Application of stabilized hypobromite for controlling membrane fouling and *N*-nitrosodimethylamine formation

Takahiro Fujioka,[1,*] Hiro Yoshikawa,[2] Masahiro Eguchi,[2]
Sandrine Boivin,[1] Hitoshi Kodamatani,[3]

[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*

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

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

Abstract

Chloramination is a conventional and successful pre-disinfection approach to control biological fouling for reverse osmosis (RO) treatment in water reuse. This study aimed to evaluate the possibility of using a new disinfectant—stabilized hypobromite—in controlling membrane fouling and the formation of a particular carcinogenic disinfection byproduct (DBP)—*N*-nitrosodimethylamine (NDMA). Our accelerated chemical exposure tests showed that the new disinfectant reduced the permeability of a polyamide RO membrane permeability from 6.7 to 4.1 L/m^{2}hbar; however, its treatment impact was equivalent to that of chloramine. The disinfection efficacy of stabilized hypobromite was greater than that of chloramine when evaluated with intact bacterial counts, which suggests its potential for mitigating membrane biofouling. Additional pilot-scale tests using synthetic wastewater demonstrated that pre-disinfection with the use of stabilized hypobromite inhibits membrane fouling. Among 13 halogenated DBPs evaluated, the formation of bromoform by stabilized hypobromite was higher than that by chloramine at a high dose of 10 mg/L, thus suggesting the need for optimizing chemical doses for achieving sufficient biofouling mitigation. NDMA formation upon stabilized hypobromite treatment in two different types of actual treated wastewaters was found to be negligible and considerably lower than that by chloramine treatment. In addition, NDMA formation potential by stabilized hypobromite was 2–5 orders of magnitude lower than that by chloramine. Our findings suggest the potential of using stabilized hypobromite for controlling NDMA formation and biofouling, which form the keys to successful potable water reuse.

Keywords: NDMA; DBPs; biofouling; reverse osmosis; disinfection.

1 Introduction

Potable water reuse has been found to be the most efficient option to augment drinking water supply in regions that experience prolonged droughts (WHO, 2017). Potable water reuse can be achieved by means of purifying secondary wastewater effluents to a level that meets drinking water standards via advanced wastewater treatment processes (AWTPs). AWTPs typically involve microfiltration (MF) or ultrafiltration (UF), reverse osmosis (RO), advanced oxidation process (AOP), and chlorine disinfection (Tang et al., 2018; Warsinger et al., 2018). In particular, RO treatment has been found to be an effective separation technology for eliminating most impurities from wastewater. However, the presence of dissolved nutrients in the pre-treatment process (i.e., MF or UF) can trigger the proliferation of microorganisms and cause biofouling (Leddy et al., 2017).

To alleviate biofouling, a pre-disinfection process via chloramination is performed prior to the RO treatment (Goh et al., 2018). However, this pre-disinfection process also leads to the formation of carcinogenic disinfection byproducts (DBPs) that include *N*-nitrosodimethylamine (NDMA) and *N*-nitrosomorpholine (NMOR) (Mitch et al., 2003b; Farré et al., 2011b; Krasner et al., 2013; Chuang et al., 2019). NDMA is formed via chloramination when there is a reaction between chloramine and secondary, tertiary, or quaternary amines (NDMA precursors). NDMA precursors include dimethylamine (DMA), trimethylamine (TMA), dimethylbenzylamine (DMBA), pharmaceuticals (e.g., ranitidine), and water treatment polymers (Le Roux et al., 2011; Shen and Andrews, 2011; Zhou et al., 2014; West et al., 2016; Sgroi et al., 2018). Because of the NDMA formed after chloramination and the NDMA present in raw wastewater, NDMA concentrations prior to RO treatment can be >20–100 ng/L (Sedlak et al., 2005; Fujioka et al., 2012). However, RO treatment can only achieve <50% NDMA rejection (Bellona et al., 2008; Fujioka et al., 2013b), and thus, ultraviolet (UV) or UV-based AOP treatment becomes the only reliable barrier to attenuate NDMA concentration within the recommended guideline levels (e.g., 10 ng/L) (Plumlee et al., 2008; McCurry et al., 2017). Thus, any reduction in NDMA formation prior to the RO process is beneficial for the improved safety of the potable water reuse.

To alleviate NDMA formation, several chloramination-based approaches have been proposed. For instance, chlorination via pre-formed monochloramine or distributed chlorine dosing can significantly reduce NDMA formation (Mitch et al., 2005; Schreiber and Mitch, 2005; Furst et al., 2018). In this context, as an alternative to the conventional chloramination, here, this study proposes a pre-disinfection process using a new disinfectant—stabilized hypobromite. Hypobromite (BrO^{-}) is an oxidizing reagent that is stronger than chloramine, and it is normally used as a strong disinfectant in industrial water applications (e.g., cooling water) (Cristiani and Perboni, 2014). It is noted that hypobromite can be stably present in water when it is stabilized with sulfamic acid at a high pH. However, the effectiveness of the new disinfectant (i.e., stabilized hypobromite) in mitigating biofouling and NDMA formation remains unclear. Moreover, bromine-based disinfectants can possibly form brominated DBPs, which can be more toxic than chlorinated DBPs (Sharma et al., 2014). Addressing these concerns is critical to adaptation of the new disinfectant to pre-disinfection process in water recycling applications.

