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Impacts of monochloramine as an antifouling agent during nanofiltration (NF) of portable water

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ABSTRACT

In this study, we investigated the potential applicability of monochloramine (MCA) for the control of membrane biofouling using a pilot-scale nanofiltration (NF) process in an advanced drinking water treatment process. It was found that membrane fouling was significantly mitigated and the increase of trans-membrane pressure was retarded more than three folds by the addition of 5 mg/L MCA. The analysis of membrane foulants after the autopsy revealed that the organic content was significantly decreased from 63.1% to 49.1% and most of the microorganisms were inactivated by the addition of MCA. Interestingly, the addition of MCA caused a dramatic decrease in protein compounds in extracellular polymeric substances extracted from biofilms, which hindered the development of dense biofilm structure. The addition of MCA also induced a significant change in the microbial community structures in the biofilm. In the presence of MCA, *Alphaproteobacteria* became the dominant class accounting for 59.8%, while *Betaproteobacteria,* which is the major bacterial community forming the biofilm in the membrane process, was decreased by 31.8%. Based on this study, the addition of MCA was effective in retarding the formation of biofilm on NF membrane surfaces by inactivating microorganisms and weakening the strength of biofilm structures.

Keywords: Biofouling; Nanofiltration (NF) process; Antifouling agent; Monochloramine (MCA); Membrane autopsy; Extracellular polymeric substances (EPS)

1. Introduction

In recent years, membrane technologies have been regarded as the most reliable solution for stable and economic water productions against the water scarcity [1]. By size exclusion, the membrane can efficiently reject the variety of contaminants (e.g., dissolved organic matters, viruses, microorganisms, and ions) from the feed water [2]. However, the accumulation and development of rejected contaminants on the membrane surface or membrane fouling lead to the rapid decline of the permeate flux and salt rejection [3], and thus, are considered as a prevalent issue [4].

Among various kinds of membrane fouling, biofouling that leads to the formation of biofilms on the membrane surface is the most challenging type of fouling in nanofiltration (NF) and reverse osmosis membrane processes [5]. The formation of biofilms includes several stages: attachment of microorganism cells, irreversible adhesion by secretion of extracellular polymeric substances (EPS) from the microorganisms, and development of mature biofilms on the membrane surface [6,7]. During the stages, the secretion of EPS, mostly composed of polysaccharides and proteins, enhances the biofilm matrix stably on the membrane surface and provides chemical resistance to the biofilm [8]. Thus, excessive biofouling results in an increase of energy requirement, a deterioration of the water quality, and frequent chemical cleanings leading to a decreased membrane lifetime [9,10].

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To reduce biofouling, various oxidants have been used as a disinfectant for the pretreatment of membrane feed waters to inactivate microorganisms. Chlorine is commonly used for sterilizing most kinds of microorganisms rapidly as a disinfectant in feed water. However, the high reaction potential of chlorine induces not only the inevitable production of disinfection by-products such as trihalomethanes [11] but also membrane oxidation, which leads to the deterioration of membrane performance [12–14]. Moreover, quenching agents, such as a sodium bisulfate, have to be used to remove the residual chlorine before the feed water enters the membrane process; thus the operating cost is increased by using additional chemicals. In addition, even when almost all the microorganisms are eliminated by the pretreatment, the remaining microorganisms can grow and multiply on the membrane surface [15]. For these reasons, the continuous dosing has been suggested with alternative disinfectants at a low concentration for effective reduction of biofouling on the membrane surface.

Monochloramine (MCA), the most stable form of chloramine, has been recognized as an attractive alternative for antifouling agents in the membrane process [16,17]. Although other chlorine-related chemicals, such as chlorine dioxide, can be used in drinking water treatment for the residual disinfection; it was reported that chlorine dioxide show a greater effect on membrane degradation than MCA [16]. In addition, other alternative disinfectants (e.g., 2,2-dibromo-3-nitrilopropionamide and methylisothiazolinone) have been investigated as antifouling agents [7,18], but these are still not approved for portable water processes due to their residual toxicological problems in ecosystems. According to the potable water guidelines of the U.S. Environmental Protection Agency (EPA), MCA can be used in the treatment of drinking water to control microorganisms, and the potable water can contain chloramine up to 4 mg/L as Cl_2 [19]. Generally, MCA is widely and commonly used as a residual disinfectant to prevent bacterial regrowth and biofilm formation on the pipe walls of distribution systems for full-scale drinking water treatment plants [20–22]. Moreover, several studies have reported that MCA is more effective in penetrating into biofilms compared with chlorine [23,24]. Nevertheless, there are only a few studies reporting on MCA as an antifouling agent to alleviate biofouling at low concentrations (3–5 mg/L) in the membrane process [25,26], and may not provide in detail the effect and mechanism of MCA on the biofilm properties during membrane operations.

