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Effect of chlorine dioxide (ClO_2) on polyamide-based RO membrane for seawater desalination process: exposure to high concentration of ClO_2

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ABSTRACT

The most popular disinfecting agents used for biofouling control in the reverse osmosis (RO) system include oxidizing biocides such as chlorine, chloramines and chlorine dioxide. Among them, chlorine (Cl_2) is a traditional water disinfecting agent of choice, and it has been used effectively in cellulose acetate membrane systems. However, it has been informed that chlorine causes an irreversible deterioration on polyamide RO membranes in a very short time. As an alternative sanitizing agent, chlorine dioxide (ClO_2) is gaining interests in many disinfect processes including membrane systems, due to its different chemistry and reactivity to chlorine. In this study, therefore, the applicability assessment of chlorine dioxide in seawater reverse osmosis process was performed. Permeate flux, salt rejection and membrane structural analyses were conducted as membrane performance indicators after exposure to chlorine and chlorine dioxide. The results showed that chlorine dioxide-exposed membrane showed very excellent performance in terms of permeate flux and salt rejection, whereas chlorine-exposed membrane showed unstable permeate flux fluctuation and lower salt rejection with increasing time of exposure to chlorine in the soaking bath. From the attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) results of chlorine-exposed membrane showing severe peak intensity decreases under chlorine existence and energy-dispersive X-ray spectrometer (EDS) results of increased chlorine atom ratio, it is suggested that flux fluctuation is a result of molecular structure deformation; chlorination. However, chlorine dioxide-exposed membrane is shown not to chlorinate but to modify polyamide structure, as shown by the results of ATR-FTIR and scanning electron microscopy/EDS analyses and permeate inclination aspect.

Keywords: Chlorine; Chlorine dioxide; Chlorination; Polyamide RO membrane

1. Introduction

Reverse osmosis (RO) is one of the most advanced technologies that has been widely used for seawater desalination, wastewater reclamation and reclaimed water reuse due to its efficient energy consumption and safe operating process [1,2]. However, the membrane fouling (especially biofouling) phenomenon, which deteriorates membrane performance (i.e., permeate flux or salt rejection) and shortens membrane life expectancy, could occur by various foulants in feed water [3–6]. Therefore, to minimize the deterioration caused by fouling, the adequate pretreatment process and membrane cleaning must be carried out to remove foulants from feed water and membrane surface. Biofouling, one of the most severe fouling phenomena, cannot be reduced by pretreatment alone, because deposited microbial cells can grow, multiply and relocate [7]. Therefore, disinfecting agent should be added to the seawater reverse osmosis (SWRO) process in order to prevent biofouling on RO membrane surface. The most popular disinfecting agents used for biofouling control in the RO system include oxidizing biocides such as chlorine, chloramines and chlorine dioxide [8].

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Among them, chlorine (Cl_2), a strong oxidizing agent, is a traditional water disinfecting agent of choice, and it has been widely used effectively in cellulose acetate membrane systems because of its characteristics; toxicity to microorganisms in water, stable usage and low cost [9].

However, it has been informed that chlorine can also lead to the formation of undesired disinfection by-products (DBPs) by reacting with natural organic matter and the halogen species in water [10,11]. Moreover, recently validated ‘stage 1 and 2 disinfectant and disinfection by-products rules (US EPA, 2006)’ strictly regulates various DBPs including the total Trihalomethanes and Haloacetic acids [12].

Besides unreliable RO permeate from harmful DBPs, there is significant possibility of failure of RO performance by chlorine. It has been proved that even a low concentration of free chlorine deteriorates the polyamide membrane, deforming the amide functional group, thereby resulting in irreversible decrease in permeate flux during long-term operation [13–15]. Normally, it is considered that the degradation of polyamide membranes mainly includes N-chlorination by substituting the hydrogen on amide nitrogen first, followed by ring-chlorination via an intermolecular rearrangement called Orton rearrangement [13]. The structural changes of polyamide by chlorine degrade membrane performances resulting in decrease in permeate flux and salt rejection and membrane life-shortening [16,17]. For these reasons, other alternative disinfectants are needed for the biofouling control in RO membrane process.

