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A comparison of fouling and cleaning properties between ceramic and polymeric micro-filtration membranes for algal rich water

Kitae Park[a], Pooreum Kim[a], Hyoung Gun Kim[b], JiHoon Kim[a,*]

[a]*Graduate School of Water Resources, Sungkyunkwan University, Suwon, Korea, Tel. +82-31-290-7647; Fax: +82-31-290-7549; email: jjtt23@skku.edu (J.H. Kim)*
[b]*POSCO E&C tower, 241, Incheon tower-daero, Yeonsu-gu, Incheon, Korea*

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ABSTRACT

This paper aimed to analyze and compare the cleaning properties and mechanisms of membrane fouling caused when filtering through ceramic and polymeric membranes using *Chlorella*. Accordingly, ceramic membranes made of silicon carbide and polymeric membranes made of polyvinylidene fluoride andchlorinated-poly vinyl chloride were used, and membrane fouling caused by *Chlorella* was analyzed using the filtration resistance model by changing the operating flux. Also, this study performed alkali cleaning for fouled membranes and aimed to derive the cleaning properties by analyzing Fourier-transform infrared spectroscopy (FTIR) of cleaning wastewater. As a result, the compactness of cake layers increased with the hydrophobicity of the membrane surface, and it is considered that the membrane material characteristics are closely related to the cake layer formation. he cleaning properties were derived by analyzing chemical cleaning wastewater of fouled membranes. The FTIR peak of polysaccharide and protein decreased with increasing specific cake resistance. These results had an effect on removing foulants depending on the cake layer characteristics of foulants attached to the membrane surface in chemical cleaning. Particularly, cake layers with a compact structure had a direct effect on removing polysaccharide among foulants in chemical cleaning. Thus, it is considered that a cake structure is an important element in cleaning efficiency.

Keywords: Algae; Membrane fouling; Ceramic membrane; Polymeric membrane; Cleaning

1. Introduction

The development of ceramic membrane manufacturing technologies has allowed becoming as competitive as polymeric membranes, and then they have received attention from the water treatment field. The excellent chemical resistance of ceramic membranes makes it possible to solve problems related to periodic repair and replacement as a disadvantage of polymeric membranes. However, little is known about the fundamental properties of ceramic membrane fouling caused by algal materials.

Previous studies have provided valuable insight into the following factors affecting membrane fouling: membrane type, material properties, process structure, operating conditions, water quality parameters, and cleaning strategies [1,2].

Also, it has been reported that membrane fouling is closely related to membrane materials, pore size, surface porosity, pore morphology, and hydrophobicity [3].

In particular, many previous studies have shown that membrane materials' surface properties (e.g. hydrophobicity, roughness, and zeta-potential) are closely correlated with foulants [4,5]. Although polymeric membranes have been mainly studied thus far, there has recently been a growing interest in alternative membrane materials.

Ceramic membrane processes have rapidly gained attention because of many more specific advantages compared to

* Corresponding author.

existing polymeric membrane processes. The excellent chemical resistance of ceramic membranes made from inorganic matter makes possible aggressive cleaning approach. The application of aggressive clean-in-place (CIP) also makes it possible to extend membrane life by removing irreversible fouling.

Ceramic membranes have been applied to drinking water treatment for 50 facilities in Japan in the last 10 years. Recently, a 2.5 mega gallons per day pilot plant has been studied in California, the United States [6,7].

Ceramic membranes have been widely applied in water treatment, but little is known about their performance properties, particularly membrane fouling caused by algae.

It has been reported that fouling is caused by algal cells and extracellular organic matter (EOM) including polysaccharides proteins, lipids, and humus when applying algae-rich water to membrane processes [8]. Membrane fouling takes the form of adsorption or gelation between algal particles and membrane surface, pore blockage, or cake layer [9].

Thus, this paper aimed to analyze and compare the cleaning properties and mechanisms of membrane fouling caused when filtering through ceramic and polymeric membranes using *Chlorella*. Membrane fouling was analyzed using the filtration resistance model by changing the operating flux based on the materials of ceramic and organic membranes. As described above, this study aimed to compare the properties of membrane fouling and CIP between ceramic and polymeric membranes by analyzing the cleaning recovery rate and cleaning wastewater of the fouled membranes with the CIP (alkali).