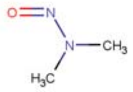
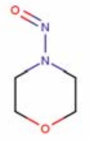
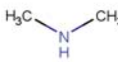
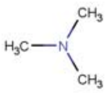
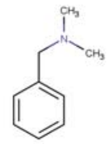
Against this backdrop, this study evaluated the potency of stabilized hypobromite treatment in controlling membrane biofouling and NDMA formation during the RO treatment of treated wastewater. The study involved three major evaluations: (a) changes in the RO membrane performance; (b) bactericidal capacity and biofouling control performance; and (c) formation potential of NDMA and other DBPs. Through every phase of the study, the results obtained using stabilized hypobromite were compared with those obtained with chloramine.

2 Materials and methods

2.1 *Chemicals*

Analytical grade chemicals (NaCl, $NaHCO_3$, $CaCl_2$, NH_4Cl, and HCl) were purchased from Kanto Chemical Co. (Tokyo, Japan). A NaOCl solution, with over 12% chlorine concentration, was purchased from Tosoh Co. (Tokyo, Japan), and a stock solution of chloramine was prepared at 0.2 M by mixing NaOCl and NH_4Cl solutions. Further, hypobromite stabilized by sulfamic acid was used as stabilized hypobromite in this study. A stock solution of stabilized hypobromite comprised of hypobromite, sulfamic acid and sodium hydroxide was supplied by Organo Co. (Tokyo, Japan). Chemicals selected as NDMA precursors were DMA, TMA, and *N*,*N*-dimethylbenzylamine (DMBA) were purchased from Kanto Chemical Co. (Tokyo, Japan) **(Table 1)**. A flat sheet polyamide composite RO membrane sample (namely ESPA2) were supplied by Hydranautics/Nitto (Oceanside, CA, USA). This study used two types of treated wastewater: an ultrafiltration (UF)-treated wastewater and membrane bioreactor (MBR)-treated wastewater, both of which were collected at wastewater treatment plants in Japan.

Table 1 – Molecular structures of NDMA and selected NDMA precursors.

Classification	*N*-nitrosamines		NDMA precursors		
Name	NDMA	NMOR	DMA	TMA	DMBA
Structure					
Molecular weight [g/mol]	74.1	116.1	45.1	59.1	135.1
pKa* [-]	3.6	3.2	10.7	9.7	9.1
Charged spices at pH 6* [%]	0	0	100 (+)	100 (+)	0
Charged spices at pH 8* [%]	0	0	99 (+)	98 (+)	8 (+)

*Calculated using MarvinSketch software (ChemAxon, Budapest, Hungary).

2.2 *Test protocols*

2.2.1 Membrane degradation tests

The deformation of RO membranes using a disinfectant agent was simulated through immersing polyamide membrane samples in a 500 mL solution dosed with a disinfectant (chloramine, stabilized hypobromite, or NaOCl) or a solution without chemical addition (Control). Each chemical reagent was dosed at a concentration of 300 mg-Cl_2/L in a synthetic wastewater (20 mM NaCl, 1 mM $CaCl_2$, 1 mM $NaHCO_3$, 1 mg-Al/L) or dosed to achieve a concentration of >200 mg-Cl_2/L in the UF-treated wastewater. It is noted that the aluminum ions were added in the synthetic wastewater to enhance oxidative degradation reactions through catalytic effects (Cran et al., 2011). The solution pH was adjusted at 7.0, and the samples were left to stand in the dark at 25 °C for 100 h, which is equivalent to the cumulative exposure during one year operation with a standard chloramine residual concentration at the membrane surface (e.g., 3 mg-Cl_2/L). Thereafter, the pure water permeability and conductivity rejection performance of each membrane sample was determined using the bench-scale RO system **(Figure S1)**. Conductivity rejection was determined at a permeate flux of 43 L/m^2h. The permeate flux in this study was as twice as high as the typical value of full-scale RO processes (i.e., approximately 20 L/m^{2}h). However, because variation in conductivity rejection between 43 and 20 L/m^{2}h is negligible (Fujioka et al., 2013a), the conductivity rejection data in this study can be considered valid.

2.2.2 Disinfection for bactericidal effects

The disinfection efficacy of stabilized hypobromite and chloramine was evaluated by determining the number of viable bacteria (denoted as “intact bacteria” in this study) in treated wastewater using epifluorescence microscopy (Section 2.3.1). A similar approach for evaluating the disinfection efficacy using intact bacterial counts has been found elsewhere (Park et al., 2016; Farhat et al., 2018). In this study, wach disinfection test was conducted using 200 mL of treated wastewater. A disinfectant (stabilized hypobromite and chloramine) was added into the sample at a dose of 10 mg-Cl_2/L. It is noted that stabilized hypobromite dose is presented in mg-Cl_2/L by converting the concentration of bromine in terms of chlorine. Thereafter, the flasks were placed in a temperature-controlled room (25 °C) for 1 or 5 h. The reaction time was determined based on a contact time of chloramination prior to RO process at full-scale water recycling systems, in which the contact time can vary considerably from 1 to 24 h (Farré et al., 2011a). Following the sample collection, residual chemical was quenched by adding a sodium sulfite solution.

