Effective Biofouling Control Using Periodic H$_2$O$_2$ Cleaning with CuO Modified and Polypropylene Spacers

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Ⓢ Supporting Information

ABSTRACT: Feed spacer biofouling is a major challenge in membrane processes such as nanofiltration and reverse osmosis. The bubbling of gas using air can be effective in partially controlling biofouling, but additional chemical control is still needed, and pressurized air systems can be difficult to integrate into existing systems. A simpler approach that combines both bubbling and cleaning was developed here on the basis of intermittently adding a low concentration hydrogen peroxide (H$_2$O$_2$) to the feedwater. With periodic dosing (every 12 h) of 0.3% (w/w) H$_2$O$_2$, no detectable biofouling occurred after 10 days of operation, while biofouling was evident without H$_2$O$_2$ dosing. A single dose of 0.3% (w/w) H$_2$O$_2$ to prefouled spacers and membranes rapidly reduced biofouling, with decreased feed channel differential pressures of 69% (CuO spacer) and 54% (polypropylene spacer). The control of biofouling mainly resulted from bubble production when H$_2$O$_2$ dissociated to shear biofilms off the spacers. Using a CuO spacer did not impact biofouling, suggesting that additional cleaning based on hydroxyl radical formation via Fenton-reaction was not necessary. The use of H$_2$O$_2$ alone had the combined advantages of physically shearing off biofilms from spacers and chemically killing bacteria, while providing a low cost approach for biofouling control in membrane-based desalination processes.

KEYWORDS: Membrane desalination, Biofouling, Bubble cleaning, Feed spacer, Hydrogen peroxide, Membrane fouling simulator
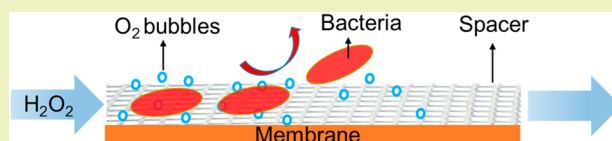
INTRODUCTION

Biofouling is a major challenge for long-term operation of nanofiltration and reverse osmosis desalination plants.[1,2] Bacteria and other biologically produced foulants are ubiquitous in membrane feed streams, and thus biofouling inevitably reduces desalination performance over time.[3,4] Bacterial growth on membranes and spacers can produce large increases in the feed channel differential pressure, which can reduce the water flux and overall efficiency of the water treatment plant.[5] Studies have shown that bacteria in the feed stream readily attach to the feed spacer, resulting in biofouling of the feed spacers and membranes.[6] Therefore, controlling feed spacer biofouling is critical for the efficient operation of nanofiltration and reverse osmosis membrane processes.

Chemical modification of spacers has been widely studied for biofouling control, although these treatments only delay but do not prevent biofouling. Greatly modifying surface hydrophilicity can decrease bacteria attachment.[7] For example, plasma polymerization of diethylene glycol ether on polypropylene spacers reduced feed spacer biofouling primarily due to the increase in spacer hydrophilicity.[5] However, increasing spacer hydrophilicity using a coating of polydopamine also only delayed bioaccumulation in the feed channel.[8] Immobilizing biocidal particles on the spacer, such as silver and copper, is another approach for controlling biofouling.[6,9] A higher percentage of dead bacteria was observed on membrane elements containing silver nanoparticles deposited on spacers, indicating a strong biocidal effect from silver.[9] A copper coating on the feed spacer also reduced the adhesion of extracellular polymeric substances.[6] While these approaches delayed biofouling,[5] no significant reduction in biofilm formation was observed over a more extended operation time,[10] suggesting active periodic cleaning was still needed using these biofouling control approaches.

