



Identification of fouling materials in the microfiltration of seawater laden with marine algae

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ABSTRACT

In this study, fouling materials were identified in the microfiltration (MF) of seawater laden with marine algae. To this end, raw seawater spiked with either the dinoflagellate species without cell walls (*Heterosigma akashiwo*) or with cell walls (*Prorocentrum micans*) was filtered through a laboratory-scale MF system. Based on the results, polysaccharides, which were excreted by the marine algae, accumulated within the MF system and subsequently resulted in membrane fouling. Cell walls are closely related with polysaccharide excretion. The dinoflagellate species without cell walls released more polysaccharides than those with cell walls based on the unit surface area of the species. High-performance size exclusion chromatography analysis revealed that organic substances (1.1 and 22 kDa, molecular weight) were accumulated in the MF system. These organic substances could be the biofouling agents in MF systems during marine algal blooms.

Keywords: Red tide; Dinoflagellate; Marine algae; Polysaccharide; Molecular weight distribution; Membrane fouling

1. Introduction

The incidence of red tides has recently increased in the Middle East, especially in Abu Dhabi. The number of red tide recordings increased to five incidences in 2006 and eight incidences in 2008 [1]. The red tide phenomenon in 2008 was remarkably immense affecting more than 1,200 km of coastline in the Arabian Gulf as well as in the Gulf of Oman [2]. Eleven to approximately 21 million cells per liter near Fujairah

were recorded on surface seawaters during the bloom period [3]. The amount reached as high as 27 million cells per liter in certain areas [4]. A major impact of marine algal blooms on water desalination plants was filter clogging; at least five seawater desalination plants in the UAE were closed by blooms due to filter clogging until the blooms disappeared [1,5,6]. At some plants, water production was decreased by 30–40% [7]. Similarly, a decrease of 50% water production in a pilot-scale microfiltration (MF) system occurred by an increase in the chlorophyll-a concentration up to

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136 mg/m³ in a marine algal bloom in the Masan bay [8]. The decline in production was followed by the incurment of large financial losses. According to the estimation of the Abu Dhabi Water Resources Master Plan, the loss for the industry amounted to more than US\$ 100,000/d during the bloom [9].

Membrane fouling could be due to substances released from algal cells rather than the algae themselves. Ridgway and Flemming reported on the importance of bacterial extracellular polymers in membrane biofouling in great detail [10]. Extracellular polymers, which aid microorganism to bind to the membrane, often envelop attached cells in a viscous hydrated gel. This gel-like matrix is referred to as extracellular polymeric substances (EPS) [11,12]. Bacterial EPS typically consist of acidic heteropolysaccharides with a high net-negative zwitterionic charge density [11,13–18].

According to Ladner, the Orange County Water District experienced a red tide event while testing their integrated membrane system consisting MF followed by reverse osmosis (RO). The infrared absorption analysis of the fouling layer coated on the MF membrane revealed peaks for carbohydrates and proteins. Subsequently, large macromolecules (sizes ranging from 10 to 100 μm) rather than algae were suspected as the main biofouling agents. The importance of carbohydrates and proteins in membrane fouling has been recognized in membrane filtration of freshwater. While studying the effect of freshwater algae on nanofiltration (NF), Her et al. detected algal organic matter (AOM) in the fouling layer of the membrane. They concluded that the AOM was more important in membrane fouling than Suwannee River humic acid (SRHA).

Polysaccharides and proteins are well recognized as foulants in membrane filtration of surface waters. Wiesner et al. identified proteins, aminosugars, polysaccharides, and polyhydroxyaromatics as strong foulants [19]. Amy and Cho identified polysaccharides as dominant foulants in ultrafiltration (UF) and NF [20]. Mackey found larger compounds such as polysaccharides and proteins to cause more fouling of UF and NF membranes [21].

Like bacteria, algal cells also excrete EPS during their growth and upon their death [22]. Algal EPS generally includes polysaccharides, proteins, lipids, vitamins, and amino acids. [23]. EPS mostly consists of polysaccharides, and the rest is proteins, nucleic acids, and lipids [24–26]. The type and amount of EPS depend on the algal species [27]. About 80% of the EPS excreted by *Chaetoceros affinis* is polysaccharides and 1.5% proteins [28].