2.2.3 Membrane fouling mitigation

The effect of stabilized hypobromite in controlling membrane fouling was evaluated using a pilot-scale RO system holding one 4-in ESPA2 RO membrane element, with a surface area of 7.9 m^2 and a nominal salt rejection of 99.6% **(Figure S2)**. Groundwater **(Table S1)** was continuously fed to the pilot-scale system as an artificial RO feedwater after being dosed with acetic acid as carbon nutrients at 5 mg/L. In addition, stabilized hypobromite was added to the RO feed reservoir at 1.0

mg-Cl_2/L for 3 h a day. The RO system was operated at a constant flux of 17–20 L/m^2h and a water recovery rate of 25–30%. The level of membrane fouling was evaluated based on the increases in pressure drop (ΔP) and transmembrane pressure (TMP) as follows:

$$\Delta P = P_f - P_c \qquad (1),$$

$$\mathrm{TMP} = (P_f + P_c)/2 - P_p \qquad (2),$$

where P_f = feed pressure (kPa), P_c = concentrate pressure (kPa), and P_p = permeate pressure (kPa).

2.2.4 DBP formation tests

The formation of halogenated DBPs was evaluated using the UF-treated wastewater. Each formation test was conducted using 1,000 mL of treated wastewater in a sealable perfluoroalkoxy alkane (PFA) flask. A disinfectant (stabilized hypobromite and chloramine) was added into the sample at a dose of 10 mg-Cl_2/L. Prior to the disinfectant addition, each sample solution's pH was adjusted by adding an HCl solution so that the sample solution pH becomes 7.0 after the disinfectant addition. The flasks were then placed in a temperature-controlled room (25 °C) for 5 h to advance the reactions. Following the sample collection, residual chemical was quenched by adding a sodium sulfite solution.

The formation of NDMA and NMOR was evaluated using the UF-treated and MBR-treated wastewaters. Each formation test was conducted using 1,000 mL of treated wastewater in a sealable PFA flask. A disinfectant (stabilized hypobromite and chloramine) was added into the sample at a dose of 3, 5, 10, or 100 mg-Cl_2/L. Prior to the disinfectant addition, each sample solution's pH was adjusted by adding an HCl solution so that the sample solution pH becomes 7.0

after the disinfectant addition. The flasks were left in a temperature-controlled room (25 °C) for 5 or 48 h. Thereafter, residual chemical was quenched by adding a sodium sulfite solution.

Formation potential of NDMA by stabilized hypobromite and chloramine was evaluated using an artificial wastewater containing one of the selected NDMA precursors. The solutions of each selected precursor (DMA, TMA, or DMBA) were conditioned at 0.1 mg/L in ultrapure water containing 10 mM of $NaHCO_3$. Each formation test was conducted using 100 mL of artificial wastewater in a sealable PFA flask. Prior to the disinfectant addition, the solution pH of each sample was adjusted by adding an HCl solution so that the sample solution pH becomes 6.0 or 8.0 after the disinfectant addition. The solution pHs were determined based on RO feed pH of typical full-scale plants, which typically varies from 6 to 8 across the entry of the first stage to the exit of the third stage (Fujioka et al., 2013b). Thereafter, a disinfectant (stabilized hypobromite and chloramine) was added into the sample at a dose of 100 mg-Cl_2/L, which was determined based on a previous study (Selbes et al., 2018). The flasks were then placed in a temperature-controlled room (25 °C) for 0, 2, 5, 24 or 120 h, and residual chemical was quenched by adding a sodium sulfite solution.

2.3 Analytical techniques

2.3.1 Bacterial analysis

Intact bacterial counts in the UF-treated wastewater before and after disinfection were determined using an epifluorescence microscope BZ-X800 (Keyence Co., Osaka, Japan). Prior to the analysis, each sample (0.2 µL) was filtered using a track-etched polycarbonate membrane filter with a pore size of 0.22 µm and a diameter of 13 mm (Meric, Tokyo, Japan). The membranes were stained with a LIVE/DEAD BacLight Bacterial Viability Kit (Thermo Fisher Scientific K.K., Tokyo, Japan) (Boulos et al., 1999). After 15 min incubation period, bacterial number deposited on approximately 3% of the filter surface area was counted as damaged bacteria (red color) and total bacteria (green color). Intact bacterial counts were determined by deducting the number of damaged bacteria stained with propidium iodide (PI) from the number of total bacteria (stained with SYTO 9).

2.3.2 Chemical analysis

Concentrations of stabilized hypobromite and chloramine were measured using a colorimeter (DR-3900, Hach Co., Loveland, CO, USA). Concentrations of trihalomethanes, haloacetic acids and bromo chloroacetonitrile were determined using gas chromatography mass spectrometry (MS) (Xie, 2001; Nikolaou et al., 2002). Concentrations of chloric acid and bromate were determined using an ion chromatography (Johns et al., 2008) and liquid chromatography-MS/MS (Snyder et al., 2005), respectively. Concentrations of NDMA and NMOR were analyzed using a high-performance liquid chromatography-inline anion exchange reaction-photochemical reaction-chemiluminescence (HPLC-AEM-PR-CL) (Kodamatani et al., 2009; Kodamatani et al., 2018). Results from the analytical method signified that the detection limit of NDMA and NMOR was 0.4 and 1.4 ng/L, respectively.