Active physical and chemical cleaning are more effective methods, compared to passive chemical modification, for
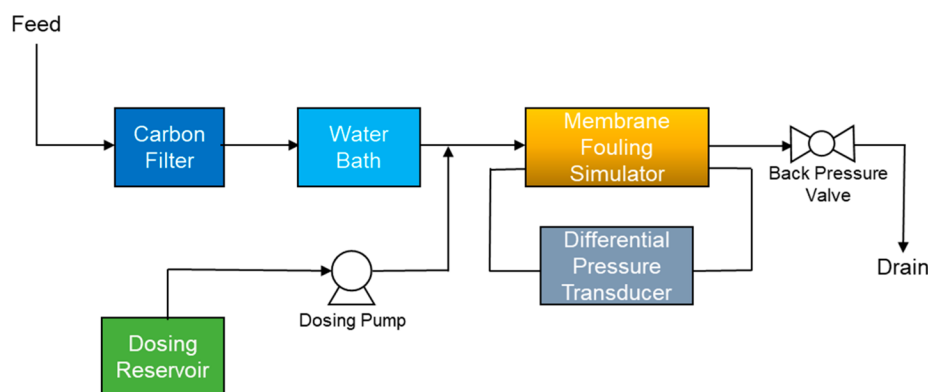
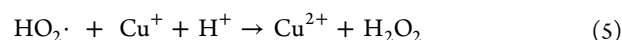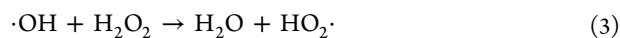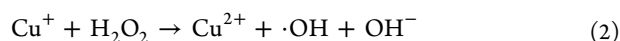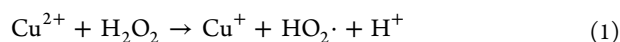**Figure 1.** Testing scheme of spacer biofouling in membrane fouling simulators.

controlling feed spacer biofouling in membrane systems. The addition of air bubbles directly into the feed stream can be an effective method to shear biofilm off membranes and spacers.[11−13] Daily cleaning of a spiral wound membrane element with feed stream at a ratio of water/air of 1:2 for 1 h resulted in only a 37% increase in feed channel differential pressure over 110 days, while more sporadic air/water cleaning resulted in a 120% increase in only 21 days.[13] Chemical cleaning is also used to enhance biofouling control. Addition of biocidal copper sulfate with daily air/water cleaning resulted in only an 18% increase in the feed pressure after 110 days, compared to a 60% increase with only air/water cleaning.[14] While a combined air bubble and copper sulfate cleaning approach can be useful, these methods have drawbacks. Dosing air into feed stream requires a complete additional system to add the air into the membrane system, which could make it difficult to integrate into existing membrane desalination plants. Dosing copper sulfate is effective, but the presence of toxic copper sulfate in the effluent would be a large environmental concern and likely difficult to implement for discharges into aquatic systems.[15]

Periodic dosing of a low concentration of hydrogen peroxide was investigated here as an inexpensive biofouling controlling strategy to provide both gas bubbles and a transient disinfectant. Hydrogen peroxide is commonly used as a disinfectant, but the generation of gas bubbles as a part of this process has not been previously addressed for membrane or spacer cleaning. The addition of a soluble chemical into a feed stream would be a much easier method of generating bubbles, and hydrogen peroxide has the additional advantage of being a strong oxidant that has long been used in water treatment.[16,17] Hydrogen peroxide can react rapidly with membrane proteins of bacterial cells, thus reducing cell integrity and killing the bacteria,[17] and it eventually degrades to oxygen and water and therefore it produces no toxic byproducts.[18] To improve the effectiveness of H_2O_2, we also examined the use of metal oxides in the system. For example, copper oxide can be used to produce hydroxyl free radicals via the Fenton reaction,[19,20] as shown in the following reactions

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + HO_2\cdot + H^+ \tag{1}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + \cdot OH + OH^- \tag{2}$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot \tag{3}$$

$$HO_2\cdot \rightarrow O_2^- + H^+ \tag{4}$$

$$HO_2\cdot + Cu^+ + H^+ \rightarrow Cu^{2+} + H_2O_2 \tag{5}$$

Therefore, the use of hydrogen peroxide alone could combine the advantages of physical bubble cleaning and chemical cleaning, with possible enhanced antibiofouling activity from the Fenton reaction. In our tests, the effectiveness of H_2O_2 was examined using metal and plastic feed spacers in membrane fouling simulators, with the feed channel differential pressure used to monitor biofouling. Hydrogen peroxide was added periodically, at 12 h intervals for 10 min, at the beginning of the tests using the membrane fouling simulators to control biofouling (preventive strategy) or to prefouled membranes as a cleaning method of biofouling (curative strategy). A chemically modified copper oxide coated spacer was fabricated to evaluate the Fenton cleaning efficiency of the H_2O_2/CuO combination, which has not been previously studied as a method of spacer biofouling control.