2. Materials and methods

2.1. Characteristics of the raw water

The single culture samples of *Chlorella* algae were collected from Danyang *Chlorella* in South Korea. To understand fouling by membrane material, the *Chlorella* concentration was adjusted to 500 mg/L (19.9 g/m^2 of algal deposition) at suspended solids.

2.2. Experimental set-up

All the experiments were conducted using a laboratory-scale membrane set-up, mainly including a raw water tank, a constant level water tank, a peristaltic pump, a pressure transducer, and a data acquisition system. The ceramic membrane was a flat type silicon carbide (SIC) Microfiltration membrane module with an effective membrane area of 0.0652 m^2 and a nominal pore size of 0.1 μm polyvinylidene fluoride (PVDF) material of submerged hollow type and membrane module of chlorinated-poly vinyl chloride (C-PVC) material of immersed flat type were used and nominal pore size of 0.1 μm. The detailed specifications of the membranes used in this study are shown in Table 1. The reactor (effective volume of 16.4 L) was fed with a raw solution through the constant level tank and the effluent was drawn directly from the membrane module by the peristaltic pump (EMS-2000S, Korea). A pressure transducer (PTP708 Tuopu Electric, Korea) was connected to a laptop, was used to continuously monitor the transmembrane pressure (TMP).

2.3. Operating conditions

The critical flux was measured based on membrane materials under the feed water conditions as shown in Table 2. The critical fluxes of SIC, PVDF, and C-PVC were 100, 20, and 40 LMH, respectively. The critical and sub-critical filtration conditions were selected based on the above experimental results, and the operating conditions were chosen as shown in Table 3. Moreover, the reactor temperature was maintained at 20°C ± 0.5°C using a water bath, and each membrane was washed and flushed by ultrapure water under the same conditions before use.

2.4. Measurement of resistance

Membrane fouling due to algal deposition was studied by measuring the following equations at a constant permeate flux and water temperature. In filtration experiments, the specific membrane resistance was first measured using ultrapure water.

$$R_c = \frac{\Delta P}{\mu J} - R_m \quad (1)$$

Table 2
Characteristics of the raw water

Parameters		Concentration
Chl-a		7,300 ± 110 mg/m^3
Cell		19.9 ± 1.2 g/m^2
Suspended solids		500 ± 45 mg/L
EPS	Protein	3.91 ± 0.8 mg/L
	Polysaccharide	44.5 ± 4.2 mg/L

Table 1
Physical characteristics of membrane

Item	Material	Supplier	Pore size (μm)	Surface area (m^2)	Type	Contact angle (°)	Clean water permeability (LMH/bar at 20°C)
Ceramic	Silicon carbide	Cembrane		0.00652	Flat type	10.53	5,000
Polymeric	PVDF	LG electronic	0.1 μm	0.06	Hollow fiber	82.99	2,300 at 20°C
	C-PVC	Pure Envitech		0.05	Flat type	63.7	1,200 at 20°C

Table 3
Operating conditions

Parameter	Ceramic membrane	Polymeric membrane	
	Silicon carbide	PVDF	C-PVC
Flux (LMH, $m^3/m^2/h$)	80, 100	10, 20	20, 40
Temperature (°C)		20	

where R_c is the resistance of algal cake (1/m); ΔP is transmembrane pressure (Pa); J is filtration flux ($m^3/m^2/s$); R_m is the resistance of membrane (1/m).

R_c can be made from the perspective of specific cake resistance as follows:

Furthermore, α is directly affected by the cake pressure gradient ΔP, and the functions of α and ΔP are taking the following forms [10–14]:

$$\alpha = \alpha_0 \left(\Delta P\right)^n \tag{2}$$

where α_0 is empirical constant; n is cake compressibility factor n has values between 0 and 1. It means non-compressibility as it approaches 0 and compressibility as it approaches 1 [15].