3 Results and discussion

3.1 Membrane properties

The impact of chemical exposure on the salt separation performance and permeability of polyamide RO membranes was evaluated through accelerated tests, in which RO membrane samples were immersed in artificial wastewater with high concentrations of chemical agents (stabilized hypobromite, chloramine, chlorine, or Control). **Figure 1** illustrates the permeability and conductivity rejection after 100 h of exposure to chlorine, chloramine, or stabilized hypobromite in a pure water matrix and UF-treated wastewater. As predicted, chlorine exposure resulted in considerably high pure water permeability (11.2 L/m^{2}hbar) and a very low conductivity rejection (91.2%) relative to Control (permeability of 7.6 L/m^{2}hbar and conductivity rejection of 99.1%) **(Figure 1a)**. This deterioration is very likely caused by the destruction of the polyamide skin layer, which can be induced by hydrolysis and degradation of the cross-linked polyamide network (Ohno et al., 2016; Gohil and Suresh, 2017). Relative to chlorine, the impact of the conventional disinfectant (chloramine) on membrane transport was significantly low; the pure water permeability and conductivity rejection after chloramine (permeability of 7.2 L/m^{2}hbar and conductivity rejection of 98.5%) were comparable with the corresponding ones of the Control (permeability of 7.6 L/m^{2}hbar and conductivity rejection of 99.1%). Further, the results show that the impact of exposing the membrane to stabilized hypobromite was insignificant.

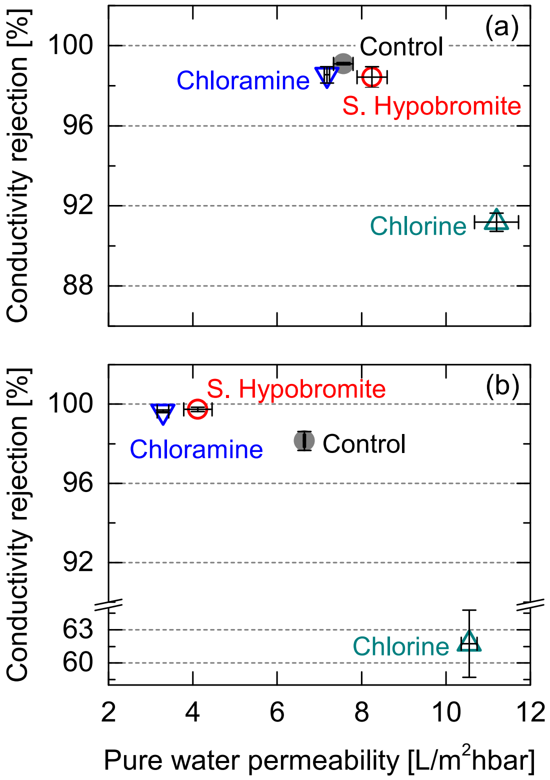


Figure 1 – Permeability and conductivity rejection after 100 h of exposure to chlorine, chloramine, or stabilized (S.) hypobromite in (a) pure water matrix and (b) ultrafiltration (UF)-treated wastewater. Symbols and error bars represent the average and range, respectively, of duplicated chemical exposure tests.

The impact of chemical exposure was more pronounced when simulated in actual UF-treated wastewater (**Figure 1b**). It is noted that during the chemical exposure tests with chloramine, chloramine concentrations reduced progressively according to reaction time. Thus, the chloramine stock solutions were dosed every 24 h to recover their chloramine concentrations above 200 mg/L **(Figure S3)**. Similar to the case of the artificial wastewater, chlorine exposure was found to increase pure water permeability to 10.5 L/m^{2}hbar and result in a considerably low conductivity rejection (61.7%). In contrast, both stabilized hypobromite and chloramine treatment resulted in a considerable reduction in water permeability to 4.1 and 3.3 L/m^{2}hbar from 6.7 L/m^{2}hbar (Control), respectively. Accordingly, the separation performance (i.e., conductivity rejection) remarkably increased to 99.6% (chloramine) and 99.7% (stabilized hypobromite) from 98% (Control). The improved separation performance and reduced water permeability in the treated wastewater indicate that stabilized hypobromite and chloramine treatment may not have caused oxidative damages to the RO membranes that can deteriorate both separation performance and water permeability (da Silva et al., 2006). Instead, stabilized hypobromite and chloramine treatment may have caused structural changes in the RO membrane matrix, because different types of RO membranes typically exhibit a tradeoff between their water permeability and separation performance (e.g., improved separation performance is achieved at the cost of decreased water permeability) (Fujioka et al., 2015). Although accelerated tests have limitations in simulating long-term exposure of chemicals to RO membranes due to differences in the degradation mechanisms (Stolov and Freger, 2019), the simulated test results suggest that stabilized hypobromite and chloramine offer comparable efficacies in terms of the level of changes in the RO membrane properties during pre-disinfection.

3.2 Disinfection

3.2.1 Bactericidal effects

The disinfection efficacy of stabilized hypobromite and chloramine was evaluated based on intact bacterial counts via epifluorescence microscopy **(Figure 2)**. Conventional heterotrophic plate count (HPC) method, which only provides the number of colony-forming bacteria that use organic carbon, is commonly used for evaluating and ensuring microbiological water quality in treated water. As compared with HPC, the methods based on fluorescence microscopy coupled with nucleic acid stains cover almost all bacterial cells in water with the information of their state (intact or damaged). In general, stabilized hypobromite is superior to chloramine in terms of reduction in bacteria. Chloramination resulted in the reduction of intact bacterial counts from 8.1 × 10^5 counts/mL to 3.2 × 10^5 (1 h) and 2.3 × 10^5 (5 h) counts/mL. Stabilized hypobromite showed a greater reduction in intact bacterial counts from 8.1 × 10^5 counts/mL to 1.7 × 10^5 (1 h) and 1.3 × 10^5 (5 h) counts/mL. Considering that biofouling layers on RO membranes can be composed of various types of bacteria in treated wastewater, intact bacterial counts can be one of the indicators for predicting the biofouling potential. Overall, the results here suggest that pre-disinfection using stabilized hypobromite is more likely to mitigate biofouling than chloramine.