■ MATERIALS AND METHODS

Materials. Flat sheet reverse osmosis membrane (Filmtec BW30LE) and polypropylene (PP) feed spacer of 31 mil (787 μm) thickness and a porosity of ∼0.85 (spacer strands at 90° position) were purchased from Dow Chemical (MI, U.S.A.). Sodium acetate, sodium nitrate, sodium hydroxide, and sodium dihydrogen phosphate were all obtained from Sigma-Aldrich (St. Louis, Mo.). Hydrogen peroxide in water (30%, w/w) was purchased from MilliporeSigma (MA, U.S.A.).

A ∼100 nm thick CuO layer was sputter-coated onto plastic polypropylene spacers using a CMS-18 sputtering tool (Kurt J. Lesker Company, PA, U.S.A.). Prior to the coating process, the polypropylene spacers were cleaned with acetone and then isopropanol and dried in a fume hood. The spacer was stabilized on a substrate and sputtered at room temperature in a 20% oxygen/argon gas mixture. The color of the coated spacers changed to black, compared to the white/yellow plain spacers, indicating the presence of the metal oxide coating (Figure S1). X-ray photoelectron spectroscopy (XPS) was used to characterize the successful deposition of CuO on the polypropylene spacers (Figure S2). The hydroxyl free radical generation from the CuO spacer reacting with H_2O_2 was identified by the decolorization of 1 mg/L methylene blue (Figure S3), as demonstrated in previous work.[19]

Fouling Simulation. Membrane fouling simulators (MFS) are a well-established method to simulate biofouling of membrane modules as demonstrated in our previous studies.[11,13,21] Here, two modules of membrane fouling simulators (MFS) were used to simulate biofouling on the spacers as previously described (Figure S4).[8] The channel dimensions of the MFS were 0.0787 cm (height) × 4.00 cm (width) × 20.00 cm (length), which could fit in one membrane and one spacer. The feedwater flowed through the channel, without any membrane permeation, as it has been shown in previous studies that

the absence of permeate production does not impact the biofouling development.[3,22] The development of fouling was monitored by measuring the pressure drop increase over the feed spacer channel of the MFS.[23]

Tap water was continuously filtered through an activated carbon filter (WGB22B-PB, ISpring, U.S.A.), to remove any natural organic matter, or chlorine residual in the water, and circulated through a water bath to provide a constant water temperature of 22 °C. The feedwater flow rate in each MFS was fixed at 16 L/h using a mass flow meter (Bronkhorst, U.S.A.) (Figure 1), resulting in a crossflow velocity of 0.16 m/s, as applied in practice installations.[24] To promote biofouling in the MFS, acetate, nitrate, and dihydrogen phosphate were dosed at 1000 μg/L-C and a C/N/P ratio of 100:20:10. Sodium acetate (3.679 g), sodium nitrate (1.308 g), and sodium dihydrogen phosphate (0.417 g) were dissolved in deionized water (2 L); sodium hydroxide was added to adjust the pH of the stock solution as needed.[8,25] Nutrient was dosed from the stock solution into each MFS at 0.03 L/h, which was low compared to the bulk water flow rate to avoid significant pH changes. The nutrient stock solution was replaced daily, and dosing levels were maintained throughout the experiments. The MFSs were operated in the dark to prevent any growth of phototrophs in the system.