In this study, we investigated the impact of MCA on the formation of membrane biofouling and on the physical and chemical properties of the foulants using a pilot-scale NF process in a drinking water treatment. A low concentration of MCA (5 mg/L) was applied as an antifouling agent to avoid excessive membrane oxidation during the operation, and the change in trans-membrane pressure (TMP) was monitored with and without the MCA. After a 35% increase in the TMP compared with the initial TMP, a membrane autopsy was done to characterize the properties of the foulants. Furthermore, the change in properties of the EPS secreted by the microorganisms and microbial communities on the fouled membrane was investigated.

2. Materials and methods

2.1. Pilot-scale NF process and monochloramine disinfection

Two spiral-wound modules of an NF membrane (NF90-2540, Dow/Filmtec, USA) were operated with the fresh water after the coagulation and microfiltration processes. The impact of MCA on the progress of the membrane fouling was performed with and without 5 mg/L of MCA in the influent of the NF process. The flow of the two solutions was controlled with a peristaltic pump, and a static mixer was used for complete mixing before adding the MCA into the influent.

The total effective area of the membrane module was 2.6 m^2 and the permeate flux was set to about 30 L/m^2/h (LMH) during the operation of the pilot-scale NF process by adjusting the TMP with 20% module recovery. Physical cleaning with a cross-flow of 8 L/min was performed for 60 min every 3 d. The temperature of the influent was varied from 10°C to 22°C depending on the season. Therefore, the TMP was calibrated based on 20°C due to the increase of the feed viscosity with the decrease in the influent temperature. After the 30% increase of the TMP compared with the initial TMP, a membrane autopsy was done to characterize the physical and chemical properties of the foulants on the membrane. The influent was taken 1–2 times a week, and the water quality is summarized in Table 1.

2.2. Characterization of membrane fouling

2.2.1. Observation of the fouled membrane

After the membrane modules were unfolded, the membrane sheets were cut into small pieces (2 cm × 2 cm) to examine the surface of the fouled membrane using a scanning electron microscope (SEM) (SU 8230, Hitachi, Japan). Membrane samples were dried in a desiccator for at least 1 d. The dried samples were coated using a platinum ion-sputter coater for 20 s at 20 mA.

Confocal laser scanning microscopy (CLSM) (LSM 880, Carl Zeiss, Germany) was used to investigate the properties of the biofilm on the fouled membrane. The staining of the fouled membrane was done with the LIVE/DEAD BacLight Bacterial Viability kit (L7012, ThermoFisher Scientific, USA). The stain solution was prepared by adding 1.5 μL of SYTO9 and 1.5 μL of propidium iodide solution in 1 mL of 0.9% NaCl solution. Briefly, the membrane samples were rinsed gently with 0.9% NaCl solution to discard unattached microbial cells. After that, 100 μL of the prepared staining solution were dropped onto the membrane samples to stain the live and dead cells. The samples were placed in the dark at room temperature for 30 min. Then, the membrane samples were rinsed with 0.9% NaCl solution again and placed on a glass slide under a coverslip to observe the biofilm using a CLSM equipped with an Argon laser at 488 nm and a DPSS561-10 laser at 561 nm.

2.2.2. Amount of foulants

The total solids (TS) and volatile solids (VS) were determined to assess the amount of foulant on the membrane surface according to standard methods [27]. The foulants were taken from the fouled membrane (800 cm^2) with a silicon

Table 1
Water qualities of the influent for the pilot-scale NF process

Constituent	Influent of pilot-scale NF process
pH	7.0 ± 0.2
Suspended solids (mg/L)	0.8 ± 0.1
Total nitrogen (mg/L as N)	1.7 ± 0.2
Total phosphorus (mg/L as P)	<0.01
Dissolved organic carbon (mg/L)	1.5 ± 0.2
Sulfate (mg/L)	14.4 ± 0.5
Calcium (mg/L)	18.0 ± 1.7
Magnesium (mg/L)	4.9 ± 0.9
Sodium (mg/L)	6.5 ± 0.4
Conductivity (μS/cm)	193 ± 6

spatula. In addition, thermal gravimetric analysis (TGA) (TG209 F1 Libra, Netzsch, Germany) was performed to detect the weight loss of the foulants, which was defined as the organic content, while the temperature was increased up to 1,000°C.