It was found in a previous study that the addition of red tide causing marine algae into seawater

induced membrane fouling [29]. They monitored the increase in TMP (transmembrane pressure) of the MF system while filtering seawater spiked either by dinoflagellates or diatoms under constant flow conditions. After observing a steeper TMP rise with the increase in algal cell numbers, they suspected that algal EPS is related to membrane fouling. Thus, they found that the polysaccharide concentration increased based on the cell numbers. They concluded that the excreted polysaccharides from the algal cells were the main culprit of membrane fouling. However, they reported on only polysaccharide measurements while the size distribution of the EPS was not determined.

The aim of this study was to determine the effect of marine algae in the red tide phenomenon which causes membrane fouling. The molecular weight distribution (MWD) of the membrane biofouling agents that accumulated on the membrane was determined by HPLC–SEC (high-performance liquid chromatography–size exclusion chromatography) analysis.

2. Experimental

2.1. Raw seawater

Surface seawater taken from Masan bay (Republic of Korea) was used in this study. Seawater samples were stored in a refrigerator at 3 ± 1 °C until used for the experiments. The characteristics of the raw seawater during the study period are summarized in Table 1.

2.2. Algae

Two dinoflagellates were used in this study. The difference between the two was the presence and absence of a cell wall. *Heterosigma akashiwo* has no cell

Table 1
Characteristics of the seawater during the study period

Parameter	Concentration
Temperature (°C)	19.8–23.5 (21.1) ^a
pH	7.75–7.90 (7.82) ^a
Conductivity (mS cm ⁻¹)	48.3–49.6 (48.8) ^a
Total dissolved solids, (g l ⁻¹)	34.1–34.8 (34.5) ^a
Total suspended solids (mg l ⁻¹)	2.2–4.3 (3.4) ^a
Turbidity (NTU)	1.2–2.1 (1.8) ^a
Particle count > 2 μm, number per ml	4,627–5,014 (4,836) ^a
COD-Mn (mg l ⁻¹)	2.0–3.1 (2.6) ^a
Chlorophyll-a (mg m ³)	2.6–4.3 (3.4) ^a

^aValues in parentheses indicate the average.

wall while *Prorocentrum micans* is protected by a cell wall, and *H. akashiwo* is smaller than *P. micans*. The characteristics of the two dinoflagellates are presented in Table 2.

First, surface seawater was filtered through 0.45- μm filter paper and sterilized at 121 °C for 30 min to eliminate other microorganisms. After cooling to room temperature, one milliliter of f/2 medium (Table 3) was prepared as described by Guillard (1975) and Guillard and Ryther (1962) and added to 1 L of the sterilized seawater filtrate. These algal species were cultured at 22 °C with 3,000 lux of illumination. Light was switched on for 14 h and off for the remaining 10 h.

2.3. Membrane experiments

Seawater spiked with marine algal cells was filtered through polysulfone hollow-fiber MF membranes with a nominal pore size of 2 μm (Kuraray, Japan). The schematic of the laboratory-scale MF system is shown in Fig. 1. Constant flow filtration was done at 20 ± 1 °C under the dead-end mode. The membrane was back-washed for 30 s after 30 min of filtration. The TMP was recorded using a digital pressure gauge (SMC, ISE60, Japan), and the permeate amount was quantified using a digital balance (A&D, EK-4100i, Korea). The filtration was terminated either when the TMP reached 100 kPa or when the filtration time reached 8 h.

2.4. Analysis

The algal cell count measurements were performed by putting one milliliter of a sample and Lugol's solution into the Sedgewick-Rafter chamber (50 mm \times 20 mm \times 1 mm). The number of algal cells was counted with a microscope. The phenol- H_2SO_4 method was used to measure the polysaccharide concentration in seawater with maltose as the standard.

Table 2
Characteristics of the dinoflagellates used in this study

Class	Raphidophyceae	Dinophyceae
Family	Raphidineae	Prorocentraceae
Genus	<i>Heterosigma</i>	<i>Prorocentrum</i>
Species	<i>akashiwo</i>	<i>micans</i>
Length (μm)	8–25	35–70
Width (μm)	6–15	20–50
Surface area ^a (m^2)	5.7×10^{-10}	6.0×10^{-9}

^aCalculation assumed that these were spheres in shape with the diameter of *H. akashiwo* and *P. micans* being 13.5 and 43.75 μm , respectively.