The CuO-coated spacer and uncoated spacers were tested in separate MFS, with the same type of membrane. Periodic cleaning with H_2O_2 was investigated by dosing 0.3% (w/w) H_2O_2 at 12 h intervals, with a nutrient medium at a pH of 7, for continuous operation over 10 days to examine the potential of this method to minimize biofilm formation. Single-dose cleaning was also investigated for prefouled membranes and spacers. Two MFSs were dosed with the nutrient medium at a pH of 7 in the first 2 days, to induce initial bacteria attachment, and then with the nutrient medium at a pH of 11 from days 3 to 20 to avoid bacterial growth in the medium and promote bacterial growth only in the MFS. Single-dose system cleaning using 0.3% (w/w) H_2O_2 was conducted on day 11 and day 17, following an increase in the feed channel differential pressure. Concentrated 30% (w/w) H_2O_2 was added to water flowing at 0.16 L/h to each MFS to achieve the final 0.3% (w/w) concentration, with a dosing duration of 10 min.

Membrane Stability Characterization. To examine membrane stability due to H_2O_2 washing, 0.3% (w/w) H_2O_2 was dosed into MFS with BW30LE membranes with either PP or CuO spacers every 12 h for 10 days. The membranes were then taken out and examined using Fourier-transform infrared spectroscopy (FTIR) to demonstrate the presence of a polyamide active layer. Water flux (LMH, L m^{-2} h^{-1}) and salt rejection [$R = (1 - C_{permeate}/C_{feed}) \times 100\%$] of the membranes were obtained using a custom dead-end filtration cell made of stainless steel, with a volume of 250 mL. A synthetic brackish water (2000 ppm of NaCl) was used as the feed solution, and the effective membrane area was 0.196 cm^2, with the cell pressurized at 13.8 bar using nitrogen gas.

■ RESULTS AND DISCUSSION

Preventive Periodic Cleaning. With the periodic dosing of H_2O_2 from the start of the experiment, we were successful in avoiding any appreciable biofouling on the spacers or membrane surfaces, as demonstrated by a lack of an increase in feed channel differential pressure. With periodic dosing of H_2O_2 for only 10 min every 12 h, no significant increases in feed channel differential pressure were observed for both MFS with either the PP or CuO spacers (~16 mbar for PP spacer; ~9 mbar for CuO spacer) over 10 days of operation, which suggested minimal biofilm growth on the spacers and membranes (Figure 2). The differential pressure in the MFS with the PP spacer in the first 2 days (day 0 to 2) was 16 ± 1.2 mbar, which was no different from 16 ± 0.8 mbar in the last 2 days (day 8 to 10) ($p < 0.05$). Similarly, in MFS tests using the CuO spacer, no significant difference in differential pressure was observed at the beginning or toward the end of the testing
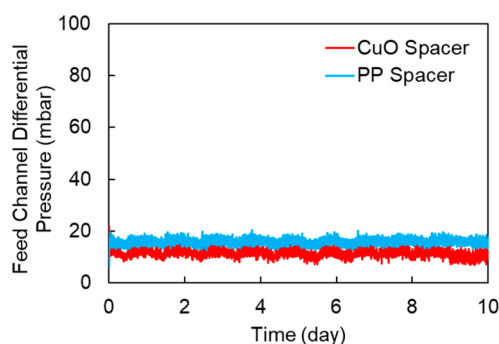

Figure 2. Preventive biofouling control: feed channel differential pressure in membrane fouling simulators with CuO coated spacer and polypropylene (PP) spacer dosed with 0.3% H_2O_2 at 12 h intervals.

(9.9 ± 1.3 mbar from day 0 to 2 and 8.9 ± 1.9 mbar from day 8 to 10; $p < 0.05$), indicating minimal bacterial accumulation on either membrane or spacer surfaces by periodical dosing of H_2O_2.