As an alternative disinfecting agent, chlorine dioxide is gaining interests in many disinfect processes including membrane systems, due to its different chemistry and reactivity to chlorine; only one-fourth chlorine dioxide dosing is required to maintain equivalent chlorine dosage. In addition, chlorine dioxide concentrations of <1.0 ppm were found to be much less damaging to the membrane than for chlorine, and it is assumed that chlorine dioxide is known to produce less DBPs with organic matter as compared with chlorine [9].

In spite of its inherent advantages, chlorine dioxide has not yet been fully studied in SWRO desalination application. In order to apply chlorine dioxide disinfection to actual SWRO process, however, the operation data, such as results of membrane performance test (i.e., permeate flux or salt rejection), are needed to be accumulated and analyzed. Thus, in this study, chlorine dioxide (ClO_2) was examined to determine whether it can be used as alternative disinfectant in RO pretreatment process.

2. Materials and methods

2.1. Preparation of disinfectants

Both disinfectants, sodium hypochlorite (NaOCl) and chlorine dioxide (ClO_2) solution, were preserved in a refrigerator under a 4°C shading condition to alleviate natural decomposition, which is accelerated with light and high temperature. To avoid error on dosing the disinfectant, the concentration of both chemicals was measured right before application. The *N*,*N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method (spectrophotometer DR-6000, Hach, USA) was used to measure both the concentration of total chlorine as well as that of chlorine dioxide, and it was conducted at least 20 min before using disinfectants. To suppressed interferences from other chlorine species, glycine was added prior to addition of DPD reagent [10].

2.2. RO membrane

The RO membrane for the lab-scale experiment was determined depending on commercialized RO membranes for seawater desalination. The RO membranes (RE2521-SHN, Toray Chemical Korea Inc., Seoul, Korea), each size measuring 128.35 cm^2 were cut into flat sheets and preserved with 3% sodium bisulfite ($NaHSO_3$) solution at 4°C prior to the experiments. Then the membrane was moved to deionized water for 1 d before being assembled on the membrane cell.

2.3. Lab-scale RO membrane filtration system

Fig. 1 describes the schematic diagram of a lab-scale RO membrane filtration system. Membrane performance was

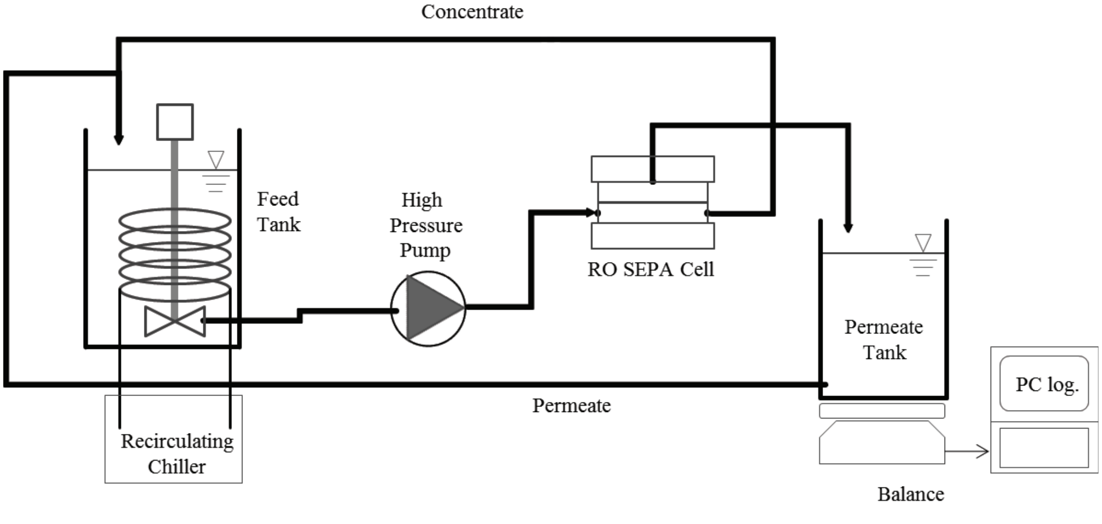


Fig. 1. Schematic illustration of lab-scale RO membrane filtration system.