Table 3

Composition of the f/2 medium agar (Guillard, 1975; Guillard and Ryther, 1962)

Parameter	Component	Quantity
Nutrients	NaNO_3	75 mg
	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	5 mg
Trace metals	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	3.15 mg
	$\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$	4.36 mg
	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	9.8 μg
	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	6.3 μg
	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	22 μg
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	10 μg
Vitamins	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.18 mg
	Thiamine-HCl	0.1 mg
	Biotin	0.5 μg
	Cyanobalamin	0.5 μg

The sample was filtered through a 0.45- μm filter paper. Thus, the polysaccharide concentration was measured at 470 nm with a UV-vis spectrometer (Shimadzu, Japan). Polysaccharides on the membrane surface were pictured with a confocal laser scanning microscope (CLSM, Eclipse 90i, Nikon, Japan).

Because proteins are an important component of the EPS, the protein concentration must be measured. Thus, both the Lowry assay method and the Bradford method were tested for their accuracy in protein concentration measurements. Both methods produced accurate calibration curves when the sample was diluted in distilled water but not in seawater. Precipitates formed upon the addition of the Lowry agent to the seawater. The Bradford method also had a problem in this study such that the protein concentration could not be measured.

The chlorophyll-a concentration was measured with an automatic chlorophyll analyzer (HK-4000, Hwan Kyeong Bio Co., Ltd, Korea). The HK-4000 functions on the principle of photosynthesis. Algal cells emit a certain wavelength of fluorescence when they are exposed to light. The HK-4000 calculates the chlorophyll-a concentration based on the emitted fluorescence. To check the integrity of the HK-4000, the instrumentally measured values were compared with chemically measured values in accordance with Analytical Methods for Ocean Environment [30]. Because the concentration difference between the two methods was insignificant, the chlorophyll-a concentration was measured with the HK-4000 in this study.

To determine the MWD of the organic substances on the fouled membrane, high-pressure size exclusion chromatography (HPSEC, Shimadzu Corp., Japan) was used with a SEC column (Protein-pak 125,

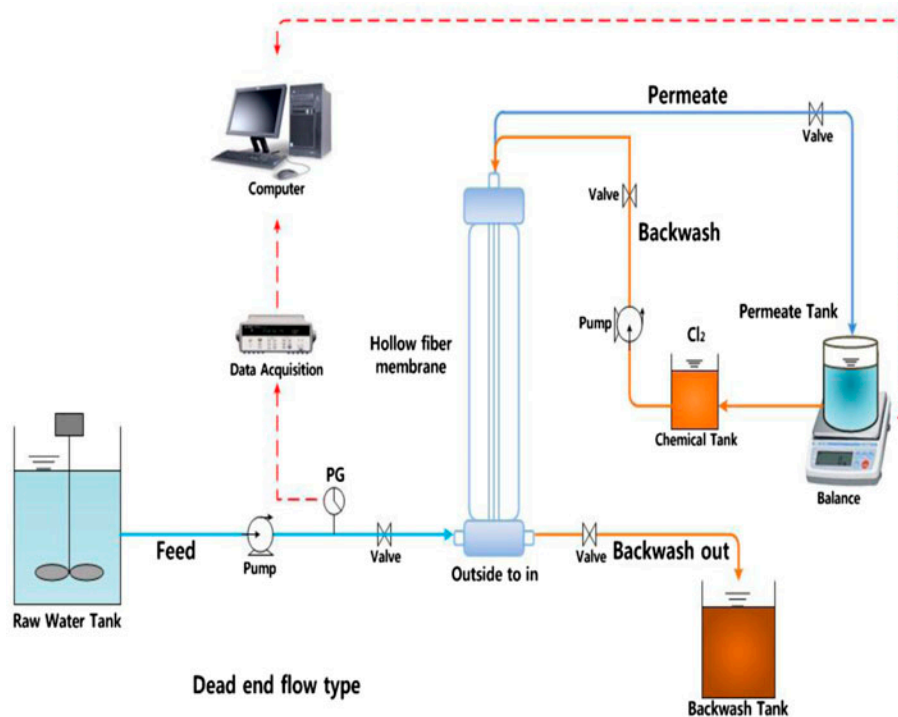


Fig. 1. Schematic diagram of the experimental setup.