Treatment with periodic H_2O_2 dosing did not impact either membrane permeability or salt rejection. When tested in a dead-end filtration cell, membranes from the MFS that had been used for 10 d with H_2O_2 dosing had water fluxes of 86 ± 8.6 LMH (PP spacer) and 83 ± 4.3 LMH (CuO spacer), which were similar to those measured for pristine membranes (83 ± 8.6 LMH) (Figure 3A). There was no significant difference in NaCl rejection (89 ± 1.7% for pristine membrane, 90 ± 1.8% for membrane with PP spacer, and 89 ± 0.2% for membrane with CuO spacer) due to exposure to H_2O_2 (Figure 3A). FTIR spectra of membranes with the PP spacer and the CuO spacer and pristine membrane all showed
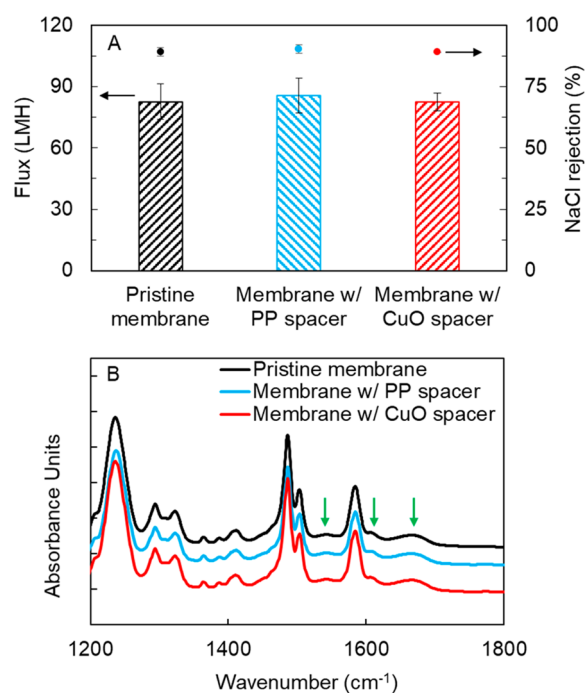

Figure 3. (A) Water flux and salt rejection for pristine membrane (no H_2O_2 washing) and membranes with PP and CuO spacers (0.3% H_2O_2 washing), at 13.8 bar with 2000 ppm of NaCl feed solution in dead-end cell. (B) FTIR spectra for pristine membrane (no H_2O_2 washing) and membranes with PP and CuO spacers (0.3% H_2O_2 washing).
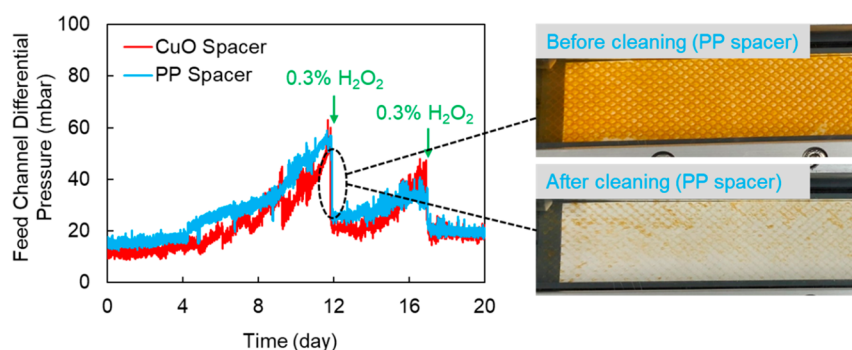
Figure 4. Curative biofouling control: feed channel differential pressure in membrane fouling simulators with CuO coated spacer and PP spacer.

similar peaks at 1663 cm^{-1} (amide I band), 1609 cm^{-1} (aromatic amide), and 1541 cm^{-1} (amide II band) (Figure 3B), which were all significant peaks for the fully aromatic polyamide,[26] suggesting the polyamide membrane stability under exposure to 0.3% (w/w) H_2O_2.

Curative Cleaning with Biofilm Removal. In the absence of H_2O_2 washing, biofilm growth followed similar trends for the PP or CuO spacers in MFS tests. The feed channel pressure with the CuO spacer increased from 13 mbar (day 0) to 60 mbar (day 12), similar to that of the PP spacer of 16 mbar (day 0) to 57 mbar (day 12) (Figure 4). The lack of an appreciable difference in pressure increases between the CuO and PP spacers indicated that the use of the CuO coating alone did not impact biofilm formation. Although previous studies have indicated that copper or copper oxides can be toxic to bacteria,[27] overall biofouling based on changes in pressure was not impacted here by the presence of a CuO layer on the spacer, which was possibly due to the low copper concentration with decreased biological toxicity in continuous flow systems. This result is consistent with other studies where coating the spacer surface with different materials can only delay biofouling but not limit biofouling[5] so that a more rigorous cleaning of the membrane and spacer was still necessary.

