RO membrane became tighter and that the chemical did not cause degradation of the layer. Similar observation (i.e., enhanced salt rejection and reduced water permeability) can be found when polyamide RO membranes are exposed to chlorine in seawater for a short contact time [9]. As hypobromite (BrO^-) is an oxidizing reagent that is weaker than chlorine, it is reasonable to assume that chemical reactions between the polyamide RO membrane and stabilized hypobromite for an

extended period of time caused similar membrane property changes that can occur during a short-term chlorination. It should be noted that the evaluation was conducted through accelerated chemical exposure tests and that the effect of membrane aging during long-term operation, which generally increases water permeability and reduces salt and boron rejection, was not simulated. It is possible that membrane aging offsets the property changes caused by stabilized hypobromite (i.e., reduced water permeability and increased rejection of salts and boron). Overall, it was demonstrated that disinfection using stabilized hypobromite in seawater is less likely to have a negative impact on membrane separation performance compared with disinfection using chlorine.

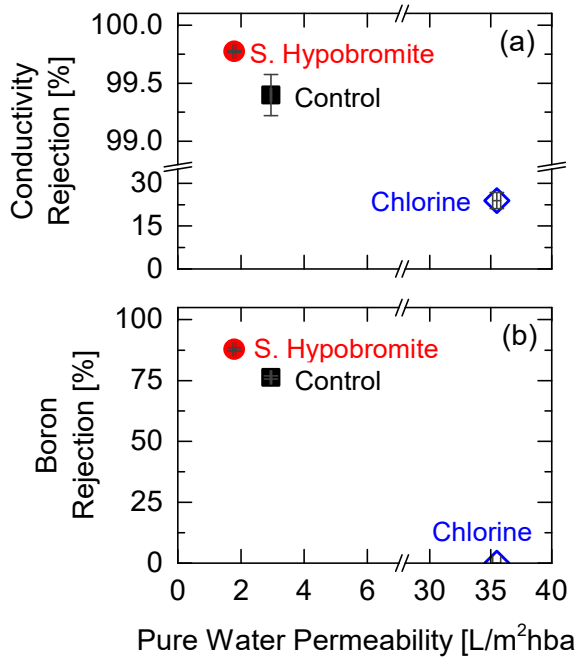

Figure 1 (a) Conductivity and (b) boron rejection as a function of pure water permeability after 96 h of exposure to chlorine and stabilized (S.) hypobromite at 500–800 mg-Cl_2/L in seawater. The symbols and error bars represent the average and range of the triplicated chemical exposure tests, respectively.

3.2 Reduction of fouling constituents

3.2.1 Bacteria

The disinfection potential of the stabilized hypobromite in seawater was assessed using viable bacterial counts determined via colony-forming bacteria **(Figure 2)**. After 1–5 mg/L treatment with either stabilized hypobromite or chlorine, the viable bacterial counts were reduced by 5.9 × 10^3 counts/mL and eliminated. Both chemicals also remained after the disinfection; the residual concentrations of stabilized hypobromite and chlorine at a chemical dose of 1 mg/L were 0.5 and 0.1 mg/L, respectively **(Figure S4)**. Thus, the results indicate that a stabilized hypobromite dose of 1 mg/L is sufficient for inactivating colony-forming bacteria in seawater and that its effectiveness is comparable to that of chlorine. It should be noted that the plate-counting method only includes colony-forming bacteria grown on the R2A medium. In fact, most bacteria in water environments, including seawater, do not form a colony; thus, the conventional plate-counting method may underestimate the possibility of biofouling on membrane surfaces.

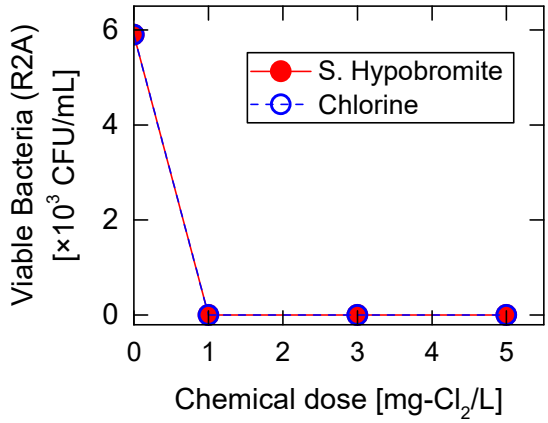

Figure 2 Viable bacteria counts determined by colony plate count during the disinfection using chlorine and stabilized hypobromite in seawater for 5 h at 25°C. Error bars indicate the standard deviations of duplicated disinfection tests.