Waters, Milford, USA). Calibration was done with a standard solution of polystyrene sulfonates with known molecular weights of 210, 1,800, 4,600, 8,000, and 18,000 Da. The MWD was measured with two detectors (a UV detector at 254 nm and a fluorescence detector) after the sample was filtered through 0.45- μm filter paper.

3. Results and discussion

3.1. TMP increase

It was determined before that the critical flux was 50 LMH ($1 \text{ m}^{-2} \text{ h}^{-1}$) by raw seawater filtration through the dead-end mode. Consequently, all experiments were done at a flux of 50 LMH. The TMP rose as the number of algal cells increased which is in agreement with the results of another study. Fig. 2 shows that higher cell concentrations had more severe TMP increases. The TMP increased to 20 kPa with 10,000 cells per ml in 8 h, 100 kPa with 30,000 cells per ml in 8 h, and 100 kPa with 50,000 cells per ml in less than 4 h. A similar TMP increase was observed for both algal species. This result indicates that the algal cell concentration was closely related to the TMP increase in the MF filtration system.

3.2. Polysaccharides excreted from the algal cells

The proportional relationship between the number of algae cells and the TMP in terms of the EPS component is an important factor. The addition of the algal cells substantially increased the polysaccharide concentration of the seawater. According to Fig. 3, the average polysaccharide concentration of raw seawater, less than 1.0 mg l^{-1} , increased to 3.3 mg l^{-1} upon the addition of 10,000 *H. akashiwo* cells per ml, to 4.4 mg l^{-1} at 30,000 cells/ml, and to 6.3 mg l^{-1} at 50,000 cells/ml, respectively. Polysaccharides released from *H. akashiwo* attached onto the membrane surface were visually confirmed by CLSM. Red spots as shown in Fig. 4 correspond to polysaccharides. Similar results were obtained when the algal species was changed to *P. micans*. This result also shows that polysaccharides excreted from algal cells are responsible for the TMP increase rather than the algal cells themselves.

Furthermore, the calculation of the polysaccharide mass balance around the MF system with *H. akashiwo* in the feed water is summarized in Table 4. The polysaccharide mass was calculated based on one cycle of filtration (30 min) as shown in Fig. 5. The positive values mean that the polysaccharides

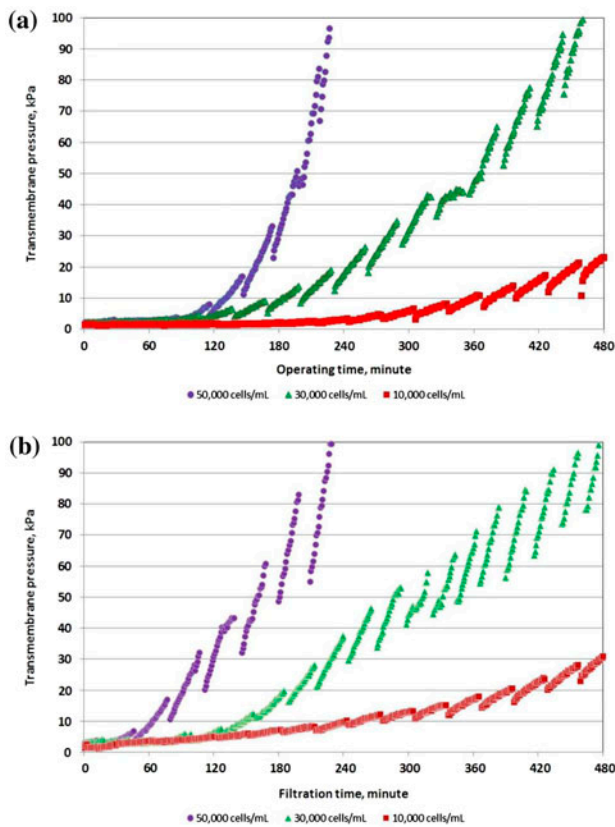


Fig. 2. TMP increase as a function of the number of algal cells in seawater—(a) *H. akashiwo* and (b) *P. micans*.