evaluated with a commercial bench-scale cross-flow filtration unit, a stainless steel SEPA CF membrane element cell was used in this study. The lab-scale RO membrane filtration system was prepared, which included a recirculating chiller for maintaining constant feed water temperature, bypass valve for satisfying general operating pressure requirements and damper for stable flow circulation. The lab-scale RO system was made up of marine grade 316 stainless steel, which has strong corrosive durability to oxidizing exposure. 15 L of feed water were prepared right before every experiment cycle and feed water goes into SEPA cell through the pipeline and pressurizing with high-pressure pump (D/G-03-S, Hydra-Cell, USA). The concentrate coming out from membrane cell flow back to the feed tank and permeate water is stored at permeate tank whose weight is measured by electric balance (FX-3000i, AnD, USA). The electrical conductivity meter (Orion 013005MD, Thermo Electron Corp., USA) was used to measure NaCl concentration in the feed and permeate water. Experiments were run under following operation conditions: the feed flow rate of 3 ± 0.3 L/min, operating pressure of 4 ± 0.5 MPa and temperature of 25.0°C ± 1.0°C. At first, the membrane was assembled on the membrane cell and then operated with deionized water for 20 min of base circulation under 7 bar at 4 LPM to remove air bubbles in the pipeline, and 20 min more under target pressure and flow rate for acquiring stable flux data. The permeate flux and salt rejection were measured with data from the electrical balance and electrical conductivity meter by following Eqs. (1) and (2):

$$\text{Permeate flux}\left(\frac{\text{L}}{\text{m}^2\times\text{hr}}\right)=\frac{\text{volume of permeate}}{\text{effective membrane area}\times\text{time}} \quad (1)$$

$$\text{Salt rejection (\%)}=\left(1-\frac{\text{conductivity of permeate}}{\text{conductivity of feed solution}}\right)\times 100 \quad (2)$$

2.4. Protocols for membrane performance measurement

Membrane performance tests were conducted using lab-scale cross-flow RO system. Once the virgin membrane was assembled in the membrane cell, the performances (i.e., permeate flux and salt rejection) were measured with 35,000 mg/L of NaCl solution. After measurement of virgin membrane performance, membrane taken out from membrane cell was soaked in 100 ppm sodium hypochlorite (NaOCl) or chlorine dioxide (ClO_2) solution. Exposure time lasted for 1, 2 and 3 h in the dark at 25°C. After exposures, each membrane was completely rinsed with deionized water and assembled in the membrane cell again. The RO membrane system with chlorine- or chlorine dioxide-exposed membrane was operated 2 h, and the membrane performances were measured. After each experimental cycle, small coupons of the RO membrane were conserved for membrane surface analysis, such as attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy/energy-dispersive X-ray spectrometer (SEM/EDS).

2.5. Membrane surface characterizations

To identify membrane characteristics, the RO membrane surfaces were analyzed by ATR-FTIR (Nicolet iS50, Thermo Fisher Scientific Instrument, Madison, WI, USA) and field-emission SEM/EDS (FE-SEM/EDS; JSM-7600F, JEOL Inc., Tokyo, Japan). ATR-FTIR was used to identify the molecular functional group of membrane. Spectral range and wave number accuracy was 7,800–50 cm^{-1} and 0.09 cm^{-1}, respectively. Atomic constitutions of membrane were observed with FESEM/EDS. The voltage controlled for analysis has 15 kV (resolution: 1.0 nm), which offering high spatial resolution. The average working distance was 8.4 nm. For the membrane surface analysis, each membrane was either soaked in 100 ppm sodium hypochlorite (NaOCl) or chlorine dioxide (ClO_2) solution for 3 h under a 25°C shading condition. After exposures, all membranes were rinsed with deionized water and dried in desiccator for 4 d before surface analysis.

3. Results and discussion

3.1. RO membrane performance

Normalized permeate fluxes of chlorine dioxide- and chlorine-exposed membranes in the cross-flow system with time are shown in Figs. 2(a) and (b), respectively.