The reversibility and irreversibility according to the coagulant injection rate were analyzed using the following methods: Membrane fouling was calculated by the following equations in defining the filtration resistance obtained by filtering ultrapure water through the initial membrane, the final filtration resistance of the fouled membrane by filtering using the target raw water to be treated, and the filtration resistance obtained by filtering using ultrapure water after physical cleaning as R_0, R_1, and R_2, respectively:

$$\text{RF} = \frac{R_2 - R_1}{R_0 - R_1} \tag{3}$$

$$\text{IF} = \frac{R_0 - R_2}{R_0 - R_1} \tag{4}$$

$$\text{TF} = \text{RF} + \text{IF} = 1 \tag{5}$$

RF means reversible fouling, IF means irreversible fouling, and the total membrane (TF) becomes 1.

3. Results and discussion

3.1. Flux curves and reversibility analyses

Fig. 1 shows the changes in TMP according to membrane materials and flux. As for the rate of change in TMP with the passage of time, C-PVC showed 0.082 and 0.110 kgf/cm^2/min at 20 and 40 LMH, respectively. PVDF showed 0.089 and 0.262 kgf/cm^2/min at 10 and 20 LMH, respectively.

Furthermore, SIC showed 0.068 and 0.083 kgf/cm^2/min at 80 and 100 LMH, respectively. The hydrophilicity of membrane materials made possible operations at high flux and low TMP.

It is known that fouling is caused by algae cells and EOM including polysaccharides proteins, lipids and humus [8] and these substances form hydrophobicity by amino group functions. Additionally, membrane materials are closely related to fouling evolution. It has been reported that fouling is accelerated due to interactions with hydrophobic membranes when foulants to be removed are hydrophobic [16]. Based on these experimental results, high flux and low rate of change in TMP were found according to the hydrophilicity of the membrane surface (inversely proportional to the contact angle). It is considered that membrane materials are important factors when applying algal-rich water to membrane processes.

Fig. 2a shows the reversible (Rr) and irreversible (Rir) filtration resistance based on membrane materials. As shown in the figure, polymeric membranes show higher filtration values than ceramic membranes. Also, relatively hydrophobic PVDF showed higher fouling resistance values than C-PVC, and the results showed that the membrane contact angle was an important factor in filtering feed water including algae.

Fig. 2b shows the fouling ratio by operating conditions. In the same membrane, irreversible fouling increased with increasing flux. As a result of analyzing reversible and irreversible filtration resistance according to membrane materials, irreversible filtration resistance increased in proportion to hydrophobicity.

3.2. Mechanisms of membrane fouling

Fig. 3 shows R_a and R_c behaviors to analyze the fouling mechanism according to membrane materials. As shown in Fig. 3, fouling resistance against R_a is dominant in the whole. Figs. 3a and b show the fouling resistance of C-PVC among polymeric membranes with time. ΔR_a shows a tendency to increase from 0.00721 to 0.00877 at a flux of 20 to 40 LMH.

On the other hand, ΔR_c showed a tendency to decrease from 0.00256 to 0.00179. Figs. 3c and d show the fouling resistance of PVDF with time. ΔR_a shows a tendency to increase from 0.00774 to 0.0174 at a flux of 10–20 LMH.

ΔR_c showed a tendency to increase from 0.00116 to 0.00154. Figs. 3e and f show the fouling resistance of SIC

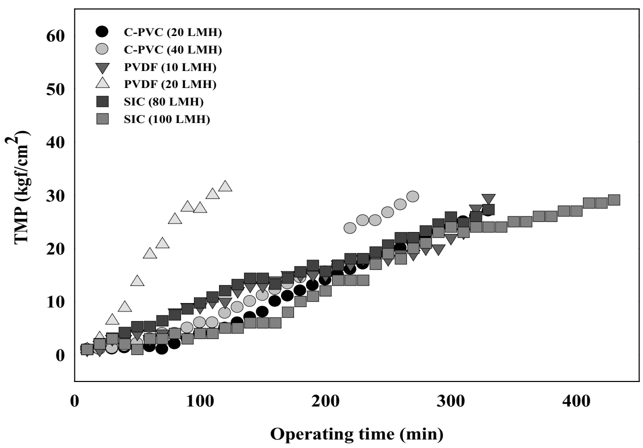


Fig. 1. Comparison of TMP according to membrane materials.