2.2.3. EPS contents of the biofilm

For quantifying the EPS contents in the biofilm, EPS extraction was prepared according to previous studies [6,14]. Briefly, the foulants on the fouled membrane (400 cm^2) were scarped with a silicon spatula and dissolved in 50 mL of 0.9% NaCl. Then, the solution was mixed using a vortex mixer and centrifuged at 12,000 rpm for 10 min. The supernatant was removed softly using a pipette. The precipitants were re-suspended with 10 mL of 0.9% NaCl using a vortex mixer, and the suspension was heated in a water bath at 80°C ± 1°C for 30 min to extract the EPS. Finally, the solution was centrifuged at 12,000 rpm for 10 min again, and the supernatant was collected to analyze the polysaccharides and proteins which are considered as the major compounds of the EPS [8,28]. The contents of polysaccharide-like and protein-like compounds in the biofilm were analyzed with the phenol-sulfuric acid method and the Coomassie (Bradford) Protein Assay kit (Thermo Scientific, USA), respectively.

2.3. Microbial community analysis

The variation of the microbial community between the microorganisms in the influent and on the fouled membrane was evaluated by amplifying their 16S rRNA genes with the FastStart™ High Fidelity PCR system as described in previous research [29]. After the foulants were obtained from the fouled membranes with and without the MCA, the samples were immediately stored at –20°C before DNA extraction. 10 L of influent were filtered through a 0.2 μm pore size filter. Then, DNA was extracted from the filter with a DNA isolation kit (DNeasy® PowerSoil® kit, QIAGEN, Germany) following the manufacturer's instructions. Sequencing was done by a 454 pyrosequencing Genome Sequencer FLX Titanium at a commercial sequencing facility (Macrogen, Republic of Korea).

3. Results and discussion

3.1. Operation of the pilot-scale NF process with monochloramine

Before the operation of pilot-scale NF process, the accelerated oxidation test was performed to assess the potential of the membrane oxidation by MCA dosage. The MCA solution in a concentration of 100 mg/L at pH 7.0 ± 0.1 was used for an accelerated oxidation test. As a result, salt rejection of NaCl and $MgSO_4$ has remained constant during the 28 d (supplementary material, Fig. S1). Therefore, it was determined that the addition of 5 mg/L MCA does not contribute to the membrane oxidation during the operation of pilot-scale NF process. The detailed experiment was described in the supplementary material.

To evaluate the effect of the MCA dosage on the operation of the membrane process, TMP was monitored shown in Fig. 1. As the operation began, the TMP increased quickly for both membrane processes due to the high permeate flux (30 LMH) and the poor pretreatment by the 0.2-micron filtration of the effluent from the coagulation process in the water treatment. During the 10 d, the TMP without the MCA dosage increased by 20% compared with the initial TMP. With further operation, 14 d were needed to reach 35% of the initial flux without the MCA. Even though physical cleaning was performed every 3 d, the increases of the TMP were maintained during the operation. On the other hand, the TMP increases were retarded by the MCA dosage of 5 mg/L during the operation. After 43 d of operation, about 35% of the TMP was reached. It was found that membrane fouling was significantly mitigated by the addition of MCA

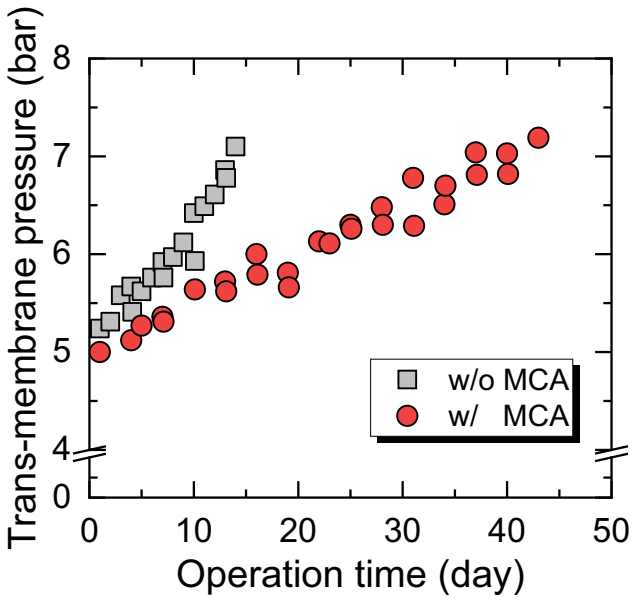

Fig. 1. Change in trans-membrane pressure (TMP) with operation time in the presence and absence of 5 mg/L monochloramine (MCA).