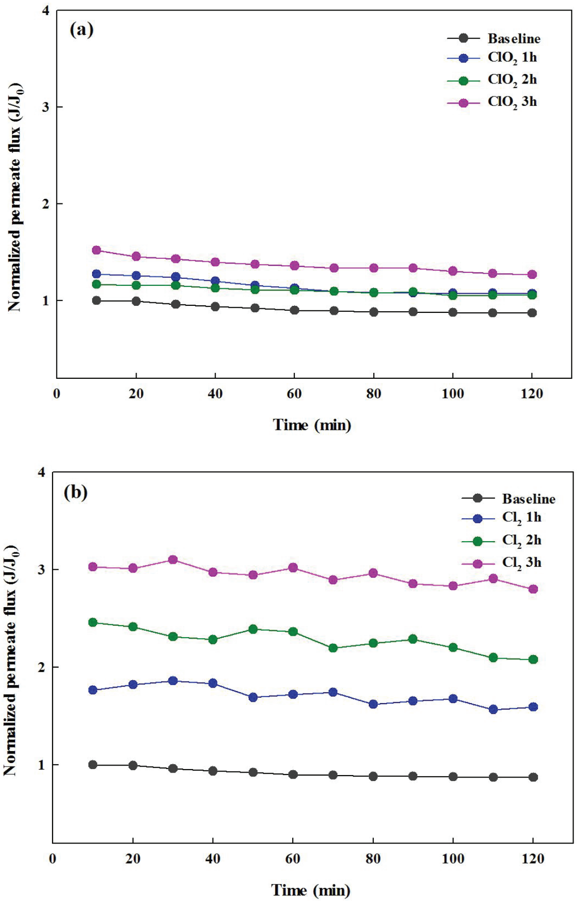


Fig. 2. Normalized permeate flux of (a) chlorine dioxide-exposed membranes in comparison with (b) chlorine-exposed membranes. Each membrane was either soaked in 100 ppm chlorine dioxide or sodium hypochlorite for 1, 2 and 3 h. (feed flow rate: 3 ± 0.3 L/min, operating pressure: 4 ± 0.5 MPa, temperature: 25.0°C ± 1.0°C).

As shown in Fig. 2(a), the normalized permeate flux of chlorine dioxide-exposed membranes was in a similar manner with the virgin membrane. On the other hand, a significant flux increased, and unstable fluctuation were observed in the case of chlorine-exposed membrane (Fig. 2(b)). In addition, it is investigated that longer chlorine exposure time induced permeate flux to be increased. It was assumed that increased permeate flux was due to reduced cross-linking density of the polymer matrix, as suggested by decline in tensile strength of the polyamide layer [18,19]. It was also suggested that increased permeate flux was attributed to increased membrane surface hydrophilicity [20,21]. According to previous studies, membrane surface hydrophilicity is influenced by physicochemical characteristics of the membrane surface [22–24].

Salt rejection results of chlorine- and chlorine dioxide-exposed membrane are shown in Fig. 3. Chlorine dioxide-exposed membrane showed outstanding rate of salt rejection, whereas that of chlorine-exposed membrane showed poor performances with increasing concentration of chlorine in the soaking bath. The salt rejection of chlorine dioxide-exposed membrane showed >96% (Fig. 3(a)), while the salt rejection of chlorine-exposed membrane (300 ppm h) was greatly decreased after 2 h (Fig. 3(b)). A noticeable decrease in chlorine-exposed membrane salt rejection should be attributed to the conformational deformations of polyamide chains. The partial destruction of polyamide rigid structure caused conformational changes of the polymer chains, such as the increase of free volume and flexibility, resulting in larger salt passage through membrane [14]. Increased salt passage upon chlorine-exposed membrane was consistent with membrane surface damage as shown in Fig. 4(c).

