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Membrane fouling in seawater desalination processes caused by harmful dinoflagellate *Cochlodinium polykrikoides*

Miho Kuroiwa[a], Takako Masuda[b], Takuo Omura[b], Aunnop Wongrueng[a], Kumiko Oguma[a], Hiroshi Sakai[a], Michio Murakami[c], Satoshi Takizawa[a,*]

[a]*Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
Tel. +81-3-5841-6241; Fax: +81-3-5841-8532; email: takizawa.satoshi@gmail.com
[b]*Asian Natural Environmental Science Center, The University of Tokyo, 1-1-1 Yayoi,Bunkyo-ku, Tokyo 113-8675, Japan*
[c]*"Wisdom of Water" (Suntory), Corporate Sponsored Research Program, Organization for Interdisciplinary Research Projects, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

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ABSTRACT

Eutrophication of the world's marine environment has been exacerbated due to discharge of a large volume of wastewater from rapidly growing cities. Between 2008 and 2009, a serious red tide appeared in the Gulf that brought about a temporary shutdown of water desalination plants in Oman and the UAE. In this study, a harmful dinoflagellate *Cochlodinium polykrikoides* known to be the cause of many red tides, including the one in the Gulf between 2008 and 2009, was cultured in the laboratory to investigate its impacts on a coagulation-microfiltration/ultrafiltration (MF/UF)-reverse osmosis (RO) desalination process. The culture medium for *C. polykrikoides* contained high amounts of dissolved organic matter that possessed fluorophores for fulvic-like, humic-like, and protein-like organic matter that can be detected by excitation-emission matrix (EEM). Although EEM peaks were diminished by coagulation-MF/UF, the reduction in dissolved organic carbon concentrations was not significant by MF and was small by UF. Both MF and UF filtrates showed strong RO filtration resistance, so that they have to be diluted 10 times to be able to be filtered by RO membranes. RO membrane fouling was more serious with MF filtrate than with UF filtrate possibly because of the difference in quantity and quality of organic contents in MF and UF filtrates. However, the RO membrane could reject most of the organic matter in both MF and UF filtrates.

Keywords: Biofouling; *Cochlodinium polykrikoides*; EEM; Red tide; Seawater desalination

1. Introduction

Although the amount of available fresh water resources on the Earth is limited, water demand has been increasing due to rapid population and economic growth, especially in developing countries. In order to fill the gap between water demand and available water resources, seawater desalination plants have been employed to produce drinking water in the arid regions and their use is expected to continue to expand to countries including Australia, China, and

*Corresponding author.

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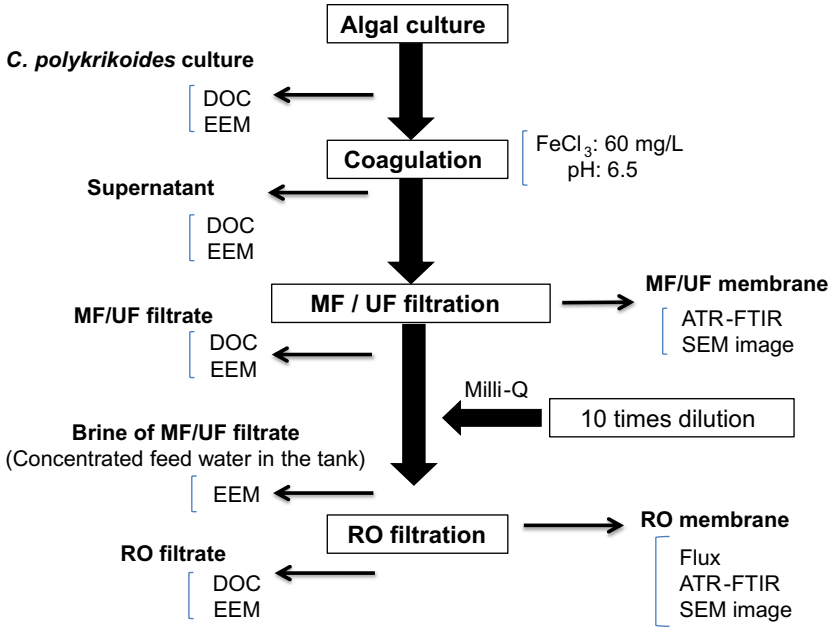

Fig. 1. Flow chart of the experiments.

the USA. However, marine water pollution in many coastal and enclosed seas has increased and has drawn wider concern with regard to the effects of pollution on desalination processes.