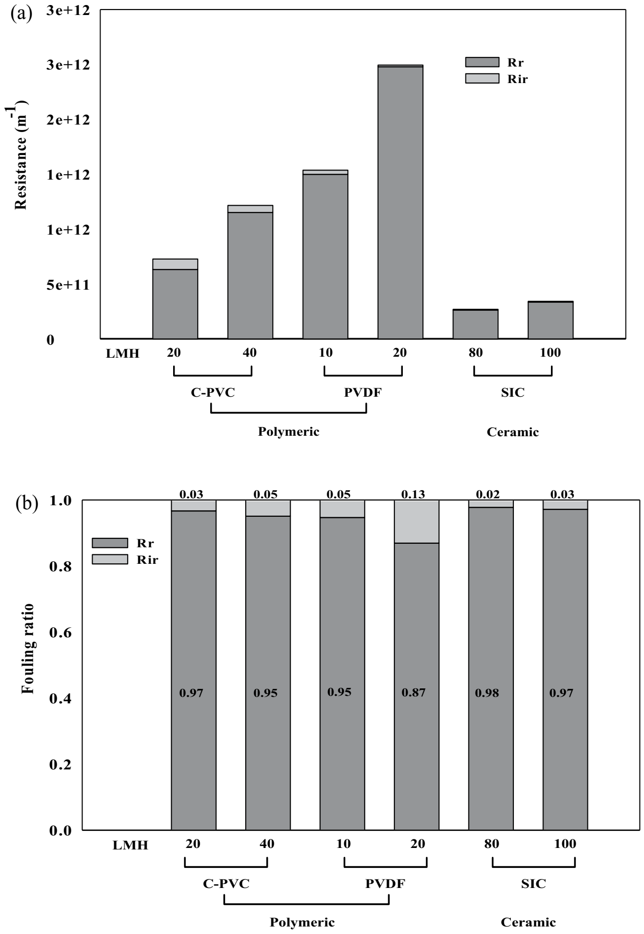


Fig. 2. Analysis results of the fouling ratio based on membrane materials and flux (a) Rr, Rir and (b) (b) fouling ratio.

among ceramic membranes with time. ΔR_a shows a tendency to decrease from 0.00504 to 0.00587 at a flux of 80–100 LMH.

However, ΔR_c showed a tendency to increase from 0.00038 to 0.00074. Polymeric membranes showed dominant cake fouling resistance in the initial filtration, but subsequently, the adsorption resistance of foulants became dominant. Conversely, in ceramic membranes, the adsorption resistance of foulants was dominant even in the initial filtration.

Fig. 4 shows the specific cake resistance based on membrane materials and flux. The specific cake resistances of C-PVC among polymeric membranes were 2.69E + 13 and 9.00E + 12 m/kg at a flux of 20 and 40 LMH, and those of PVDF was 1.33E + 14 and 1.19E + 14 m/kg at a flux of 10 and 20 LMH.

The specific cake resistances of SIC among ceramic membranes were 2.24E + 12 and 9.29E + 11 m/kg at a flux of 80 and 100 LMH. Specific cake resistance of both polymeric and ceramic membranes showed a tendency to decrease with increasing flux.

Park [17] reported that rapid cake fouling occurred with increasing effective pressure but rapidly formed cake fouling layers consisted of a large and loose structure.

It is considered that specific cake resistance decreased because cake layers with a relatively loose structure are formed by high effective pressure on the membrane surface with increasing flux also in this experiment.

The specific cake resistances according to membrane materials were PVDF, C-PVC, and SIC, in that order. It is considered that the specific cake resistance showed high values because hydrophobic membrane materials formed a cake layer with a compact structure due to interactions with a hydrophobic foulant *Chlorella*.