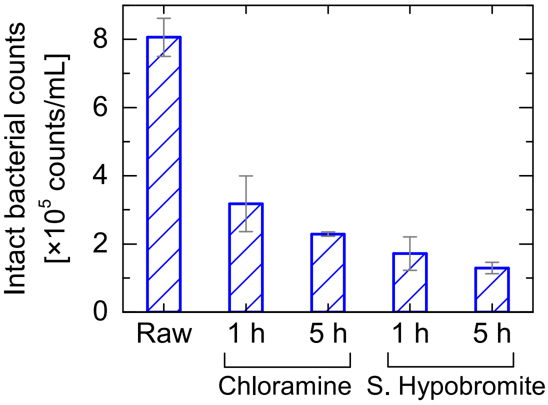


Figure 2 – Effects of disinfection using chloramine and stabilized hypobromite in ultrafiltration-treated wastewater: intact bacterial counts determined by epifluorescence microscopy. Error bars indicate the standard deviations for duplicated disinfection tests.

3.2.2 Fouling mitigation

The degree of membrane fouling mitigation with the use of stabilized hypobromite was next evaluated at the pilot scale by comparison with that without disinfection addition (Control). Due to the limitations of the facility available for this pilot-scale test, this study used filtered groundwater dosed with acetic acid as synthetic wastewater in this study. Stabilized hypobromite treatment was conducted by intermittently applying stabilized hypobromite pre-disinfection at a dose of 1.0 mg-Cl_2/L for 3 h/d; **Figure 3** shows the corresponding results. Over the course of the

17-day test, the pressure drop (Δ*P*) across the feed stream of the Control system was observed to increase remarkably from 6 to 20 kPa **(Figure 3a)**, thereby indicating clogging in the RO feed channel. Here, it is noted that full-scale clogging can cause a reduction in the RO feed pressure in the inlet of the subsequent RO elements. In contrast to the Control system, the pressure drop in the stabilized hypobromite system remained almost constant (at 7–8 kPa). This result indicates that stabilized hypobromite effectively suppresses bacterial growth (clogging) in the RO feed channel. Next, from **Figure 3b**, the transmembrane pressure (TMP) in the Control system progressively increased from 490 to 590 kPa during the tests. This increase in TMP indicates increased hydraulic resistance across the RO membrane, which means that a higher energy is required to maintain a specific permeate flux. In contrast, the stabilized hypobromite system achieved a stable TMP in the range of 440–500 MPa. It is noted that another membrane fouling test using chloramine pre-disinfection at a dose of 3.0 mg-Cl_2/L resulted in a constant decrease in transmembrane pressure (TMP) and conductivity rejection during over a period of only 18 days **(Figure S4)**. The decreased TMP (i.e., increased water permeability) and decreased separation performance indicate that chloramination in the synthetic wastewater may have induced deterioration of the RO membrane.

Despite the differences in the membrane fouling levels between the two RO systems (i.e., Control and stabilized hypobromite), the ion separation performances of both systems were comparable **(Figure 3c)**. These results indicate that intermittent pre-disinfection with stabilized hypobromite can mitigate membrane fouling. Further investigations focusing on the mechanisms associated with membrane fouling mitigation with the use of stabilized hypobromite are necessary to ensure that the versatility of stabilized hypobromite in water recycling applications is taken into consideration, particularly because actual wastewaters contain diverse ranges of foulants and their concentrations vary considerably depending on seasons and locations.

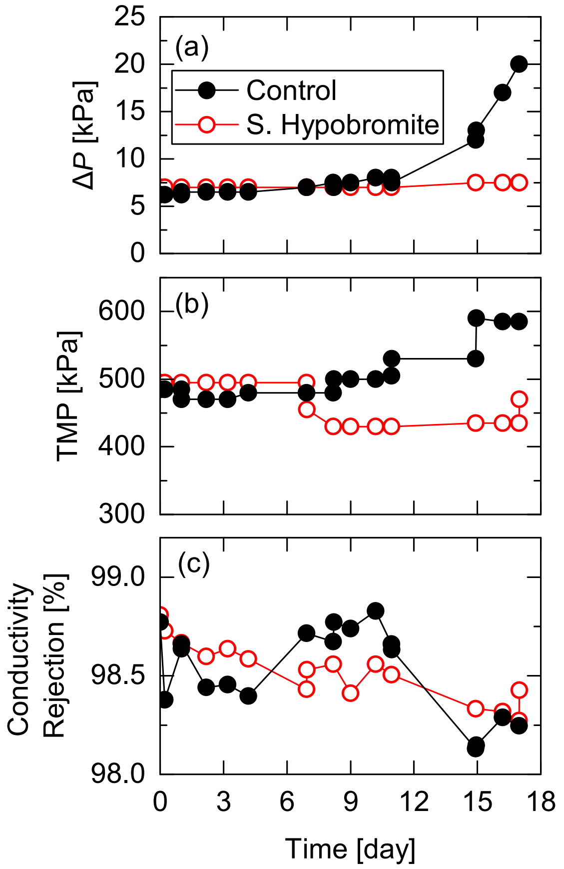


Figure 3 – Change in (a) pressure drop (Δ*P*) across feed channel, (b) transmembrane pressure (TMP) across reverse osmosis (RO) membrane, and (c) conductivity rejection during RO treatment of synthetic wastewater (Permeate flux of 19–20 L/m^{2}h, permeate recovery of 25–30%, and feed temperature of 14–17 °C). Throughout the tests, no hypobromite was detected in the RO permeate.