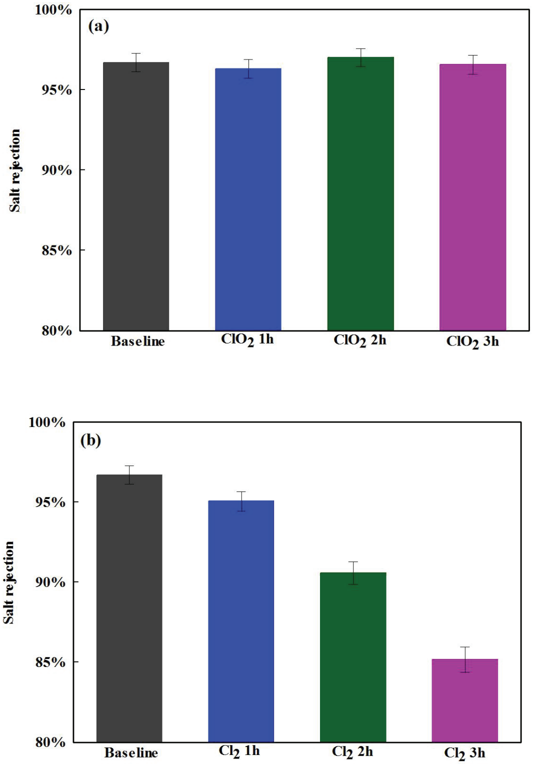


Fig. 3. Salt rejection of (a) chlorine dioxide-exposed membranes in comparison with (b) chlorine-exposed membranes. Each membrane was either soaked in 100 ppm chlorine dioxide or sodium hypochlorite for 1, 2 and 3 h (feed flow rate: 3 ± 0.3 L/min, operating pressure: 4 ± 0.5 MPa, temperature: 25.0°C ± 1.0°C).

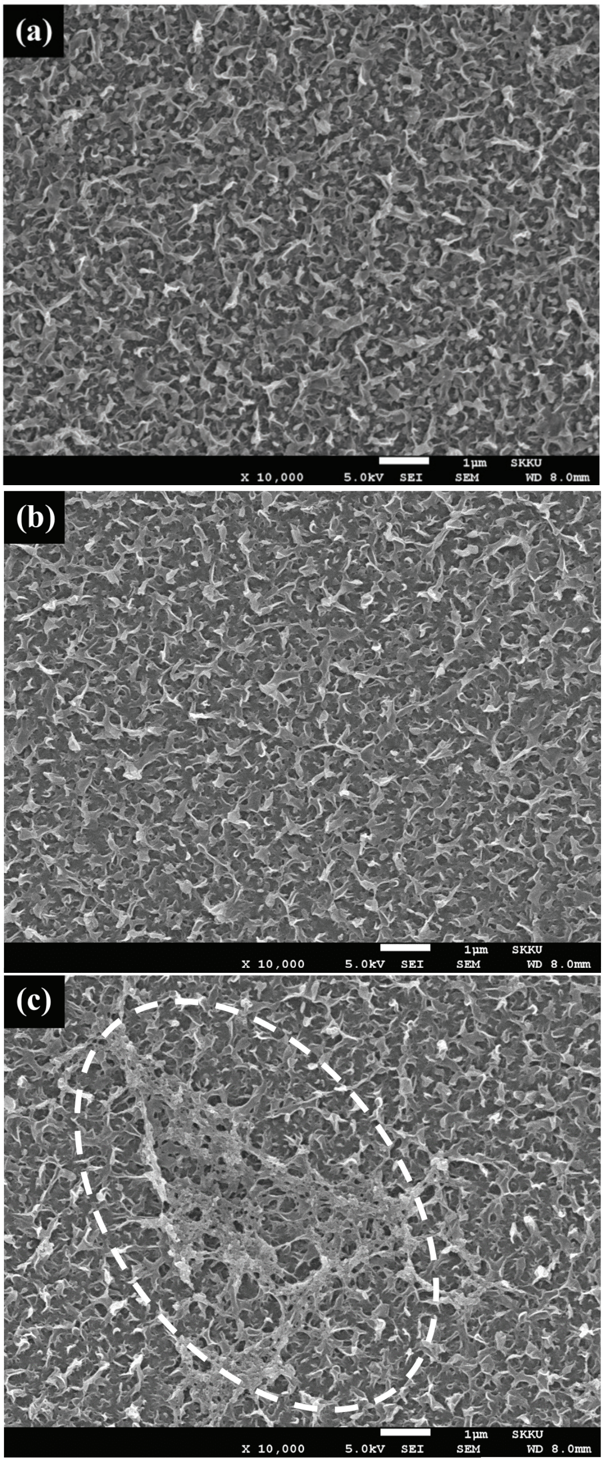


Fig. 4. 10,000× magnified, SEM images of RO membrane surface: (a) virgin, (b) chlorine dioxide-exposed membrane and (c) chlorine-exposed membrane exposure to 100 ppm chlorine dioxide or sodium hypochlorite solution for 3 h. An area of evident membrane surface degradation is circled in white.