and that the operational time of the membrane process was extended from 14 to 43 d by the MCA dosage. In addition, it was found that the continuous increase of the TMP with the MCA was relieved by the periodic physical cleaning. This result indicates that loose deposits were formed on the membrane surface resulting from the addition of a low concentration of MCA into the influent. To understand the characteristics of the foulants formed on the NF membrane surfaces, the NF membranes were autopsied, and the membrane foulants were analyzed.

3.2. Characterization of the foulants

The fouled membranes were inspected at the membrane surface. SEM images of the deposits on the membrane surface are shown in Fig. 2. Thick deposits were found on both membrane samples, but the morphologies of the foulants were significantly different. Compact cake layers were formed on both fouled membranes; however, scale formation was observed dominantly on the fouled membrane with 5 mg/L MCA (Fig. 2b) compared with the foulants without the MCA (Fig. 2a).

To quantify the amount of foulants deposited on the membrane surface, the total TS and VS were measured (Fig. 3a). Interestingly, it was found that more foulants were formed on the membrane surface when MCA was injected during the membrane operation. The amount of TS per unit area was 516.9 ± 105.9 mg/m^2 with the MCA while it was 311.5 ± 13.7 mg/m^2 without the MCA shown in Fig. 3a. However, the contents of VS in the TS were found to be 70% and 55% without and with 5 mg/L MCA, respectively. As shown in Fig. 3b, the TGA results indicate that the amount of mass changed, which was defined as the organic content, while the temperature was increased up 1,000°C. The decomposition temperature of the organic foulants was from 260°C to 800°C with both foulants obtained from the fouled membrane. Considering the mass changes of the foulants, the organic content in the membrane foulants was significantly decreased from 63.1% to 49.1% with the MCA. Although more foulants were found on the membrane surface with the MCA, the organic content was reduced from 63.1 wt.% to 49.1 wt.%. In terms of organic contents, it can be expected that the addition of MCA oxidizes and inactivates the organic matter such as microorganisms which hinders the development of a biofilm layer on the membrane surface.

3.3. Properites and microbial community of the biofilm structures

Fig. 4a shows the CLSM images for the viability of the microorganisms on the fouled membrane with and without 5 mg/L MCA. The majority of the membrane surface was covered with live cells (stained as green fluorescence) in the absence of MCA while most of the microorganisms

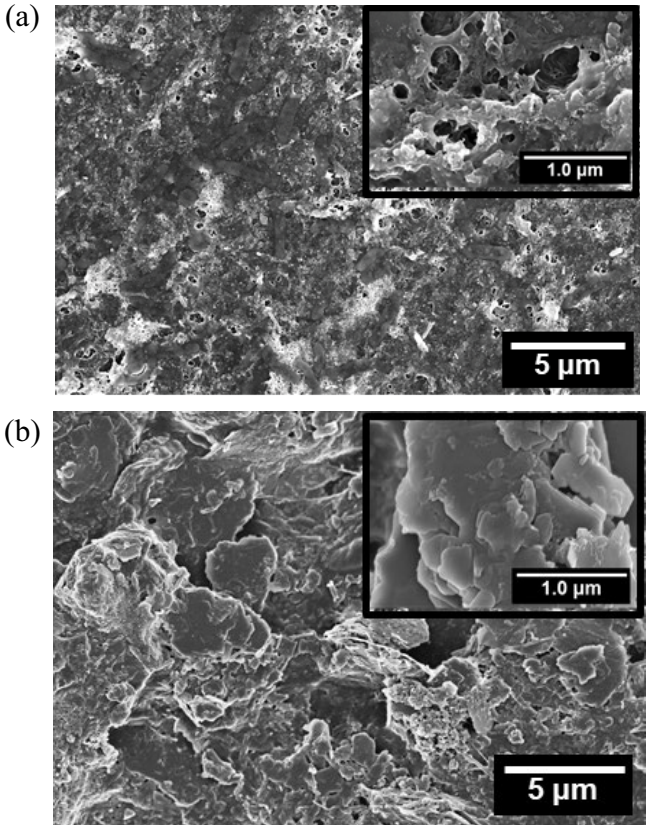

Fig. 2. Scanning electron microscope (SEM) image of the deposits on the fouled membrane (a) without and (b) with 5 mg/L MCA.