3.3. Chemical cleaning

Chemical cleaning is performed to recover the membrane performance with reduced flux by resolving the foulant structure and removing foulant species. The efficiency of chemical cleaning depends on the mass transfer of chemicals and foulants, the diffusion of active species, and the effects of reactions to physical properties. The experiments were conducted to examine the cleaning properties of chemical cleaning for fouled membranes depending on membrane material and flux under the cleaning conditions at 3 h and pH 12. Fig. 5 shows the analysis results of cleaning wastewater depending on membrane materials using Fourier-transform infrared spectroscopy (FTIR) spectroscopy. Although the peak values of fatty acid and protein components were high in proportion to the hydrophilicity of SIC (80 LMH), C-PVC (20 LMH), and PVDF (10 LMH) membranes, they were high in proportion to the hydrophobicity of polysaccharide.

Fig. 6 shows the FTIR peak values depending on membrane materials with flux. With regard to fatty acid and protein, C-PVC and SIC showed a high peak on the critical flux, but PVDF showed a higher peak on the subcritical flux. As for polysaccharide, C-PVC and SIC showed a high peak on the subcritical flux, and PVDF showed a similar peak regardless of flux. As shown in Fig. 4, the specific cake resistance is related to the FTIR peak of cleaning wastewater, and protein and polysaccharide showed a higher peak inversely proportional to the compactness of the structure foulants deposited on the membrane. On the other hand, fatty acid was related to the membrane surface properties, and it seems easy to remove fatty acid under alkaline conditions proportional to the hydrophilicity of the membrane surface. Based on the above results, the foulant structure depending on membrane material properties directly affected chemical cleaning for *Chlorella* foulants.

4. Discussion

This paper aimed to analyze and compare the cleaning properties and mechanisms of membrane fouling caused when filtering through ceramic and polymeric membranes using *Chlorella*. Accordingly, ceramic membranes made of silicon carbide and polymeric membranes made of PVDF and C-PVC were used, and membrane fouling caused by *Chlorella* was analyzed using the filtration resistance model by changing the operating flux. Also, this study performed alkali cleaning for fouled membranes and aimed to derive the cleaning properties by analyzing FTIR of cleaning wastewater. The conclusions were drawn as follows:

This study derived the fouling properties according to membrane materials at critical and subcritical flux using