Epifluorescence microscopy along with the staining of bacteria can cover almost all bacteria in water. Thus, the disinfection potential of stabilized hypobromite was further evaluated via

the counting of intact bacteria having no damage on their cell membranes. With the highest chlorine dose of 5 mg/L in seawater, the intact bacterial counts decreased from 19.0×10^5 to 9.6×10^5 counts/mL **(#1 in Figure 3)**. At the same time, the 5 mg/L dose of stabilized hypobromite in seawater resulted in an even higher reduction from 19.0×10^5 to 1.3×10^4 counts/mL. A similar reduction trend was also obtained when using the treated seawater collected on a separate occasion **(#2 in Figure 3)**. Chlorine, which is not allowed to remain on polyamide RO membrane surfaces, is a powerful disinfectant that damages bacterial membrane cells, enzymatic functions, and nucleic acids [20]. The results of this study indicate that stabilized hypobromite is superior to chlorine with respect to its reduction of intact bacteria counts, suggesting that it has great potential for effective use in biofouling control. We will undertake investigations on the inactivation mechanisms of stabilized hypobromite in a future study.

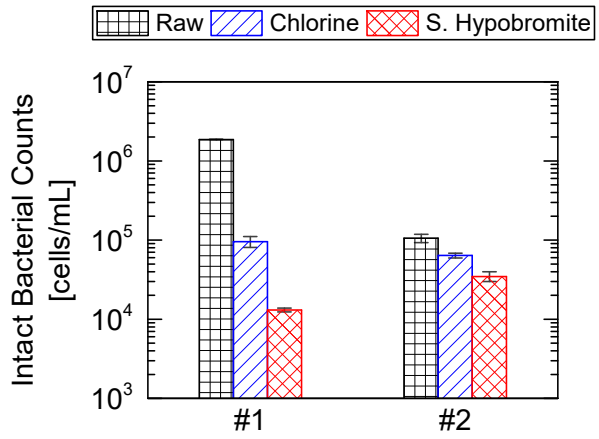

Figure 3 Disinfection effects using chlorine and stabilized hypobromite in two seawater samples collected on separate occasions (#1 and #2) at a chemical dose of 5 mg/L for 5 h. Errors indicate the standard deviations for duplicated disinfection tests.

3.2.2 Dissolved organics

In addition to biofouling, organic fouling is often a major contributor to membrane fouling during seawater desalination [21, 22]. In this study, the organics in the disinfected seawater were further characterized through LC–OCD **(Figure 4)**. The raw seawater pretreated using

an ultrafiltration membrane showed two major organic fractions: humics and LMW organic compounds. Overall, the seawater showed negligible reduction in these two peaks when treated with either chlorine or stabilized hypobromite, and no changes in organic foulants caused by the disinfection treatments were identified through LC–OCD analysis.

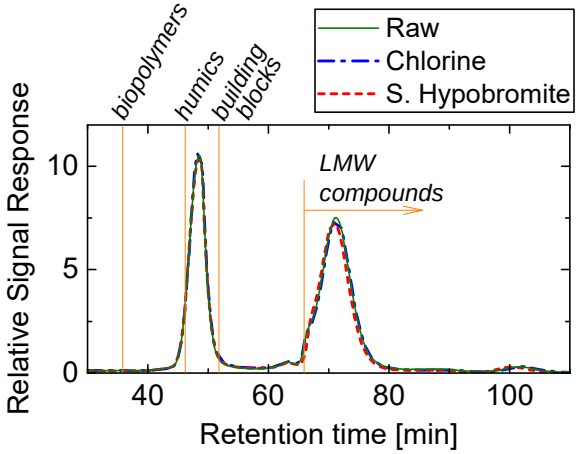

Figure 4 Liquid chromatography–organic carbon detection (LC–OCD) chromatogram of raw seawater and seawater after chlorine and stabilized (S.) hypobromite treatments at a chemical dose of 5 mg/L for 5 h.