There are a large number of desalination plants in the Middle East, many of which employ reverse osmosis (RO) membrane processes. Although this region has been free of troubles in operation of desalination plants caused by marine pollution, a serious red tide appeared in the Gulf between 2008 and 2009. This red tide brought serious damage to the marine products industries in the region. The tide also forced some desalination plants in Oman and the UAE to suspend operations due to clogging of intake filters or the fouling of RO membranes. The disruption of desalination plant operations is a serious threat not only to the water supply, but also to national security in this region. The cause of the red tide was later identified to be the harmful dinoflagellates *Cochlodinium polykrikoides*, which cause serious red tides in many coastal areas of the world [1].

In general, algae impart soluble organic matter called extracellular organic matter (EOM) and intracellular organic matter (IOM). Algal extracellular products increase a coagulant demand and lead to increased turbidity and the impaired disinfection efficiency in the chlorination process. Furthermore, algal extracellular products are viscous and known to cause membrane fouling [2,3]. However, the mechanisms of fouling and the nature of the cake deposited at the membrane surface due to algae have not yet been well understood and reported.

Hence, the purpose of this study is to characterize the EOM and IOM produced by *C. polykrikoides*, and to evaluate the removal efficiency by various pretreatment processes for desalination, including coagulation, microfiltration (MF), and ultrafiltration (UF). Furthermore, the effluents from these pretreatment processes were used to evaluate the RO membrane fouling.

2. Materials and methods

2.1. Algal culture

The experimental protocol for this study is presented in Fig. 1. A strain of *C. polykrikoides* was obtained from National Research Institute of Fisheries and Environment of Inland Sea Fisheries Research Agency in Japan. The culture was incubated in a 50 mL culture flask filled with the modified f/2 medium at 25˚C under fluorescent lights with a 12 h:12 h L:D cycle.

The modified f/2 medium used in this study was lacking $Na_2EDTA\ 2H_2O$, $CuSO_4\ 5H_2O$, $Na_2SiO_3\ 9H_2O$ and included H_2SeO_3 to the original f/2 medium. Seawater was collected from the surface of a subtropical sea off the coast of the Miyako Island, Japan, and was stored in the laboratory at 25˚C until being used as the culture medium after adjustments of its salinity to 30 psu. After gently shaking the culture bottles to uniformly suspend *C. polykrikoides*, 0.1 mL of culture medium was transferred with a pipette on a glass slide for counting cell numbers of *C. polykrikoides* under a

microscope. When the growth rates of *C. polykrikoides* reached a stationary stage, the cells were transferred to a new culture medium.

The mean cell count per volume was ~1,493 cells/mL with a minimum of 1,280 cells/mL and maximum of 1,640 cells/mL. During the red tide incident in the Gulf in 2008, algal cell concentrations of 11,000–21,000 cells/mL were recorded in the seawater samples obtained off the coast of UAE. Hence, the cell concentrations used in this study are one-tenth of the cell concentration during the red tide event of 2008.

2.2. Coagulation

By a jar test, the optimum concentration of ferric chloride was found to be 60 mg/L and the optimum pH for coagulation to be 6.5. Hence, 900 mL of the *C. polykrikoides* culture was coagulated under this condition. The coagulation sequence was as follows: rapid mixing at 120 rpm for 45 s, slow mixing at 30 rpm for 15 min, and settling for 30 min. After settling, a 650 mL sample of supernatant was collected, of which 50 mL was used for water quality analysis and 600 mL was used for either MF or UF filtration.

2.3. Membrane filtration

2.3.1. MF and UF filtration

After coagulation, 600 mL of supernatant was transferred to the filtration chamber for filtration experiments using either MF membranes (polytetrafluoroethylene [PTFE], 0.45 μm, Millipore) or UF membranes (regenerated cellulose, molecular weight cut-off [MWCO] 10 kDa, YM-10, Millipore). The MF was operated by vacuum filtration, whereas the UF was operated by pressurized filtration at 0.2 MPa. The 600 mL of supernatant was filtered through the MF membrane, while 400 mL of the supernatant was filtered through the UF membrane. After MF or UF filtration, 50 mL of the filtrate was used for water quality analysis, while the rest of the filtrate was used for the RO filtration experiments.