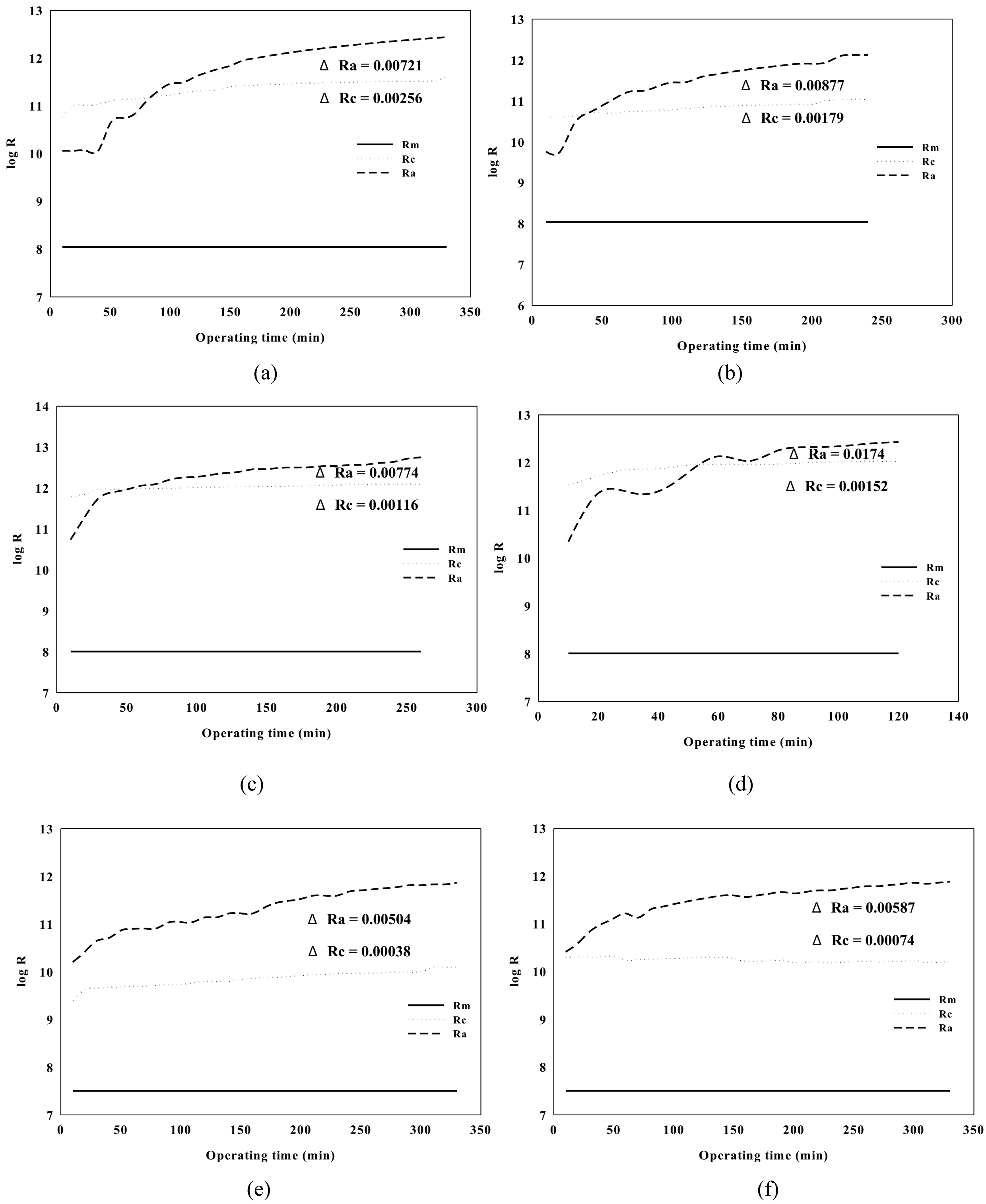


Fig. 3. R_a and R_c behaviors with time (a) C-PVC 20 LMH, (b) C-PVC 40 LMH, (c) PVDF 10 LMH, (d) PVDF 20 LMH, (e) SIC 80 LMH, and (f) SIC 100 LMH.

Chlorella feed water. Based on the results, membrane fouling by *Chlorella* directly affected the membrane surface characteristics. In particular, fouling reversibility increased with decreasing contact angle of the membrane surface.

With regard to the membrane fouling mechanism, polymeric membranes showed dominant cake fouling resistance in the initial filtration, but adsorption fouling became dominant with the passage of filtration. Conversely, in ceramic

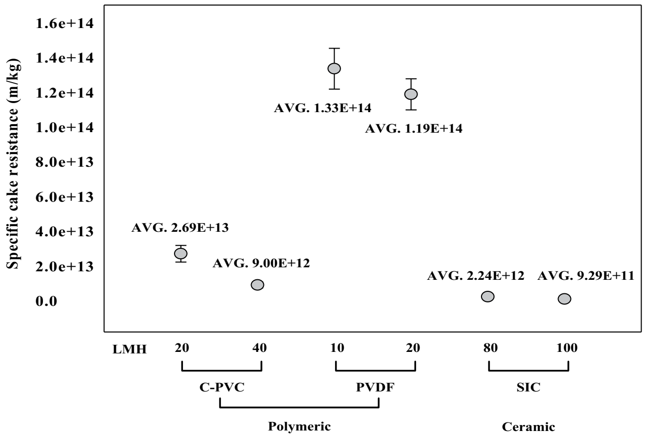


Fig. 4. Comparison of specific care resistances according to membrane materials.