The state of the organics in the raw and disinfected seawater was characterized by EEM fluorescence spectra **(Figure 5)**. The spectrum of the non-disinfected seawater showed three major peaks: Ex/Em at 230/300 nm (aromatic protein including tyrosine, denoted by "A"), Ex/Em at 270/300 nm (protein-like substances containing tryptophan, denoted by "B"), and Ex/Em at 340/425 nm (humic-like substances, denoted by "C") [23-25]. The peaks at these regions in the raw seawater **(Figure 5a)** were consistent with those found in previous studies concerning the characterization of organics in seawater [13]. Overall, chlorine treatment reduced the major peaks of regions A, B, and C **(Figure 5b)**, while stabilized hypobromite treatment caused a smaller reduction in the peaks of these regions **(Figure 5c)**. Although the EEM data cannot be used for quantitative analysis, the results indicate that stabilized hypobromite is capable of decomposing some proteins and humic acid-like substances in seawater, while its impact may be lower than that of chlorine in this respect. As some organics in seawater (i.e., protein-like and humic-like substances) remain in the RO feed after

disinfection, these are able to assist in the formation of biofilms in the RO membrane elements during seawater desalination [26]. In addition, the degradation of organics through chemical reactions can lead to the formation of DBPs, including THMs [25, 27]. Therefore, the effectiveness of stabilized hypobromite on fouling mitigation and the potential of DBP formation were assessed in the following sections.

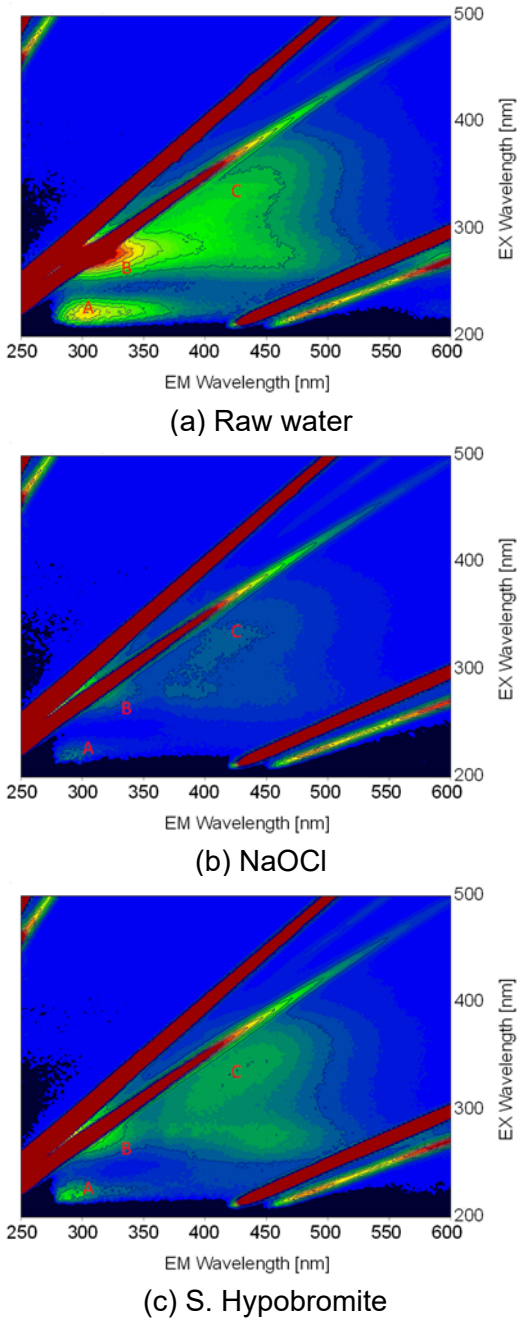

Figure 5 EEM of (a) raw seawater and (b–c) seawater after (b) chlorine and (c) stabilized (S.) hypobromite treatment at a chemical dose of 5 mg/L for 5 h.