2.3.2. RO filtration

Because the RO membrane was unable to filter the MF filtrate directly, both the MF filtrate and UF filtrate were diluted 10 times by taking 50 mL of the filtrate and adding 450 mL of Milli-Q water in a 500 mL measuring flask. The RO membrane filtration of the diluted sample was performed at 0.8 MPa using a polyamide RO membrane (UTC-70U Toray). Changes in the flux were recorded and filtration was stopped when the flux became constant after 250 mL of the feedwater had been filtered. After RO membrane filtration, the filtrate, RO membrane, and brine of MF/UF filtrate (feedwater which was concentrated in the feed tank), were subject to analyses as explained in the following section.

2.4. Analyses of water quality and membrane foulant

Dissolved organic carbon (DOC) (Shimadzu, TOC-5000A) and Excitation-Emission Matrix (EEM) (HITACHI, F-4500 fluorescence spectrophotometer) were analyzed in the algal culture, in the supernatant of coagulation, and in the MF, UF, and RO filtrates. The functional groups of foulants attached to the MF, UF, and RO membranes were also analyzed by attenuated total reflection-fourier transform infrared (ATR-FTIR) spectroscopy (Jasco International Co. Ltd, ATR-FT/IR-610). Additionally, changes in the membrane surfaces were observed by a scanning electron microscope (SEM) (KEYENCE, VE-8800).

3. Results and discussion

3.1. MF and UF filtration

3.1.1. EEM of MF and UF filtrates

The EEM of *C. polykrikoides* culture, the supernatant of the coagulated culture, and the MF and UF filtrates are presented as Fig. 2(a)–(d). Four fluorophores, labeled A, B, C, and D, were observed in the *C. polykrikoides* culture. Peak A occurs at an excitation wave length of 280 nm and an emission wavelength of 336 nm (Ex: 280 nm/Em: 336 nm). Peak A and B (Ex: 230 nm/Em: 344 nm) were assigned to protein-like substances. Peak B is close to the peaks of tyrosine-like (Ex: 230 nm/Em: 300 nm) and tryptophan-like (Ex: 230 nm/Em: 350 nm) aromatic proteins [4]. Peak A may be caused by a mixture of several fluorophores of various organic matter origins. According to Chen [5] and Leenheer [6], peaks at an excitation wavelength between 250 nm and 280 nm and at an emission wavelengths less than 380 nm are related to soluble microbial byproduct-like material such as tyrosine-like and protein-like (Ex: 270–280 nm/Em: 300–320 nm) substances, which have peaks within the region of Peak A. Furthermore, tryptophan-like, protein-like, or phenol-like (Ex: 270–280 nm/Em: 320–350 nm) substances are related to biological matter (Ex: 275–285 nm/Em: 340–350 nm). Peak C (Ex: 260 nm/Em: 460 nm) is assigned to the so-called fulvic acid-like fluorescence, while Peak D (Ex: 345 nm/Em: 436 nm) belongs to the humic acid-like region [5,6].

After coagulation, all the intensities of Peaks A–D diminish significantly (Fig. 2(b)) indicating the