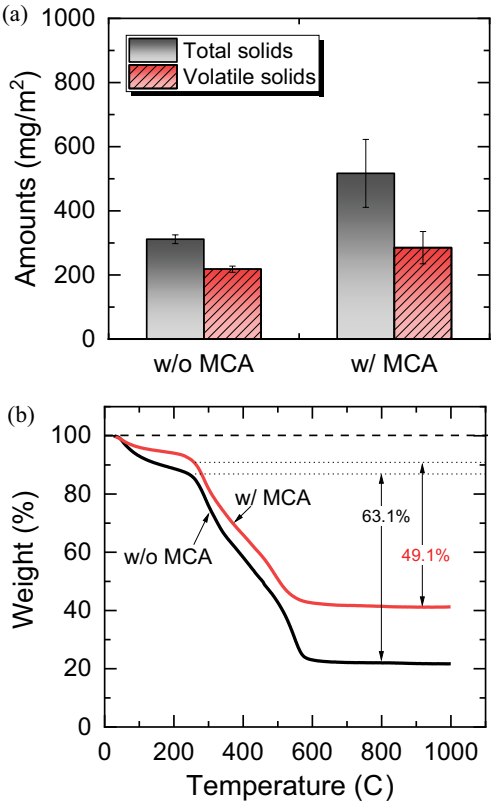

Fig. 3. (a) Amount of total solids (TS) and volatile solids (VS) per unit area of fouled membrane with and without 5 mg/L MCA. (b) Thermogravimetric analysis (TGA) of the foulants obtained from the membrane samples.