Dosing with low concentration H_2O_2 rapidly decreased the differential pressure, indicating that it was possible to reduce, but not eliminate, biofouling in MFSs with either the CuO or PP spacers. After dosing with 0.3% (w/w) H_2O_2 for 10 min on day 12, the feed channel differential pressure in the MFS with the CuO spacer dropped from 60 to 22 mbar (Figure 4), which was a 63% reduction in pressure. However, the reduced differential pressure of 22 mbar was still ~69% more compared to 13 mbar of the initial clean surface, suggesting only partial biofilm removal. The MFS with PP spacer also showed a 54% decrease in the feed channel differential pressure from 57 to 26 mbar (Figure 4), also without a complete recovery of the initial differential pressure (16 mbar). By day 17 without intermittent treatment, the pressure had again increased in both MFSs indicating biofilm development, with a maximum of 45 mbar, using the CuO spacer, and 38 mbar using the PP spacer. After H_2O_2 dosing, the differential pressure for both spacers decreased to about 20 mbar (Figure 4), showing that infrequent doses of H_2O_2 were ineffective in complete biofilm removal. The colors on the membrane and the spacer surfaces in the MFS with the PP spacer changed from bronze to light yellow after the first H_2O_2 dosing, suggesting substantial biofilm removal (Figure 4). However, complete biofilm removal was not achieved using this intermittent cleaning method, indicating that the preventive 12 h periodic cleaning method was a more effective biofouling control strategy.

The main mechanism of biofilm removal was likely the shear created by the production of gas bubbles in the feed, combined with disinfection due to H_2O_2. When the H_2O_2 was added into the solution, oxygen bubbles were immediately formed at the point of chemical addition, which were further catalyzed by catalase in the bacterial periplasm in response to oxidative stress[28] and carried into the chamber. The rapid biofilm removal was therefore accomplished within several minutes, as indicated by the sharp decrease in the feed channel differential pressure (Figure 4). These bubbles and the rapid removal of the biofilm were visually observed through the MFS glass window (Figure S5). Typical chemical cleaning using disinfectants such as sodium hydroxide or sodium dodecyl sulfate can take longer than 1 h for biofouling control in reverse osmosis membrane systems.[29] Even though H_2O_2 is a strong disinfectant, it is unlikely that disinfection was the main factor in biofilm removal which required only a few minutes, but there may be an additional benefit relative to disinfection for even this small amount of time due to the combined effects of both bubble shear and disinfection. The reaction between CuO and H_2O_2 can generate hydroxyl free radicals (Figure S3),[19] but no significant enhancement of biofouling control was observed in this study with the use of CuO in comparison to a plastic spacer. Since the use of a CuO spacer did not show any noticeable advantages over the PP spacers, bubble cleaning was concluded to be the dominant mechanism for biofouling control.

Bubble generation from direct H_2O_2 dosing is a simpler and easier method compared to other explored processes such as bubble injection or chemical reactions. For example, air bubbles of 150 to 250 nm generated using an electrically powered bubble generator (220 V, maximum flow rate of 65 L/min) that were pumped into a membrane cell disrupted external membrane concentration polarization as shown by a 16% increase of permeate flux with a 35 g/L NaCl feed solution.[30] However, the impact on biofouling or other types of fouling was not examined, and the continuous bubble generation is likely not practical based on its high energy cost. CuO nanoparticles were immobilized on a polydopamine coated reverse osmosis membrane surface and reacted with H_2O_2 to generate oxygen bubbles on the membrane surface.[19] The generated bubbles were able to clean the silica foulants on the membrane surfaces and also restore the membrane surfaces to initial water flux. However, the immobilization of the CuO nanoparticles required the preparation of an additional polydopamine coating and the use of multiple chemicals,

which required a more complex (and likely more expensive) membrane production process. The stability of the CuO particles on the membrane over time was not examined for repeated reaction with H_2O_2 as only two intermittent dosing tests were performed, but it could be expected that the hydroxyl radical formation would result in the loss of adhesion of the CuO particles over time. Thus, the direct addition of H_2O_2 would likely be a simpler and more efficient method to generate bubbles than these other processes, and this process could be used in any existing system without the prior need for CuO particles to be immobilized on the membrane.