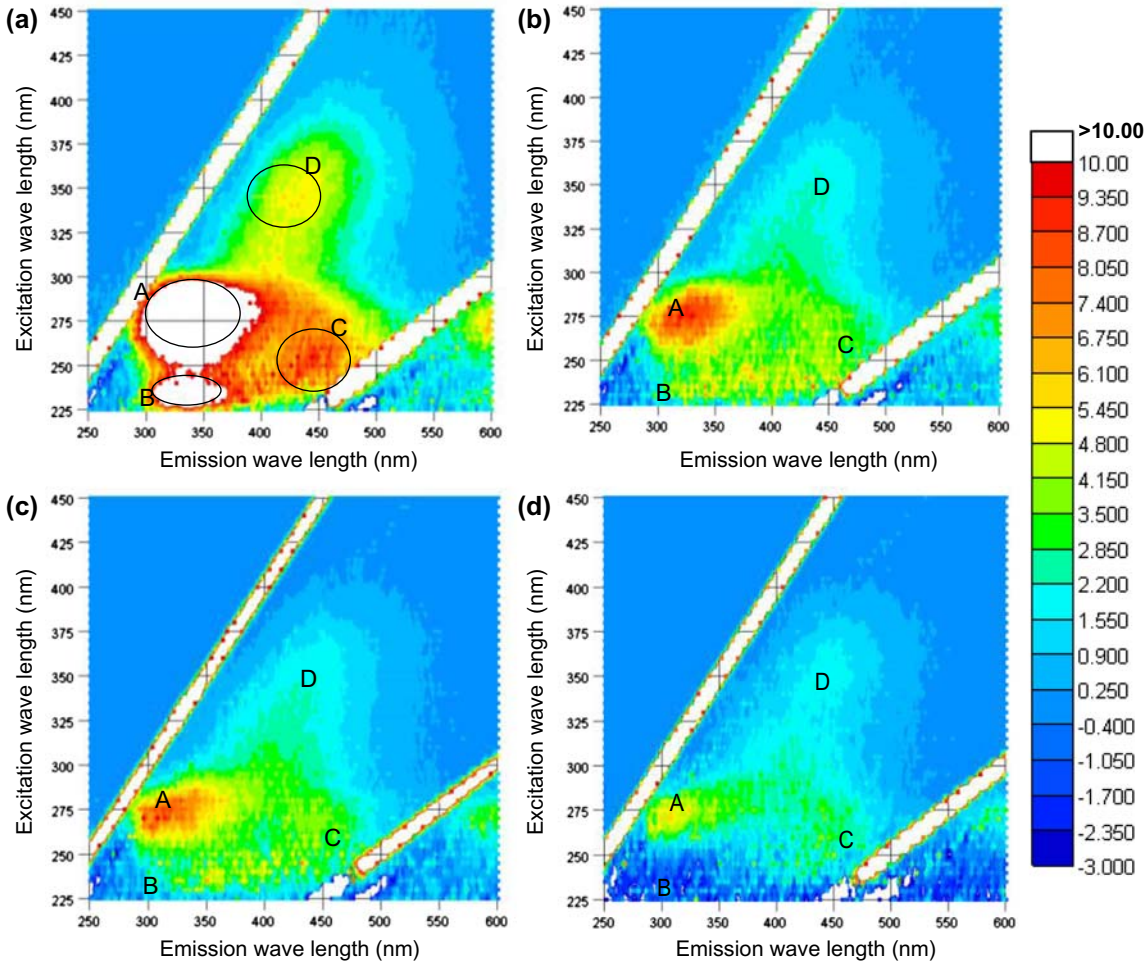

Fig. 2. EEM fluorescence spectra of (a) *C. polykrikoides* culture, (b) Supernatant (after coagulation), (c) MF filtrate, and (d) UF filtrate.

effectiveness of coagulation as a pretreatment of algae-laden water. These peaks are further diminished by MF filtration, but Peak A remained in the filtrate (Fig. 2(c)). These peaks were much diminished in the UF filtrate (Fig. 2(d)) compared to the MF filtrate indicating the presence of organic molecules in the size range between 10 kDa and 0.45 μm in the supernatant of coagulated water.

3.1.2. DOC results of MF and UF filtrates

The concentration of DOC at each treatment step is presented in Fig. 3. The *C. polykrikoides* culture and the supernatant after coagulation were filtered through cartridge membranes (pore size 0.45 μm, PTFE, Millipore) before measuring DOC. The MF and UF filtrates were measured without filtering by the cartridge filters. DOC was analyzed in duplicate for all samples. The *C. polykrikoides* culture contained 28.0 mg/L of DOC. There was no significant difference in DOC between the *C. polykrikoides* culture before coagulation and the supernatant after coagulation (*t*-test, $p = 0.13$). There was also no DOC reduction after MF filtration (*t*-test, $p = 0.19$). These results are contradictory to the EEM results shown in Fig. 2, in which all the peaks were decreased

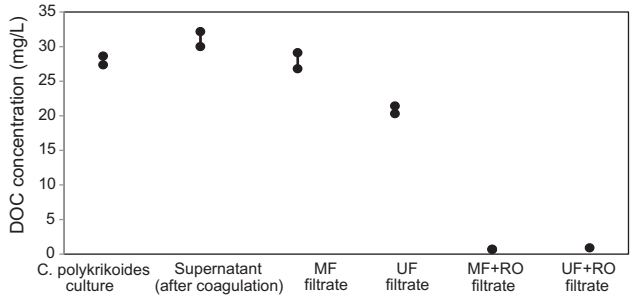

Fig. 3. DOC concentration after various treatments.