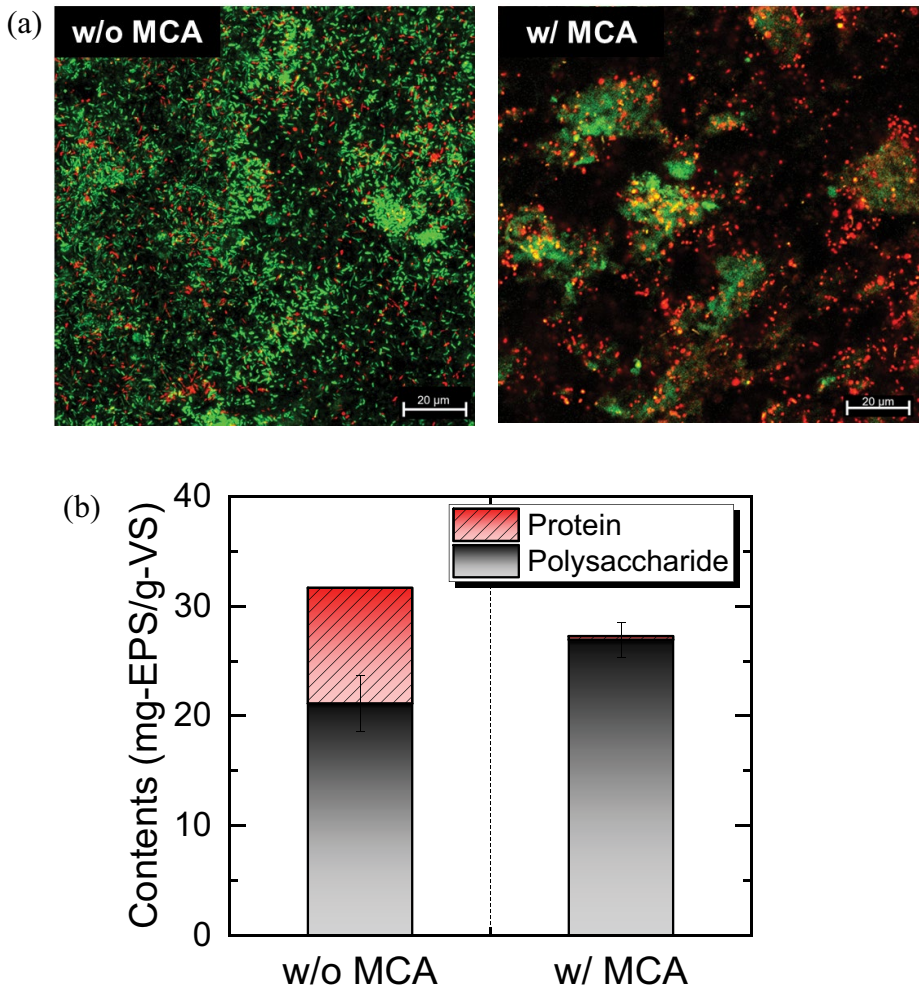

Fig. 4. (a) Impact of the MCA on the viability of the microorganisms on the fouled membrane using CLSM and (b) quantitative and qualitative analysis of the EPS. Note that the cells were stained with SYTO9 (green: live cell) and propidium iodide (red: dead cell).

were inactivated (stained as red fluorescence) when 5 mg/L of MCA was introduced. Moreover, fewer microbial aggregates were found on the membrane surface with the MCA. Considering the operational time of the two NF membranes, it can be concluded that the addition of MCA resulted in a significant mitigation of the biofilm by inactivating the microorganisms. Interestingly, the addition of MCA resulted in a dramatic decrease in protein-like compounds in the EPS which are the primary constituents in biofilms (Fig. 4b). EPS are mostly composed of protein-like and polysaccharide-like EPS leading to cross-linking and the formation of the biofilm. Although the contents of the polysaccharide-like EPS were somewhat increased with the MCA, the protein-like EPS were significant decreased by 97% with the MCA (10.5 ± 0.04 mg/VS) compared to without the MCA (0.33 ± 0.01 mg/VS).

The total contents of the EPS were decreased from 31.7 to 27.3 mg/g-VS with the MCA on the membrane surface. This result is in accordance with the CLSM observation (Fig. 4a), implying that the biofilm was mitigated by the continuous exposures to MCA. Mainly, the addition of MCA resulted in a dramatic decrease in protein-like compounds in the EPS extracted from the membrane biofilms. Yuan et al. [30] reported that protein-like EPS were shown to have crucial roles in embedding cells and forming clusters and further resulted in the quick growth of a biofouling layer; thus, the hindered secretion of protein-like matters in the EPS resulted in a weak and retarded growth of the biofilm which could easily be removed by the applied cross-flow.

The microbial community in the influent and foulants with and without 5 mg/L MCA was analyzed by 16S rRNA gene sequencing. At the phylum level, the most abundant bacteria in the influent were *Proteobacteria* (87.9%), followed by *Bacteroidetes* (9.77%), *Planctomycetes* (1.14%), *Cyanobacteria* (0.83%), *Actinobacteria* (0.15%) and *Firmicutes* (0.01%). Similarly, the *Proteobacteria* was the leading bacteria in both foulants that accounted for 74.0% and 67.2% of the whole microbial community with and without 5 mg/L MCA, respectively (Fig. 5a). *Proteobacteria* was the most abundant in all samples. Interestingly, the abundances of *Actinobacteria* in the foulant with the MCA were significantly higher (13.8%) than that of the case without the MCA (0.03%). At the class level of the *Proteobacteria* (Fig. 5b), *Betaproteobacteria* was detected as the dominant