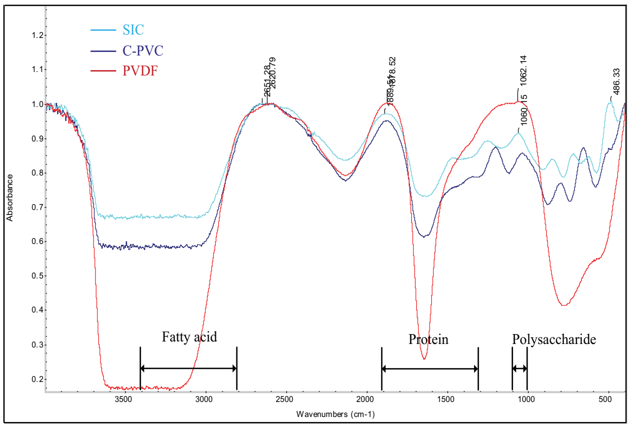
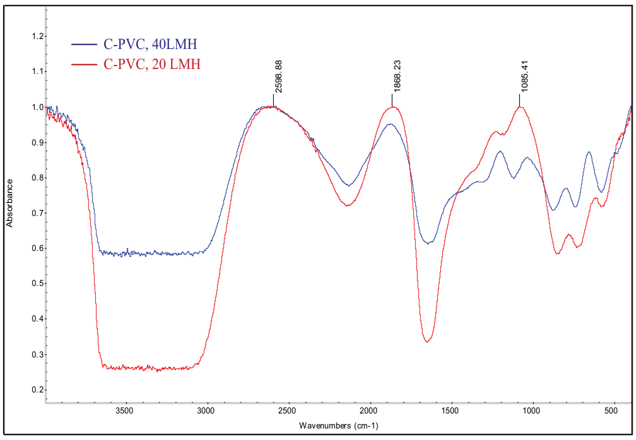


Fig. 5. FTIR peak according to membrane materials.-

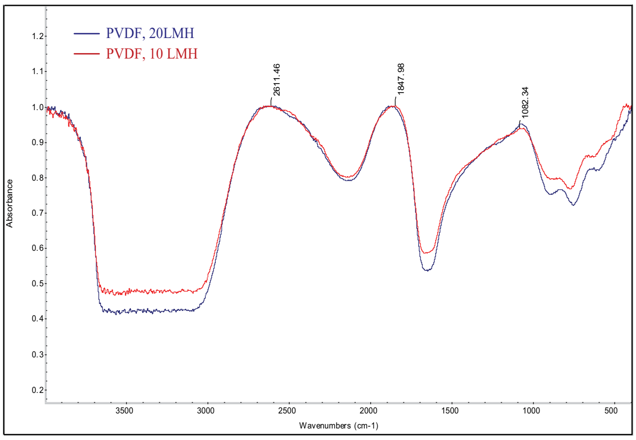
membranes, the adsorption resistance was dominant even in the initial filtration, and fouling form varied depending on the membrane surface properties. Moreover, this study aimed to examine the cake layer characteristics on the membrane surface by analyzing the specific cake resistance.

As a result, the compactness of cake layers increased with the hydrophobicity of the membrane surface, and it is considered that the membrane material characteristics are closely related to the cake layer formation.

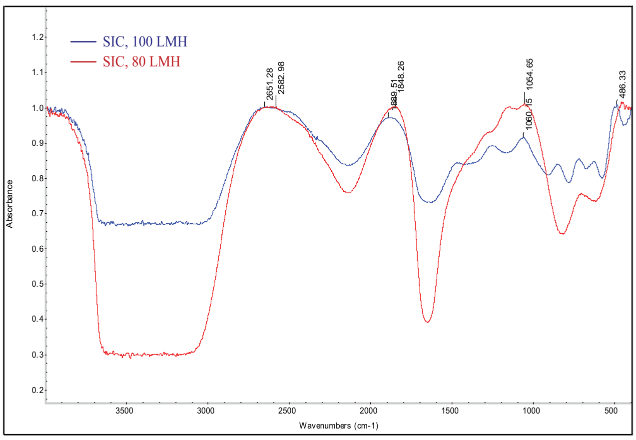
The cleaning properties were derived by analyzing chemical cleaning wastewater of fouled membranes. The FTIR peak of polysaccharide and protein decreased with increasing specific cake resistance. These results affected removing foulants depending on the cake layer characteristics of foulants attached to the membrane surface in chemical cleaning. Particularly, cake layers with a compact structure had a direct effect on removing polysaccharide among foulants in chemical cleaning. Thus, it is considered that a cake structure is an important element in cleaning efficiency.



(a)



(b)



(c)

Fig. 6. Comparison of FTIR peaks of chemical cleaning wastewater by membrane materials and flux (a) C-PVC, (b) PVDF, and (c) SIC.

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