3.2. ATR-FTIR characteristics of the RO membrane

ATR-FTIR detects bonds between atoms in a molecule and can, thus, provide information about functional groups and the chemical structure of the membrane [21]. Thus, by comparing a certain peak or its intensity between a virgin sample and treated one, a modified molecular structure can be identified, especially when chemical modification had occurred. The typical spectrum of virgin RO membrane is shown in Fig. 5. The region I at wave number in 3,444 and 3,310 cm^{-1} presents the stretching vibration of the NH group including bands, which are corresponded to free and hydrogen-bonded N–H stretching modes, respectively [14,25]. The wave numbers of 1,667 cm^{-1} (region II) and 1,542 cm^{-1} (region IV) indicating amide I (C=O) and amide II (N–H, N–C) modes in secondary amides. A small but well resolved peak at 1,610 cm^{-1} in region III indicates the hydrogen-bonded carbonyl of the amide [14,26,27].

Fig. 6 shows ATR-FTIR spectrum of the membranes exposed to chlorine and chlorine dioxide solutions (300 ppm h), respectively. As shown in Fig. 6(a), the peak around 3,310 cm^{-1}, which was corresponding to a hydrogen bond in N–H group, changed remarkably after disinfectant exposed. A gradual decrease of the peak intensity was consistent with the reduced hydrogen bond. According to Fig. 6(b), a remarkable peak intensity change was observed. Chlorine-exposed membrane cases show more reduced amide I and amide II band than that of chlorine dioxide-exposed cases. Although the spectrum of chlorine dioxide-exposed membrane was also slightly changed, the differences were much less than that of chlorine-exposed membrane. The shift of amide I and the disappeared peak at 1,610 cm^{-1} both indicated that hydrogen bonds between C=O and N–H were destroyed or weakened. By the same reasons, the peak of amide II even buried due to too much shift to lower frequency [14,17]. All these results suggested that molecular bonds in amide group were modified due to attachment chlorine to the polyamide chains, of which previous studies defined that kind of membrane property modification [14].

3.3. SEM/EDS characteristics of the RO membrane

The SEM/EDS analysis was conducted to identify morphological change in membrane surface and atomic constitution. Fig. 4 shows the SEM images under the magnification of 10,000 times of virgin and disinfectant-exposed membrane. As shown in Fig. 4(b), the SEM images of chlorine dioxide-exposed membrane, which is not observed the membrane surface damaged area. It implies that chlorine dioxide exposure rarely affects morphological change in membrane surface. On the other hand, the SEM images of chlorine-exposed membrane (Fig. 4(c)) show that it present the white circled area on the membrane, which provides evident of membrane surface degradation by chlorine.

EDS results showed noticeable differences between chlorine- and chlorine dioxide-exposed membrane, and the results are summarized in Table 1. Compared with chlorine amount of virgin membrane constitution (0.09%), chlorine dioxide-exposed membrane cases did not increase chlorine atom ratio support that chlorine dioxide does not chlorinate amide structure. On the other hands, chlorine-exposed membrane cases increase the chlorine atom ratio. It was assumed that such increased chlorine amount of membrane by chlorine exposure was a typical result of chlorination.