accumulated; in contrast, the negative values mean that the polysaccharides descended because of wash out from the MF system. According to Table 4, all the values of the accumulation term were positive which indicates that the polysaccharides accumulated within the membrane system as the filtration proceeded. Twenty-nine milligrams of polysaccharides per unit membrane area accumulated within the system with 10,000 cells/ml of algae. The amount increased to 74 mg at 30,000 cells/ml and to 170 mg at 50,000 cells/ml. The mass balance calculation also confirmed that polysaccharide excretion from algal cells influenced the TMP increase.

Table 4 also shows the ineffectiveness of backwashing to dislodge the polysaccharides from the membrane. There seems to be a limit in the amount of polysaccharides which can be detached by backwashing. Backwashing could detach 83% of the polysaccharides from the system when the algae was low (10,000 cells/ml), and the amount of polysaccharide accumulation was not substantial (29 mg/m²). As the cell number increased, the effectiveness of

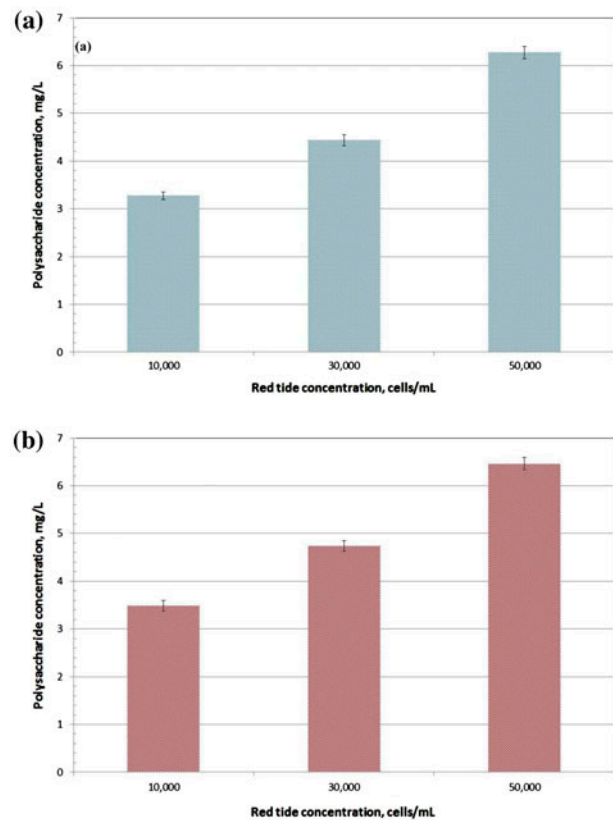


Fig. 3. Polysaccharide concentration as a function of the number of algal cells in seawater: (a) *H. akashiwo* and (b) *P. micans*.

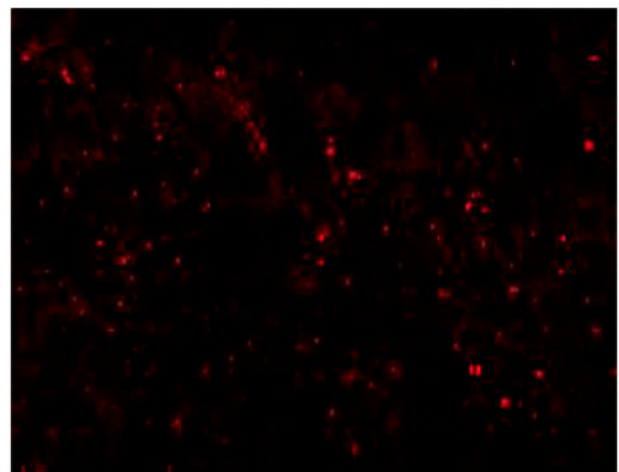


Fig. 4. Confocal laser scanning microscope image of the polysaccharides on the membrane.

backwashing diminished. Less than 30% of the polysaccharides were dislodged from the system when the algae amount was increased to 50,000

Table 4

Mass balance calculation of the polysaccharides in the MF system that received seawater spiked with *H. akashiwo* (filtration time of 30 min)