3.3 DBP formation

3.3.1 Halogenated DBPs

The formation of 13 halogenated DBPs was evaluated at a chloramine or stabilized hypobromite dose of 10 mg-Cl_2/L and a reaction period of 5 h; the results are listed in **Table 2**. In general, the formation potentials of DBPs by chloramine and stabilized hypobromite appeared comparable. Here, it is important to note that the formation of bromate (BrO_3), a carcinogenic DBP, via stabilized hypobromite treatment was found to be negligible at 1 μg/L, which is below the WHO guideline value for drinking water (10 µg/L) (WHO, 2011). Stabilized hypobromite is an intermediate form of transformation from bromine to bromate, and bromate formation can only be achieved by strong oxidants such as ozone and hypochlorite (Fang et al., 2017; Yang et al., 2017). Therefore, stabilized hypobromite cannot transform to bromate in the absence of these strong oxidants. Among the four trihalomethanes (THMs)—chloroform, bromodichloromethane, dibromochloromethane, and bromoform—the concentration of bromoform after stabilized hypobromite treatment (90 µg/L) was greater than that after chloramine treatment (24 µg/L). The high bromoform concentration of the treated wastewater resulted in its THM concentration being greater than the maximum contaminant level (MCL) of THMs, which has been established for drinking water in CA, USA. However, trihalomethanes, including bromoform, are typically rejected by 40–50% (Doederer et al., 2014); thus, THM concentration in the RO permeate will be substantially lower than that in the RO feed. It is to be noted that the formation potential of THMs can vary considerably depending on the source of treated wastewater and disinfection conditions (e.g., reaction time and chemical dose). To identify whether the formation of halogenated DBPs by stabilized hypobromite is acceptable, evaluations of various wastewaters used for potable reuse and the optimization of operating conditions are necessary in future.

Table 2 – Disinfection byproduct (DBP) concentrations after chloramine or stabilized hypobromite treatment of ultrafiltration-treated wastewater (chemical dose of 10 mg-Cl_2/L, reaction time of 5 h, temperature of 25 °C, and initial pH of 7.0). The residual concentrations of chloramine and stabilized hypobromite after the reaction were 5.5 and 2.4 mg-Cl_2/L, respectively.

DBP	Unit	MCL in CA, USA	Before pre-disinfection	Chloramine	Stabilized hypobromite
Trihalomethane	µg/L	80	<8	36	100
-Chloroform	µg/L	-	<2	<2	<2
-Dibromochloromethane	µg/L	-	<2	9	6
-Bromodichloromethane	µg/L	-	<2	3	<2
-Bromoform	µg/L	-	<2	24	90
Chloroacetic acid	µg/L	60	<2	<2	<2
Dichloroacetic acid	µg/L	-	<2	2	<2
Trichloroacetic acid	µg/L	-	6	6	6
Bromoacetate	µg/L	-	<2	n.a.	2
Dibromoacetic acid	µg/L	-	<2	n.a.	19
Bromochloroacetonitrile	µg/L	-	<1	n.a.	<1
Chloric acid	µg/L	1,000	<3,000	<3,000	<3,000
Bromate	µg/L	10	<1	n.a.	1

*-: Not established, n.a.: Not analyzed.

3.3.2 *N*-nitrosamines

The potential of DBP formation upon the chloramine and stabilized hypobromite treatment of two different treated wastewaters was evaluated at a chemical dose of 3–10 mg-Cl_2/L and a reaction time of 5 h. Chloramine treatment of the UF-treated wastewater resulted in a considerable increase in NDMA concentration from 4 to 21 ng/L **(Figure 4a)**. In contrast, the NMOR concentration after the chloramine treatment was low at <3 ng/L **(Figure 4b)**. It is noted that the health-based guideline value of NMOR has been set at as low as 1 ng/L for recycled water intended for potable water reuse in Australia (NRMMC et al., 2008). However, NMOR is strongly rejected by RO (typically >90%); thus, NMOR concentrations greater than the regulatory value in the specific treated wastewater are less likely to form an issue. A similar increasing trend for the formation of NDMA and NMOR by chloramine was observed for the MBR-treated wastewater, whereas

NDMA formed by stabilized hypobromite reached only up to 3 ng/L. It is important to note that the residual chloramine concentration in the full-scale RO process in water recycling is usually maintained at >2–3 mg-Cl_2/L; thus, it is safe to say that a residual chloramine concentration of 3.7 mg-Cl_2/L under the 10 mg-Cl_2/L dose condition in UF-treated wastewater simulated the actual chloramination **(Figure 4c)**. The formation of NDMA by chloramine possibly occurred through a reaction between monochloramine and NDMA precursors in the treated wastewater because chloramine species at the test solution pH of 7 include monochloramine and a small fraction of dichloramine (Kinani et al., 2012). Throughout the tests, the oxygen concentration and solution pH, which can influence NDMA formation by chloramine (Le Roux et al., 2012; Spahr et al., 2017), remained almost stable **(Figure S5)**. This implies that any further extension of the chloramine reaction time can lead to the formation of greater amounts of NDMA, as previously reported in literature (Farré et al., 2011a). In contrast to chloramine, stabilized hypobromite showed a negligible increase in NDMA and NMOR for both treated wastewaters **(Figures 4a and 4b)**. This result indicates that the yield of NDMA by stabilized hypobromite was significantly lower than the one by chloramine.