3.3 Formation of disinfection by-products

Among the four THMs analyzed in this study, the disinfection of seawater using chlorine and stabilized hypobromite at varied doses of 1–10 mg/L resulted only in the formation of bromoform ($CHBr_3$). The other three THMs, chloroform ($CHCl_3$), dibromochloromethane (CHBrCl), and bromodichloromethane ($CHBr_2Cl$), were not identified at above the detection limit (2 μg/L). Generally, bromoform is the most abundant halogenated organic chemical formed through the chlorination of seawater [3]. On the whole, the formation of bromoform increased along with the increasing chemical dose in the present study. In particular, during chlorine treatment, the bromoform formation increased along with the dose of chlorine up to 35 μg/L **(Figure 6a)**. It should be noted that the formation of bromoform by chlorine is a rapid reaction that takes place within an hour, which is not the case with respect to the other three THMs [28]. In contrast, the stabilized hypobromite treatment resulted in a lower bromoform formation of up to 23 μg/L, while the residual concentration of stabilized hypobromite was higher than that of chlorine at all chemical doses **(Figure 6b)**. Altogether, the results indicate that stabilized hypobromite is less reactive than chlorine.

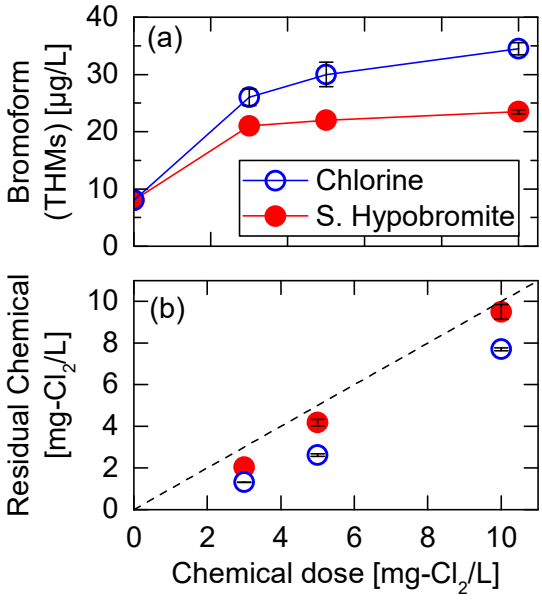

Figure 6 (a) Concentrations of bromoform in seawater as functions of chlorine and stabilized (S.) hypobromite doses and (b) residual chemical concentrations after each test (reaction time of 5 h, temperature of 25°C, and initial pH of 7.0). The symbols and error bars represent the average and range of duplicated formation tests, respectively. The dashed line indicates the equality line with a slope of 1.0.

As the formation of THMs can vary depending on reaction time, the maximum formation potential of THMs caused by stabilized hypobromite or chlorine treatment was also evaluated for an extended reaction period of 96 h **(Figure 7)**. Among the four evaluated THMs, neither the formation of chloroform nor of bromodichloromethane was detected. In addition, a minor formation of dibromochloromethane (<4 µg/L) was identified after the extended reaction period. Compared with these three THMs, bromoform formation was high for both chlorine (80 µg/L) and stabilized hypobromite (55 µg/L) treatments. Most formed bromoform permeates through RO membranes because its rejection by RO membranes is below 50% [29]. Thus, bromoform concentrations after RO treatment can be above the guideline value adopted in many countries (25–250 µg/L) [3] and are a potential threat to the public health. Moreover, the bromoform rejected by RO membranes remains in the RO concentrate and is discharged into the ocean. Bromoform exposure has been reported to alter the behavior of some marine species (e.g., shrimp and menhaden) [30]. Therefore, the fact that stabilized

hypobromite leads to a lower formation of bromoform gives it an advantage over chlorine with respect to THM formation.

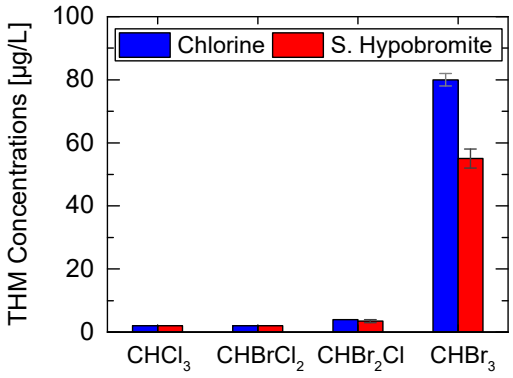

Figure 7 Concentrations of THMs at a chemical dose of 5 mg-Cl_2/L and a reaction time of 96 h (temperature of 25°C and initial pH of 7.0). The data represent the average and range of duplicated formation tests.