Cell count	Polysaccharides accumulated	Polysaccharides dislodged by backwashing
10,000 per ml	29 mg per m ²	24 mg per m ² (83%)
30,000 per ml	74 mg per m ²	30 mg per m ² (41%)
50,000 per ml	170 mg per m ²	49 mg per m ² (29%)

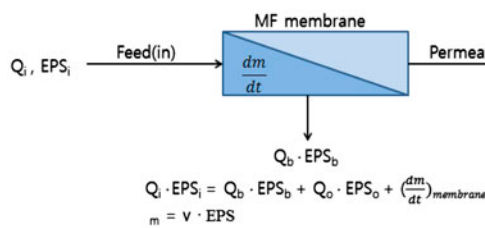


Fig. 5. Schematic of the mass balance of the polysaccharides around the MF system.

cells/ml. This result indicates that insufficient backwashing alone was responsible for retarding the TMP increase and that a separate pretreatment is necessary to reduce membrane fouling.

3.3. Effect of the algal cell wall

The results of the TMP and polysaccharide concentration variation according to the number of algal cells had no significant differences between the two species with and without cell walls. It was originally assumed that *H. akashiwo* without a cell wall would excrete more polysaccharides than that of *P. micans* with a cell wall because the cell wall could act as a barrier to polysaccharide transport. However, both species excreted similar amounts of polysaccharides resulting in similar TMP increases shown in Figs. 2 and 3. Then, the different sizes of these algal species were noted. Because polysaccharides were excreted through the surface of algal cells, larger species could excrete more polysaccharides than that of the smaller one. Because the polysaccharide excretion was counted based on the unit surface area, these species were assumed to have a spherical shape. The diameters of *H. akashiwo* and *P. micans* were assumed to be 13.5 and 43.75 μm , respectively. The surface area of *H. akashiwo* ($5.7 \times 10^{-10} \text{ m}^2$) was smaller than that of *P. micans* ($6.0 \times 10^{-9} \text{ m}^2$) by approximately ten times. Therefore, this result

revealed that *H. akashiwo* generated more polysaccharides ($0.2 \text{ kg l}^{-1} \text{ per m}^2$ of the cell surface area) than that of *P. micans* ($0.02 \text{ kg l}^{-1} \text{ per m}^2$ of the cell surface area). Moreover, this result also confirms that algal species without a cell wall excrete more polysaccharides than algal species with a cell wall. Because the polysaccharides were closely related to the TMP increase, the algal species without a cell wall could be more detrimental to membrane filtration in terms of fouling control.

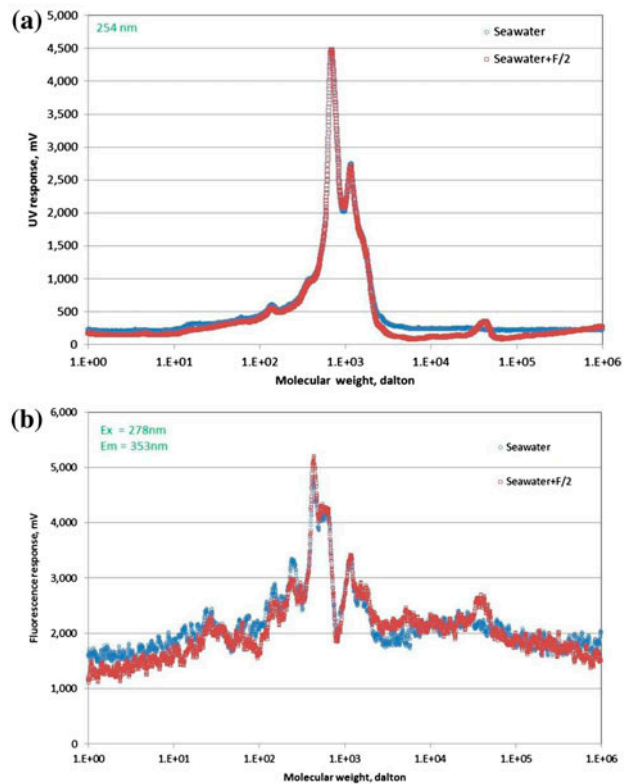


Fig. 6. MWD results of the seawater with and without the F/2 medium agar—(a) UV detector and (b) fluorescence detector.