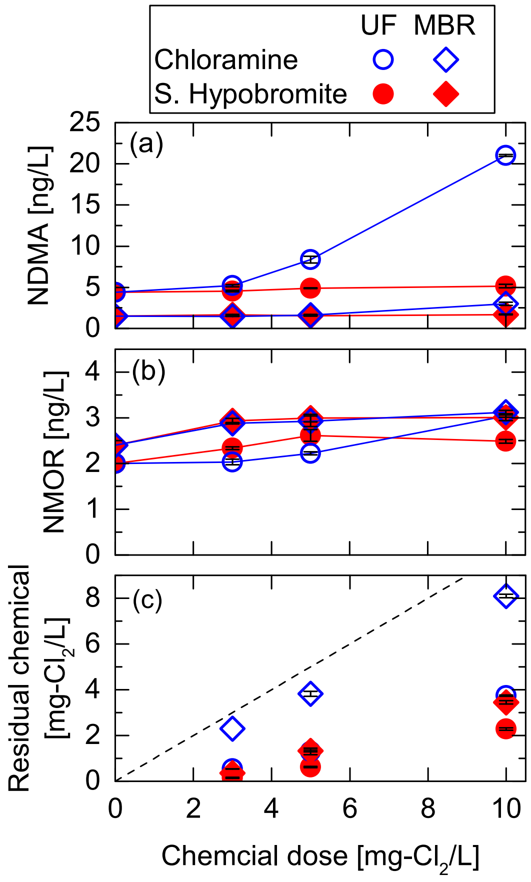


Figure 4 – (a) *N*-nitrosodimethylamine (NDMA) and (b) *N*-nitrosomorpholine (NMOR) concentrations in ultrafiltration (UF)-treated or membrane bioreactor (MBR)-treated wastewaters as functions of chloramine and stabilized hypobromite doses, and (c) residual chemical concentrations after each test (reaction time of 5 h, temperature of 25 °C, and initial pH of 7.0). The symbols and error bars represent the average and range, respectively, of duplicated formation tests. The dashed line indicates the equality line with a slope of 1.0.

The maximum formation potential (FP) of NDMA and NMOR by stabilized hypobromite or chloramine pre-treatment was also evaluated at an excessive chemical dose of 100 mg-Cl_2/L and an extended reaction period of 48 h **(Table 3)**. The results revealed that chloramine treatment resulted in a considerably high NDMA concentration of 207 and 89 ng/L in the UF-treated and MBR-treated wastewaters, respectively. The high level of formation of NDMA, which occurred as a result of the extended chloramination at a high chloramine dose, is consistent with previous studies (Mitch and Sedlak, 2002; Farré et al., 2011a). High NMOR concentrations of 5–12 ng/L by chloramine was also observed for both treated wastewaters. In contrast, stabilized hypobromite resulted in very small concentrations of NDMA (1–8 ng/L) and NMOR (2.7–2.8 ng/L) for the two wastewaters. The low formation propensity of NDMA by hypobromite has been reported in literature (Luh and Mariñas, 2012), which explains the NDMA formation from DMA by bromine species (e.g., hypobromous acid, stabilized hypobromite ion, and tribromide ion) being over one magnitude lower than the one formed by monochloramine. Overall, the results indicate that pre-disinfection of treated wastewater prior to RO using stabilized hypobromite can form far less NDMA than that using chloramine.

Table 3 – Concentrations of *N*-nitrosodimethylamine (NDMA) and *N*-nitrosomorpholine (NMOR) at dose of 100 mg-Cl_2/L and reaction time of 120 h (temperature of 25 °C and initial pH of 7.0). The data represent the average and range of duplicated formation tests.

	UF (Plant A)		MBR (Plant B)	
	Chloramine	Stabilized hypobromite	Chloramine	Stabilized hypobromite
NDMA (ng/L)	207.0 ± 1.2	7.5 ± 0.5	89.4 ± 2.5	1.4 ± <0.1
NMOR (ng/L)	12.2 ± 0.1	2.7 ± 0.1	4.6 ± <0.1	2.8 ± <0.1

3.3.3 NDMA formation potential

Because NDMA formation can vary considerably depending on the NDMA precursors and their concentrations in treated wastewaters, an investigation of the consistency of stabilized hypobromite in forming less NDMA than chloramine for various waters is important for the viability of the new disinfectant. Thus, NDMA formation tests were conducted with the use of high concentrations of three different NDMA precursors at high chemical doses and extended periods of time (up to 120 h); **Figure 5** shows these results. Throughout the tests, NDMA formation by stabilized hypobromite was 2–5 orders of magnitude lower than that by chloramine. For example, after stabilized hypobromite treatment of DMA-containing solutions, the NDMA concentrations were only up to 4 ng/L (pH 6) and 26 ng/L (pH 8), while the ones after chloramine treatment were 769 ng/L (pH 6) and 1,544 ng/L (pH 8). Similar results were observed with the TMA-containing solutions. Considerable variation in the NDMA concentration was observed with DMBA (tertiary amine)-containing solutions; NDMA concentrations after stabilized hypobromite and chloramine treatment at pH 8 were 2 and 45,318 ng/L, respectively. For both disinfectants, the impact of solution pH on NDMA formation is the same; reactions at a high pH (i.e., pH = 8) yield higher NDMA concentrations than those at a low pH (i.e., pH = 6). Because the NDMA concentration after stabilized hypobromite treatment was consistently low regardless of pH, it can be concluded that the solution pH during stabilized hypobromite treatment is only a minor factor for NDMA formation unlike in the case of chloramine treatment.