The maximum potential formations of HAAs and bromate caused by stabilized hypobromite and chlorine were also determined **(Figure 8)**, and the results revealed that disinfection at a stabilized hypobromite resulted in the formation of dibromoacetic acid (DBA) at 29 µg/L. Chlorine treatment resulted in higher formations of monochloroacetic acid (MCA), monobromoacetic acid (MBA), and DBA (2, 9, and 63 µg/L, respectively). Bromine, a precursor of bromate, is abundant in seawater with a concentration in the range of 65–80 mg/L, and high concentrations of bromate (50 µg/L) were found after chlorine treatment. In contrast, no bromate formation (<10 µg/L) was detected after stabilized hypobromite treatment. The concentration of bromate after chlorine treatment was greater than the WHO guideline value for drinking water (10 µg/L) [31]. Generally, RO processes can achieve a high rejection of bromate ion removal (>95%) [32]; however, this means that high concentrations of bromate ions can be discharged into the water environment through brine. Therefore, disinfection using stabilized hypobromite, a weaker oxidant than chlorine [33, 34], has the advantage that it results in a lower formation of bromate in seawater.

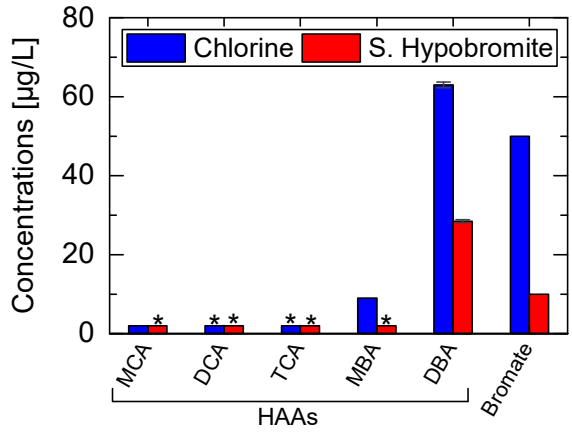

Figure 8 Concentrations of HAAs and bromate at a chemical dose of 5 mg-Cl_2/L and reaction time of 96 h and 13.5 days, respectively (temperature of 25°C and initial pH of 7.0). The data represent the average and range of duplicated formation tests. The concentration of chemicals with asterisk (*) represents below the detection limit of 2 µg/L.

The results of this study indicate that stabilized hypobromite is able to form smaller amounts of THMs, HAAs, and bromate than chlorine during disinfection in seawater. Yang et al. [13] have reported that dissolved organic matter with a MW of <1 kDa dominates the formation of THMs and HAAs during the chlorination of seawater. Small and hydrophobic neutrals in particular, including humic acid-like and aromatic protein-like substances, are major precursors of THMs and HAAs. In this study, it was found that chlorine reduced a larger amount of these small and hydrophobic neutrals compared with stabilized hypobromite **(Figure 5)**. This implies that stabilized hypobromite reacted less with these small organics in the seawater, resulting in a lower formation of THMs and HAAs. The DBP formation of THMs, HAAs, and bromate varies considerably depending on disinfection conditions (e.g., concentration, reaction time, and temperature) and water matrix conditions (e.g., precursor concentrations). To assess the efficacy of stabilized hypobromite during seawater desalination, it is important to validate the effectiveness of stabilized hypobromite for controlling membrane fouling and DBP formation with optimized disinfection conditions at pilot or full scale.