3.4. MWD of the membrane fouling substances

The MWD of seawater containing algae was analyzed with and without the f/2 medium agar to determine whether there was any possible interference from the medium. According to Fig. 6, the f/2 medium agar did not interfere with the MWD analysis. There were three peaks for the raw seawater used in this study. Two peaks were observed by the UV detector (900 and 1,100 Da) and one peak by the fluorescence detector (440 Da). The addition of algal cells significantly increased the peak intensities at 1.1 kDa (UV detector) and at 600 Da and 22 kDa (fluorescence detector) as shown in Fig. 7. This result indicates that organic substances with a MW of 0.6, 1.1, and 22 kDa were associated with these dinoflagellates. They could be excreted by *H. akashiwo* and *P. micans*. Depending on the peak location, a difference in the peak intensity between the two algal species was noted. The difference was significant at the 22 kDa peak. *H. akashiwo* produced a substantially higher peak than that of *P. micans*. The difference was insignificant at the other peaks.

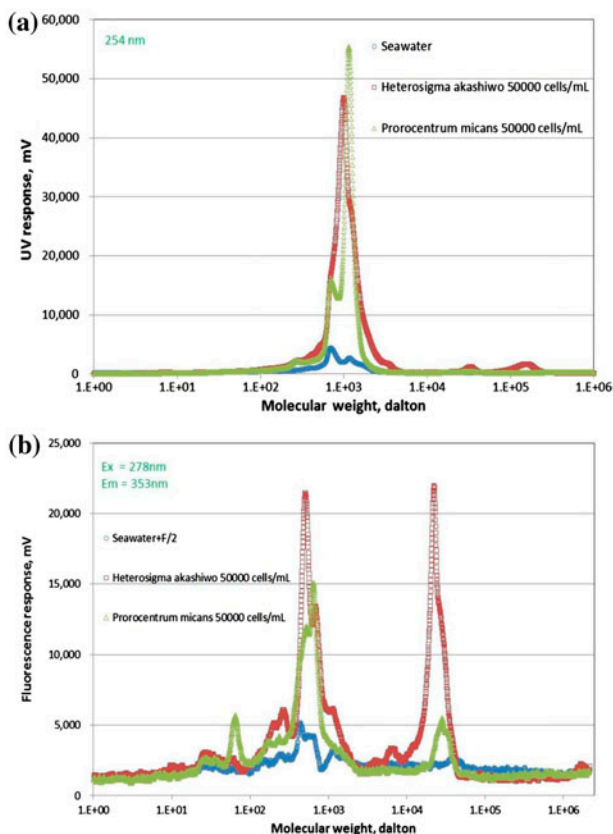


Fig. 7. MWD results of the seawater spiked with algal cells—(a) UV detector and (b) fluorescence detector.

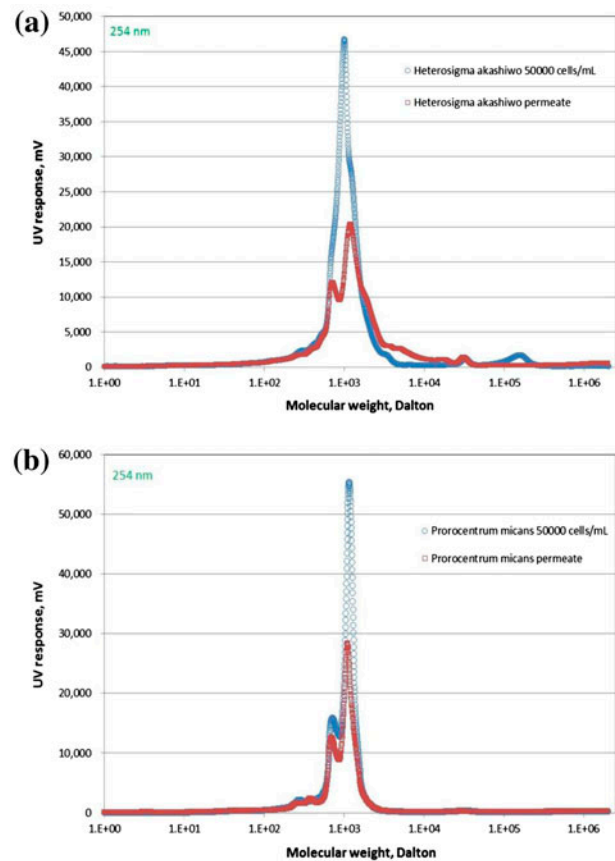


Fig. 8. Comparison of the MWD results by the UV detector before and after the membrane filtration of seawater spiked with algal cells—(a) *H. akashiwo* and (b) *P. micans*.