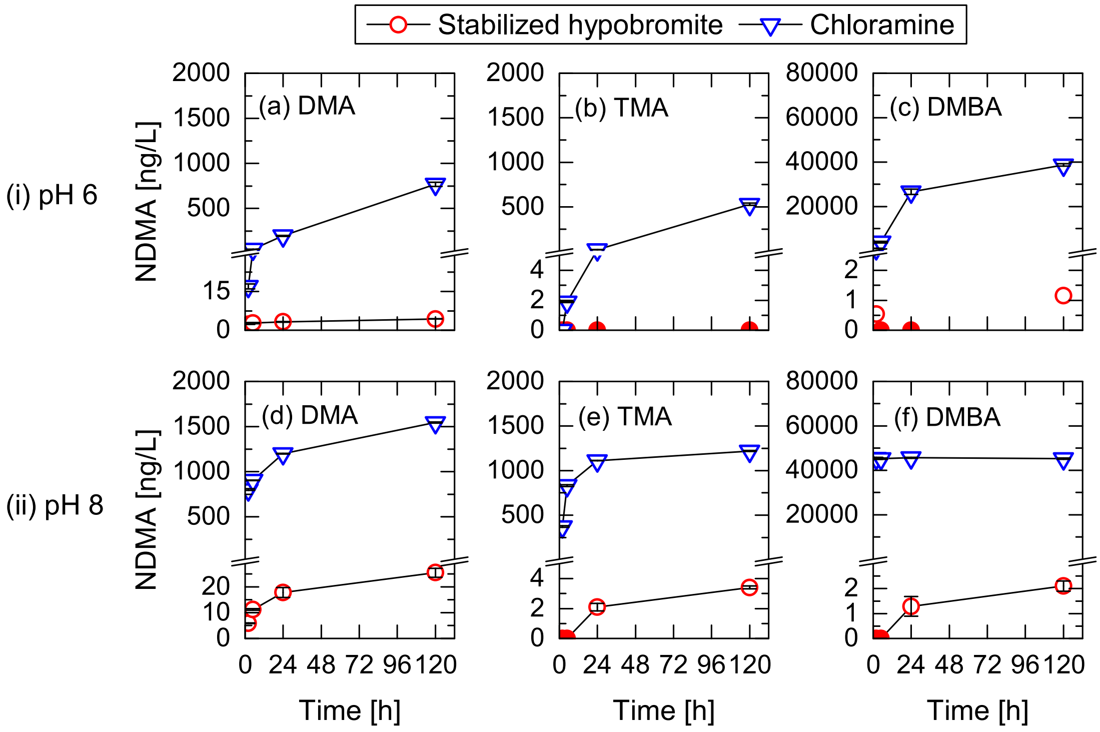


Figure 5 – *N*-nitrosodimethylamine (NDMA) concentrations in artificial wastewater containing 100 μg/L of dimethylamine (DMA), trimethylamine (TMA), or dimethylbenzylamine (DMBA) at solution temperature of 25 °C and solution pH values of (i) 6 and (ii) 8. Chloramine and stabilized hypobromite were dosed at 100 mg/L. Symbols and error bars represent the average and range,

respectively, of duplicated formation tests. Solid circle symbols represent concentrations below the detection limit.

Among the three NDMA precursors, NDMA formation by stabilized hypobromite treatment at pH 8 was higher with the secondary amine (DMA) than with tertiary amines (TMA and DMBA). This result is different from that of chloramine, which showed the highest yield with DMBA. For chloramine treatment, the maximum NDMA molar conversion rates (i.e., NDMA yields) achieved in this study were <2% for DMA and TMA, and approximately 45% for DMBA **(Figure 5)**, which are comparable with the yields reported in the literature (Mitch et al., 2003a; Selbes et al., 2013; Selbes et al., 2018). The variation among the three NDMA precursors can be attributed to the difference in charge. At pH values of 6 and 8, almost all DMA and TMA species are positively charged, whereas most DMBA species are uncharged **(Table 1)**. Amine-based NDMA precursors are more reactive with chloramine in neutral (uncharged) forms (McCurry et al., 2017); thus, a change of NDMA precursors can play an important role in NDMA formation. In contrast, change of NDMA precursors is not an important factor for stabilized hypobromite treatment, although the causes of the higher NDMA formation potential with DMA over TMA and DMBA remained unclear in this study. Overall, the results demonstrated the versatility of stabilized hypobromite treatment for forming negligible amounts of NDMA during water recycling.

4 Conclusions

This study found that pre-disinfection using stabilized hypobromite affords more potent bactericidal effects than that using monochloramine for the same chemical dose, which indicates the high potential of stabilized hypobromite for mitigating biofouling during RO treatment. Among the 13 DBPs evaluated in the study, it was found that the formation of bromoform by stabilized hypobromite was higher than that by chloramine at a high dose of 10 mg/L and reaction time of 5

h. This suggested a need for clarification of the chemical doses required to achieve a membrane fouling mitigation effect similar to that of chloramine. In addition, NDMA formation by stabilized hypobromite treatment in two different types of treated wastewaters was found to negligible and considerably lower than that by chloramine treatment. Further, NDMA formation potential by stabilized hypobromite was 2–5 orders of magnitude lower than that by chloramine. These results suggest the versatility of stabilized hypobromite treatment in terms of forming negligible amounts of NDMA during water recycling.

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