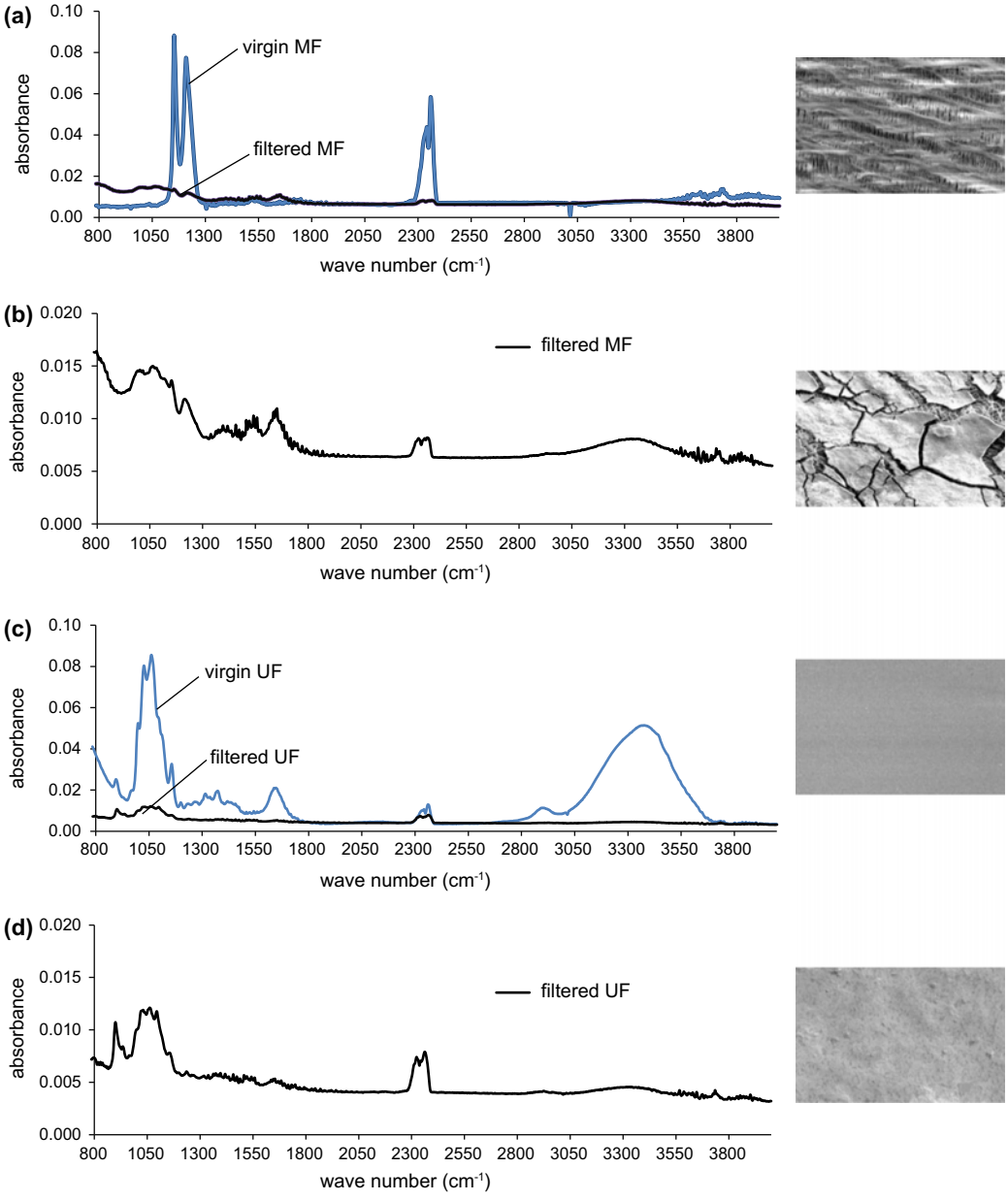

Fig. 4. FTIR spectra and SEM images (a) virgin and filtered MF membranes, (b) enlarged figure of filtered MF membrane, (c) virgin and filtered UF membranes, and (d) enlarged figure of filtered UF membrane.