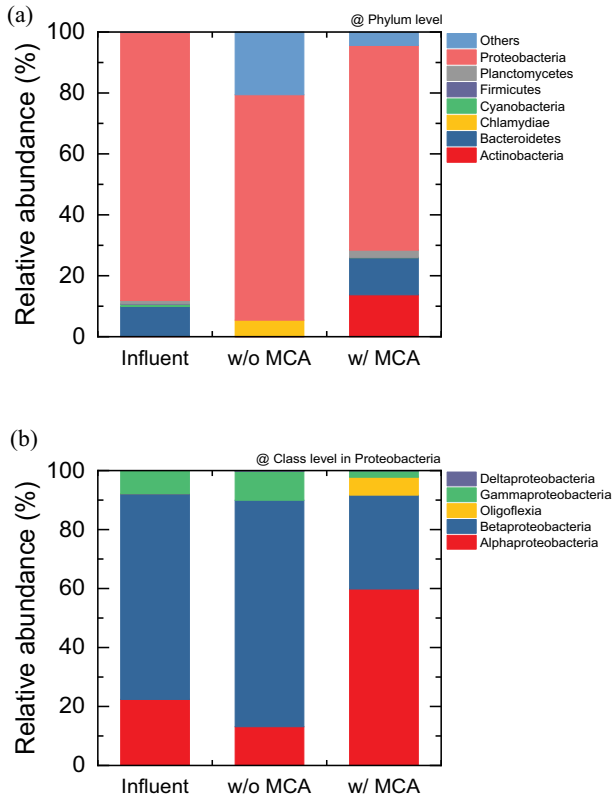

Fig. 5. Microbial community structures in the influent and foulants with and without 5 mg/L MCA shown by 16S rRNA gene sequencing at the (a) phylum level and (b) class level in *Proteobacteria*.

microorganism in the influent and the foulants without the MCA, accounting for 69.8% and 76.8%, respectively. However, in the foulant with an MCA dosage of 5 mg/L, the relative abundances of *Alphaproteobacteria* became the dominant class, accounting for 59.8%, while the relative abundances of *Betaproteobacteria* were decreased by 31.8%. A previous study reported that the microbial portion of *Alphaproteobacteria* in the foulants was increased by the chemical cleaning and the duration of the experiments [31]. It might be implied that *Alphaproteobacteria* has chemical resistance than that of *Betaproteobacteria*. In addition, the relative abundance of *Oligoflexia* (6.07%) was observed as the third abundant microorganism in the foulant with the MCA, although *Oligoflexia* in the influent only occupied 0.08%.

These results show that the addition of MCA induced a significant change in the microbial community structures of the foulants on the NF membrane. Especially, the relative abundance of *Betaproteobacteria* (*Proteobacteria* phylum), which is considered as a major bacterial community forming the biofilm in the membrane process [32,33], was dramatically reduced by the MCA dosage of 5 mg/L. In terms of the EPS, the remaining microorganisms after chlorine disinfection might secrete more EPS to protect themselves on the membrane surface [34]. In the present study, although the polysaccharide-like EPS in the biofilm with the MCA were somewhat increased (Fig. 4b), the MCA reduced the protein-like EPS in the biofilm by 97%.

4. Conclusions

In this study, a pilot-scale NF process was operated to investigate the potential applicability of MCA for the control of membrane biofouling. The continuous dosing of 5 mg/L MCA extended the operation time of the NF process more than three folds without any noticeable damage in NF membrane performance. The analysis of biofilm components exhibited that the addition of MCA was effective in retarding the formation of biofilm by inactivating microorganism and weakening the strength of the biofilm structures. Especially, 97% of the protein-like compounds were reduced in the presence of MCA, and the microbial community structures in the biofilm were significantly altered by 5 mg/L of MCA. On the basis of results, continuous dosing of MCA can be suggested as the effective and economical strategy to control the membrane biofouling, and thus, to increase membrane life by reducing the frequency of the chemical cleaning.

Acknowledgments

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Supplementary information:

Accelerated oxidation test

Accelerated oxidation test was performed with monochloramine (MCA). 100 mg/L MCA was used for the test and made by 0.2 M sodium hypochlorite and ammonium chloride solution. The pH of MCA solution was adjusted by 0.1 M HCl at 7.0 ± 0.1. Membrane coupons, cut from virgin spiral-wound modules, were exposed to MCA for 1, 3, 7, 14, and 28 d. After the MCA exposures, the salt rejections were measured with 500 mg/L NaCl and 2,000 mg/L $MgSO_4$ as a feed solution, respectively.

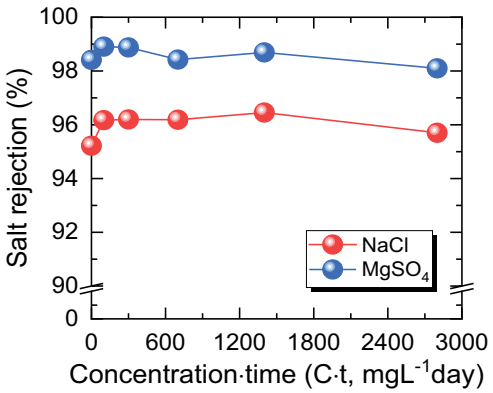

Fig. S1. Change of salt rejection after MCA exposures on the NF membrane. The applied pressure was 5 bar for the filtration test. The other conditions were as follows: 10 cm/s cross-flow velocity, feed water temperature of 23°C ± 1°C.