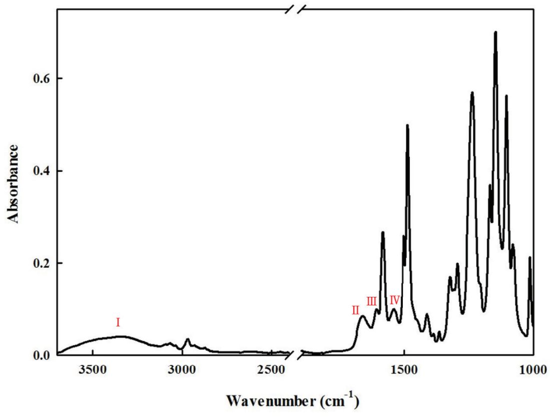
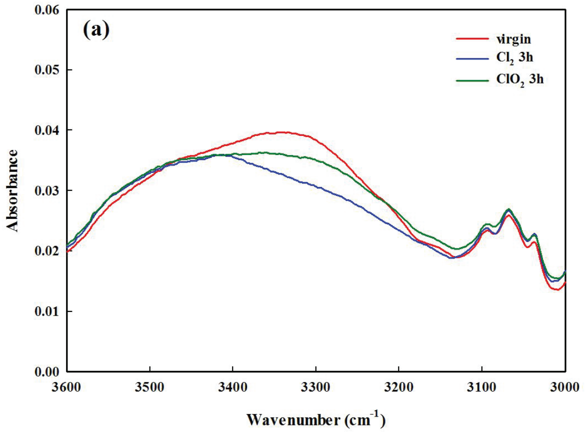


Fig. 5. ATR-FTIR spectrum of a virgin polyamide RO membrane.



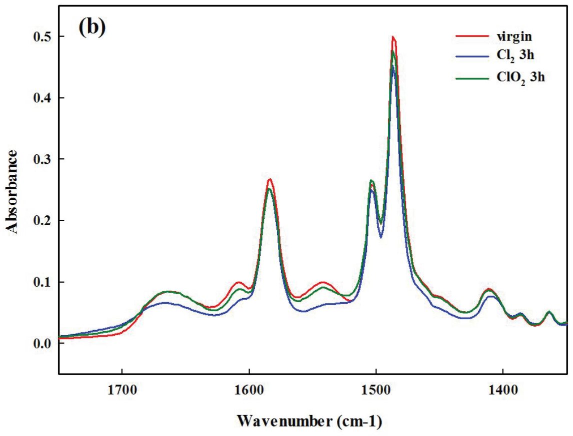


Fig. 6. ATR-FTIR spectrum of chlorine dioxide-exposed membrane in comparison with chlorine-exposed membrane. Each membrane was exposed in 100 ppm sodium hypochlorite or chlorine dioxide solution for 3 h. (a) The range of wave number is from 3,600 to 3,000 cm^{-1} and (b) the range of wave number is from 1,750 to 1,350 cm^{-1}.

Table 1
EDS analysis of disinfectant-exposed membrane

Disinfectant/exposure time	Virgin	Cl_2/1 h	ClO_2/1 h	Cl_2/2 h	ClO_2/2 h	Cl_2/3 h	ClO_2/3 h
CT* value (ppm h)	0	100	100	200	200	300	300
C (atomic %)	84.68	84.88	85.48	85.13	84.02	84.97	84.55
O	12.76	12.89	11.65	12.09	12.16	12.48	12.38
S	2.47	2.11	2.82	2.64	3.13	3.02	3.00
Cl	0.09	0.12	0.05	0.14	0.08	0.14	0.07

* It means the product of the concentration of a disinfectant and the contact time with the water being disinfected.

4. Conclusions

This study focuses on the effect of chlorine dioxide used for an alternative disinfectant agent on SWRO membrane process. Several experiments were conducted to observe polyamide RO membrane performance change under different disinfectant exposure. In addition, ATR-FTIR and SEM/EDS analyses were conducted to identify membrane structural change on disinfectants exposure. Following conclusions are drawn from the experimental results: in the case of chlorine-exposed membrane, chlorine solution has a negative effect on permeate flux and salt rejection. From the ATR-FTIR results showing severe peak intensity decreases under chlorine existence and EDS results of increased chlorine atom ratio, it is suggested that flux fluctuation is a result of molecular structure deformation; chlorination. However, chlorine dioxide-exposed membrane showed excellent results in terms of permeate flux and salt rejection. Based on the ATR-FTIR results, chlorine dioxide influences similar peaks that were distinctively deformed by the chlorine, but the peak changes are relatively moderate. In addition, From the EDS results showing that chlorine constitution was not significantly changed after exposure to chlorine dioxide, it could be concluded that chlorine dioxide does not chlorinate amide structure.

This study shows the applicability of chlorine dioxide as an alternative disinfectant agent in SWRO membrane process.

Acknowledgments

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