Feasibility of H_2O_2 Cleaning. The use of H_2O_2 for biofouling control provides an economical and in situ method to prevent biofouling or clean biofouled membranes. By the injection of H_2O_2 directly into the feed stream, biofilm removal can be accomplished within minutes, and thus, it could be conducted intermittently with a minimal impact on the overall membrane operation process. The pressure in the feed system might need to be reduced, however, in order to achieve sufficient bubble formation. Moreover, the low concentration and the short time of dosing (0.3% w/w H_2O_2, for 10 min every 12 h) did not do damage to the membranes. This lack of observed damage to the membrane was consistent with data provided by the manufacturer (Dow Chemical) that polyamide membranes were not adversely impacted after continuous exposure to a higher H_2O_2 concentration (0.5% w/w).[31] In practice, the H_2O_2 can be directly dosed at the inlets of the membrane modules with maintained concentration to maximize the cleaning efficiency.

The cost of periodic cleaning with H_2O_2 can be very low based on the small amount of H_2O_2 used here for cleaning. The bulk order price for concentrated 30% (w/w) H_2O_2 is only \$0.46/kg,[32] which is much lower than that of acids or bases that might be used for chemical cleaning. Due to limited information on chemical cleaning in real desalination plants, the cost comparison was based on overall desalination cost and pretreatment cost. With periodic dosing at 12 h intervals, the cost of 30% (w/w) H_2O_2 consumption for each MFS would be equivalent to \$0.009/m^3 or 0.024 kWh/m^3, assuming a water flux of 15.3 LMH based on a typical seawater desalination operation.[33] This H_2O_2 cost of \$0.009/m^3 was only ∼0.8% of the total cost of water of \$1.1/m^3 in a typical seawater reverse osmosis plant and ∼6.5% of the current pretreatment cost.[33] While periodic dosing of H_2O_2 at 12 h intervals was used here to avoid biofouling, it is likely that a reduction in the frequency of dosing or the amount of chemical could further lower this cost. For example, frequent dosing can be applied when the biofouling risk is high such as during times where there is an algal bloom,[34] with reduced frequency of dosing during normal seasons. The next series of tests using this procedure should be performed using membrane modules to determine the translation of these findings to the more complex conditions present in larger-scale systems, with both the concentration and dosing frequency examined to optimize biofouling control and minimize chemical consumption.

CONCLUSION

The use of an intermittent low concentration of H_2O_2 was investigated as a combined physical and chemical cleaning strategy for biofouling control in membrane systems using CuO or PP spacers. The periodic dosing of 0.3% (w/w) H_2O_2 at 12 h intervals led to the avoidance of any increase in feed channel differential pressure in the test system, indicating a lack of appreciable biofouling with periodic H_2O_2 dosing. In tests with membranes fouled over a period of 11 days, a single-dose of 0.3% (w/w) H_2O_2 removed most of the biofilm on the spacers and membranes within minutes, as demonstrated by a feed channel differential pressure, by 69% (CuO spacer) and 54% (PP spacer). The biofouling reduction was primarily due to the high shear created by the generated oxygen bubbles in the system, combined with the disinfection effect of H_2O_2. The use of a CuO spacer, which would have produced hydroxyl radicals, did not show significant advantages in comparison to the PP spacer. The overall low cost of \$0.009/m^3 from periodic H_2O_2 dosing was only 0.8% of the total estimated cost for seawater desalination and 6.5% of the current pretreatment process, making it a potentially economical method for effective biofouling control.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssusche-meng.9b01086.

> Pictures of plain and CuO coated polypropylene spacers with identical geometry, XPS spectra of spacers, decolorization of methylene blue with CuO and PP spacer, setup of membrane fouling simulators, bubble generation (PDF)

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Notes
The authors declare no competing financial interest.

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