by MF or UF filtration. DOC measures all the carbon in organic matter, whereas EEM can show only fluorescent fractions of DOC. Therefore, one possible explanation why the DOC concentration did not decrease while EEM peaks diminished by coagulation and MF/UF filtration is that, after coagulation and MF filtration, IOM and/or EOM attached to the algal cells was released due to cells lysis. These organic materials may not be fluorescent and, hence, cannot be detected by EEM. From previous research, it is known that these metabolic products are difficult to flocculate [3]. DOC in the UF filtrate was significantly less than the DOC from the coagulated supernatant. This observation indicates that a fraction of DOC greater than the MWCO of 10 kDa of the UF membrane was removed. However, 74.5% of DOC still remained after coagulation-UF filtration, which may affect subsequent RO filtration.

3.1.3. FTIR spectra of MF and UF membrane

Fig. 4(a)–(d) presents the ATR-FTIR spectra and a SEM image of the virgin MF membrane, the MF

membrane filter after filtration of the coagulation supernatant, the virgin UF membrane, and the UF membrane after filtration of the coagulation supernatant, respectively.

As seen in Fig. 4(a), the FTIR spectrum of the virgin MF membrane disappears after filtration of *C. polykrikoides* culture due to the formation of the cake layer. In Fig. 4(b), some peaks develop as a consequence of foulants deposited on the MF membrane. The absorption peaks at 3,331, 1,652, and 1,540 cm^{-1} are characteristic bands for proteins due to stretching N–H bonds, stretching of C=O bonds (amide I band), and deformation of N–H bonds (amide II bands), respectively. The peak at 1,400 cm^{-1} indicates that the membrane foulants contain some lipids [7,8]. Her et al. identified the peak near 1,000–1,120 cm^{-1} as being associated with alcoholic C–O absorption, which may be derived from polysaccharide-like substances [9]. Furthermore, both protein- and polysaccharide-like compounds are associated with algogenic organic matter (AOM). AOM containing both EOM and IOM, such as polysaccharide-like substances including amino sugars and proteins have been recognized as playing a significant role in membrane fouling [7,10,11].

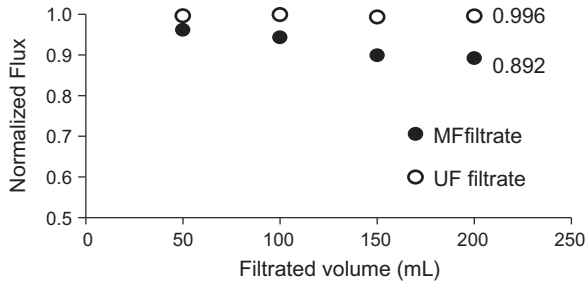

Fig. 5. Normalized flux reduction along with the filtrated volume.

Based on the results of EEM, one can conclude that protein-like substances between 45 μm and 10 kDa are associated with membrane fouling. Other researchers have suggested that the extracellular mucoid polysac-