3.4 Pilot-scale demonstration

The pilot-scale test demonstrated the effectiveness of pre-disinfection with stabilized hypobromite on biofouling mitigation **(Figure 9)**. Over the course of the 180-day test, the differential pressure of the feed stream (ΔP) in the system containing stabilized hypobromite remained stable at approximately 8 kPa, while that in the system without pre-disinfection (control) increased proportionally from 8 to 28 kPa after 100 days of filtration **(Figure 9a)**. Biofouling typically becomes evident after a certain period of the treatment, when substantial biofilm formation along with biological growth begins to occur. The ΔP represents the level of clogging in the feed stream, which is related to hydrolytic resistance. Thus, the results indicate that stabilized hypobromite is able to alleviate the deposition of foulants between the membranes and spacers in the feed stream. Similarly, the mitigation of biofouling by stabilized hypobromite was observed in normalized flux ($J_t/J_{t=0}$), corresponding to the level of membrane fouling on the membrane surface. A notable difference between the control and stabilized hypobromite systems was observed after 70 days of operation **(Figure 9b)**. At this time, the normalized flux of the control system decreased to 0.6, while the stabilized hypobromite system maintained a normalized flux above 0.8. This indicates that the stabilized hypobromite system requires a lower energy than the control system to maintain a specific permeate flux. It is noted that the conductivity rejection of both systems was above 99.3% throughout the evaluation **(Figure S5)**, which means that the changes in the membrane properties during the half-year test were insignificant. The pilot-scale evaluations demonstrated that pre-disinfection of seawater using stabilized hypobromite was capable of alleviating bacterial growth in the RO feed channel as well as on the membrane surface without compromising the separation of salts, maintaining the permeance of the seawater RO membrane for half a year. Despite successful demonstration of controlling membrane fouling and DBP formation using stabilized hypobromite, it requires higher costs than conventional

disinfectants (e.g., sodium hypochlorite). A future study that focuses on the chemical dose optimization and chemical cost analysis will clarify the potential of stabilized hypobromite as an alternative disinfectant to chlorine.

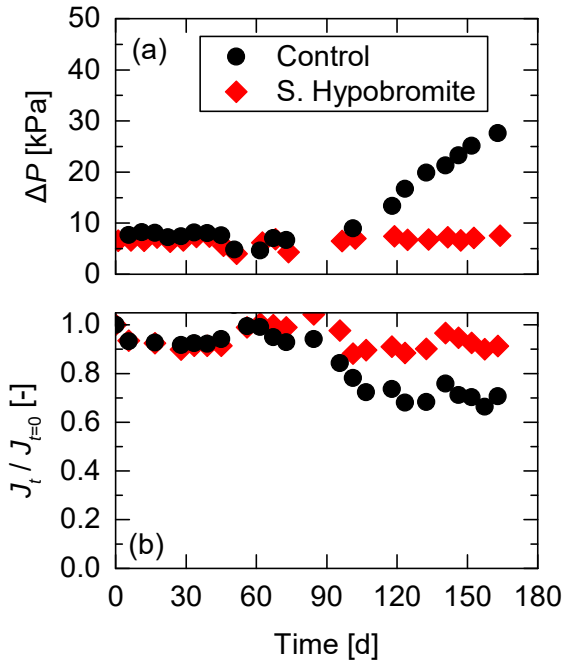

Figure 9 Changes in (a) differential pressure across the feed channel (ΔP) and (b) normalized permeate flux ($J_t/J_{t=0}$) during RO treatment of seawater with and without 0.2 mg-Cl_2/L of stabilized (S.) hypobromite.

4 Conclusion

A new disinfectant, stabilized hypobromite, was found to be a viable alternative to chlorine for controlling membrane fouling while maintaining sufficient disinfection capacity during seawater treatment. The stabilized hypobromite did not cause degradation of the tested RO membrane, indicating that it can be used continuously for disinfection on polyamide RO membrane surfaces. Hypobromite and chlorine were also found to be equally effective in reducing potential fouling constituents (bacteria and organics). The formation of major DBPs including THMs, HAAs, and bromate caused by stabilized hypobromite was found to be lower than that caused by chlorine, indicating the superiority of stabilized hypobromite over

chlorine in this respect. Pilot-scale RO treatment of seawater with a continuous dose of stabilized hypobromite further revealed a half-year continuous operation without major fouling. Altogether, the results of this study indicate the great potential of stabilized hypobromite for use as a disinfectant of RO membranes for controlling DBP formation and membrane fouling during seawater desalination.

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