To identify the fouling substances, seawater spiked with algal cells was filtered through the MF system, and the MWD results before and after the membrane filtration were compared. The results are summarized in Fig. 8 (UV detector) and 9 (fluorescence detector). Fig. 8 shows a reduction in the peak at 1.1 kDa after filtration, which indicates that an organic substance with a MW of 1.1 kDa could accumulate within the MF system, possibly leading to fouling. Fig. 9 shows that the peak at 600 Da did not change after filtration; however, the 22 kDa peak was significantly reduced after filtration. This result suggests that small substances of 600 Da could pass through the MF system, but large substances of 22 kDa could accumulate within the membrane system. In summary, organic substances with a MW of 1.1 and 22 kDa could be related with the biofouling of MF systems. This result suggests that pretreatment should be adopted to reduce the membrane fouling caused by *H. akashiwo* and *P. micans*.

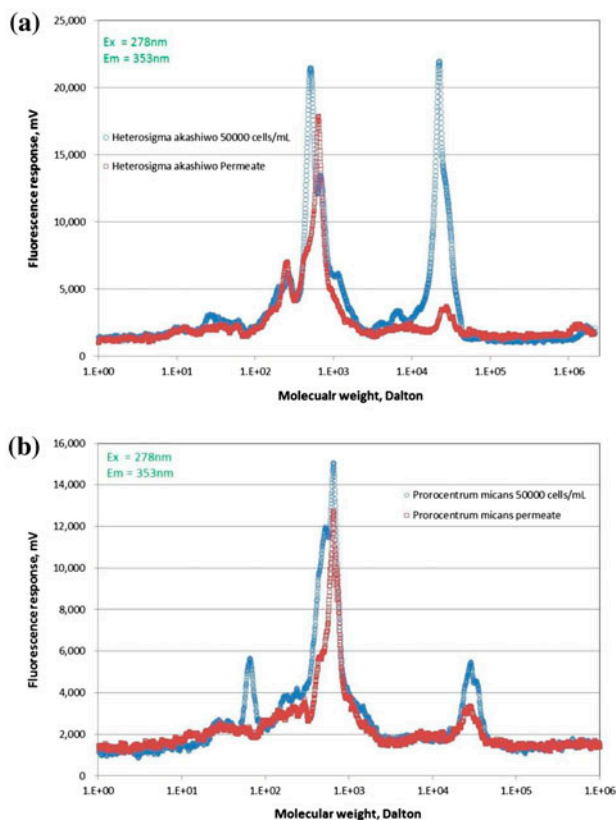


Fig. 9. Comparison of the MWD results by the fluorescence detector before and after the membrane filtration of seawater spiked with algal cells: (a) *H. akashiwo* and (b) *P. micans*.

4. Conclusions

In this study, the effect of marine algal cells on membrane fouling in an MF filtration system was investigated. Surface seawater spiked with two dinoflagellate species, *H. akashiwo* (without a cell wall) and *P. micans* (with a cell wall), was filtered through the MF system. Based on these study results, polysaccharides excreted from the algal cells were the primary cause of membrane fouling. The MWD analysis detected that the peak intensities increased at 0.6, 1.1, and 22 kDa after the addition of dinoflagellates into seawater. The organic substances related to the MWs were the polysaccharides from the algal cell excretion. Fouling could occur from the accumulation of 1.1 and 22 kDa organic substances in the MF system. These molecular weights (MW) are also present in the algal bloom phenomenon. Based on the unit surface area, *H. akashiwo* (without a cell wall) excreted more polysaccharides than that of *P. micans* (with a cell wall) which indicates that the presence of a cell wall has an important role in marine algal membrane fouling.

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