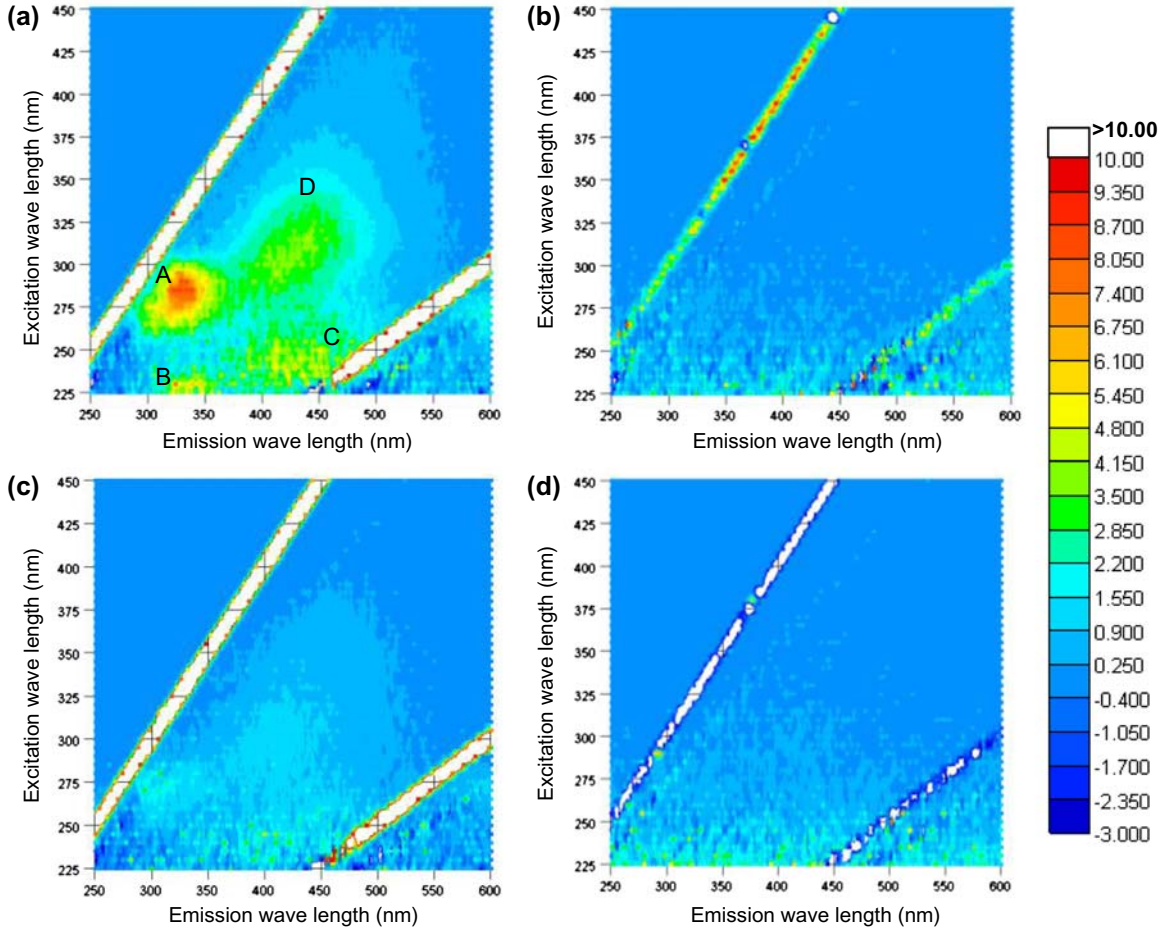

Fig. 6. EEM fluorescence spectra of each step (a) Brine of MF filtrate, (b) RO filtrate of (a), (c) Brine of UF filtrate, and (d) RO filtrate of (c).

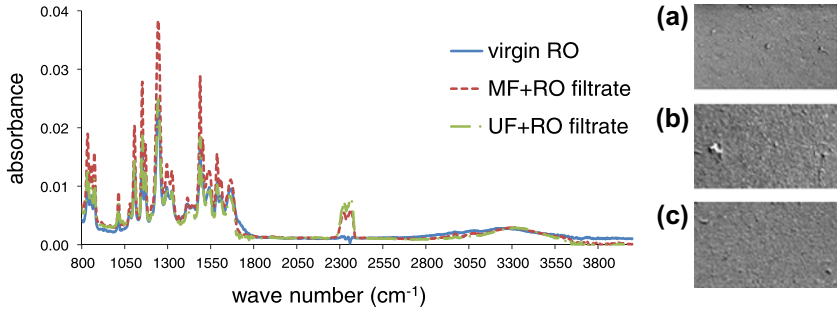

Fig. 7. FTIR spectra and SEM images comparing virgin/filtrated RO membranes. SEM photos: (a) virgin RO membrane (top), (b) RO membrane after filtration of MF filtrate (middle), and (c) RO membrane after filtration of UF filtrate (bottom).

charide substances produced by *C. polykrikoides* may be involved in the indirect mechanism of mortality [12,13]. Thus, further research on the rejection of polysaccharides is important to affirm the safety of desalinated water.

The FTIR spectrum of the virgin UF membrane was significantly attenuated after filtering the *C. polykrikoides* culture medium (Fig. 4(c)–(d)), but the deposited foulant on the UF membrane was different from the foulant on the MF membrane (Fig. 4(b)). As shown in Fig. 4(d), the FTIR peaks of the virgin UF membrane are still present after filtration of *C. polykrikoides* culture. This result, combined with the photo of the filtered UF membrane in Fig. 4(d), indicates that a thick cake, such as the one that deposited on the MF membrane, did not deposite on the UF membrane because of stirring.

3.2. RO filtration

Fig. 5 shows the normalized flux of RO filtration. Because the RO membrane filtration was carried out in a dead-end mode, the feedwater was gradually concentrated during the course of filtration; hence, the flux gradually decreased. In order to offset changes in the feedwater concentration during filtration, the flux of the feedwater containing the *C. polykrikoides* culture was normalized by the flux of the culture medium without *C. polykrikoides* at filtered volumes of 50, 100, 150, and 200 mL. Before the flux of the culture medium with or without *C. polykrikoides* was measured, the flux of pure water was measured using the same RO membrane because of slight differences in the pure water flux for each RO membrane. Then, the flux of the culture medium with or without *C. polykrikoides* was measured and normalized by dividing the flux by the pure water flux for each RO membrane. Finally, the flux of *C. polykrikoides* culture was divided by the flux of the culture medium without *C. polykrikoides* to obtain the normalized data shown in Fig. 5.

As shown in Fig. 5, there was a clear difference between MF filtrate and UF filtrate in the declining trend of RO fluxes. There was no significant reduction of RO flux with UF filtrate, whereas RO flux reduction was significant with the MF filtrate. The difference in the RO flux may be a result of the difference in DOC in MF and UF filtrates (Fig. 3), which is also in agreement with the EEM results shown in Fig. 2.

Fig. 6(a)–(b) show EEM of the brine solution of MF filtrate concentrated by the RO membrane and the RO filtrate that filtered the MF filtrate. Fig. 6(c)–(d) are similar to Fig. 6(a)–(b) except that the UF filtrate was used as the feedwater to the RO membrane. From the results presented in Fig. 6(a)–(d), one can conclude that most of the soluble organic matter including microbial products—such as tryptophan-like or protein-like substances; aromatic proteins; and humic acid-like and fulvic acid-like organic matter—were completely rejected by the RO membrane. By comparing Fig. 6(a) and 6(b), one can see that the fluorophores associated with this organic matter, potential foulants of the RO membrane, were completely removed by the RO membrane.

Fig. 7 shows the FTIR spectra and SEM images of the virgin RO membrane and the RO membranes filtered with either MF or UF filtrates. Although the RO membranes after MF/UF filtration appear slightly rougher than the virgin RO membrane as can be seen in the SEM images (Fig. 7(a)–7(c)), no significant changes to the FTIR spectra are observed after RO filtration of MF/UF filtrates. There appears to be a difference between the virgin and filtered RO membranes at the peak 2,300–2,400 cm^{-1}; however, this change may be due to adsorption of carbon dioxide during RO membrane filtration.

4. Conclusions

A coagulation-MF/UF filtration pretreatment of a *C. polykrikoides* culture was used to find the potential

problems associated with eutrophication and algal blooms in seawater desalination processes that employ membrane filtration processes. The *C. polykrikoides* culture contained high DOC and showed an EEM spectrum with fulvic-like, humic-like, and protein-like organic matter. The EEM spectra were significantly attenuated after MF and UF filtration. However, there was no concurrent reduction in DOC by coagulation-MF filtration, whereas DOC was reduced by 25.5% through coagulation-UF filtration. After filtration, the MF membrane was fouled with a deposited cake layer, whereas no thick cake layer was observed on the UF membrane. The RO membrane could not filter the MF filtrate, so it was necessary to dilute the MF and UF filtrates by a factor of 10 with pure water. This required dilution suggests a serious problem of desalinating algal-laden seawater with RO processes alone. However, the RO membrane was quite effective in removing dissolved organic matter from the diluted MF and UF filtrate, which may minimize any adverse effects of AOM in seawater.

Acknowledgments

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