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Harvesting of microalgae via submerged membranes: flux, fouling and its reversibility

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Abstract. The purpose of this study was to investigate membrane fouling caused by microalgal cells in submerged membrane systems consisting of polymeric and ceramic microfiltration membranes. In this study, one polymeric (flat-sheet, pore size: 0.2 μm) and two ceramic (flat-sheet, pore size: 0.2 μm and cylindrical, pore size: 1 μm) membranes were used. Physical cleaning was performed with water and air to determine the potential for reversible and irreversible membrane fouling. The study results showed that substantial irreversible membrane fouling (after four filtration cycles, irreversible fouling degree 27% (cleaning with water) and 38% (cleaning with air)) occurs in the polymeric membrane. In cleaning studies performed using water and air on ceramic membranes, it was observed that compressed air was more effective (recovery rate: 87-91%) for membrane cleaning. The harvesting performance of the membranes was examined through critical flux experiments. The critical flux values for polymeric membrane with a pore size of 0.20 μm and ceramic membranes with a pore size of 0.20 μm and 1 μm were $\leq$95 L/m^{2}hour, $\leq$70 L/m^{2}hour and $\leq$55 L/m^{2}hour, respectively. It was determined that critical flux varies depending on the membrane material and the pore size. To obtain more information on membrane fouling caused by microalgal cells, the characterization of the fouled polymeric membrane was performed. This study concluded that ceramic membranes with a pore size of 0.2-1 μm in the submerged membrane system could be efficiently used for microalgae harvesting by cleaning the membrane with compressed air at regular intervals.

Keywords: membrane; microalgae; critical flux; fouling; reversibility

1. Introduction

In recent years, the membrane filtration method has been developed as a promising and improved method for harvesting microalgae. The membrane technology method is generally less costly than centrifugation (Bilad *et al.* 2012). Nearly all of the algal biomass can be recovered through membrane filtration (Bilad *et al.* 2012). In addition, these systems do not require any chemicals, such as coagulating agents (Bilad *et al.* 2012) and their energy consumption is fairly low (Bilad *et al.* 2013). Also, it is possible to remove wastewaters effectively using integration two step processes such as microalgal treatment followed by membrane filtration (Ibrahim *et al.* 2015).

Many studies on the harvesting of microalgal cells confirm the effectiveness of the crossflow

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filtration method (Zhang *et al.* 2010), (Ahmad *et al.* 2012). The high crossflow velocities in this system generate high shear rates that prevent the accumulation of microalgal cells on the membrane surface, thus enabling high harvesting performances (Bilad *et al.* 2012). However, the high crossflow velocities and transmembrane pressures applied in this system result in considerable energy consumption (Bilad *et al.* 2012). In addition, high shear rates may cause the breakdown of microalgal cells and the secretion of extracellular organic materials (Bilad *et al.* 2012).

Another method proposed for the efficient harvesting of microalgae is the submerged membrane microfiltration technique (Bilad *et al.* 2013). Submerged microfiltration can be performed at low operating pressures, which prevents any crossflow velocity in this system; consequently, microalgal biomass is not damaged during harvesting, and can be utilized for the production of various valuable products (Bilad *et al.* 2012). Bilad *et al.* (2012) previously examined the harvestability of the species *Chlorella vulgaris* and *Phaeodactylum tricornutum* with the submerged membrane system by using PVDF membranes with three different porosities. Based on their study results, they reported that submerged microfiltration is a low-cost process for harvesting microalgal cultures that allows for high harvesting efficiencies when combined with the centrifuge method (Bilad *et al.* 2012). Babel and Takizawa (2010) investigated membrane fouling caused by microalgal cells on cellulose ester and polyvinylidene difluoride (PVDF) membranes using the vacuum filtration method, and reported that microalgal cells cause significant membrane fouling in both types of polymeric membrane (Babel and Takizawa 2010).

Membrane fouling is most significant disadvantage that limits the widespread use of membrane systems in microalgae harvesting (Zhang *et al.* 2014, Qu *et al.* 2015). Membrane fouling decreases permeate flux and membrane lifespan, thereby increasing energy consumption and operating costs. Many studies have reported that membrane fouling caused by microalgal cells mainly results from the extracellular organic materials secreted by these cells (Zhang *et al.* 2014, Zhang *et al.* 2010, Qu *et al.* 2014). The major components of the extracellular organic materials are polysaccharides, proteins, nucleic acids, lipids, and small organic materials (Ahmad *et al.* 2014).

Other important factors that are believed to affect membrane fouling include system operating conditions (such as transmembrane pressure, crossflow velocity) and membrane properties (such as pore size, thickness and surface charge) (Ahmad *et al.* 2014).

Qu *et al.* (2014) investigated the effect of membrane pore size and surface hydrophobicity on membrane fouling caused by the extracellular organic materials in polymeric polyethersulfone membranes. It has been reported that while membranes with larger pore sizes have more flux reduction, they also have less adsorptive fouling, which leads to higher recoverable flux (Qu *et al.* 2014). In addition, Sun *et al.* (2013) investigated the performance of polymeric microfiltration and ultrafiltration membranes in harvesting microalgal biomass. The results of their experiments showed that the membrane materials play an important role in the harvest of microalgal biomass (Sun *et al.* 2013). Bilad *et al.* (2014) reported that ceramic membranes with high mechanical strength can be used instead of polymeric ultrafiltration membranes for harvesting algal biomass. Bhave *et al.* (2012) studied the effective dehydratibility of microalgal biomass by using the polymeric hollow fibers and tubular ceramic membranes in crossflow membrane systems. They reported that the polymeric membrane and ceramic membrane ensured 90-95% and >99% dehydration, respectively (Bhave *et al.* 2012).

Although there are many studies on harvesting microalgal cells with membrane systems, the membrane fouling problem caused by microalgal cells has not yet been fully elucidated. The effect of membrane properties on flux reduction and the effect of fouled membrane cleaning methods on

flux recovery need to be investigated in detail. Therefore, the aim of this study was to investigate membrane fouling caused by microalgal cells in low operating cost submerged membrane systems by using one polymeric (flat sheet) microfiltration membrane with a pore size of 0.2 μm and two ceramic (flat sheet and cylindrical) microfiltration membranes with pore sizes of 0.2 μm and 1 μm. This study examined the critical flux values of membranes, and the reversible and irreversible fouling potentials after the cleaning process with water and air. Moreover, SEM, ATR-FTIR, and hydrophobicity / hydrophilicity analyses of the polymeric flat-sheet membrane were performed to gain more information about membrane fouling caused by microalgal cells.

2. Materials and methods

2.1 Cultivation of the microalgae

In this study, the unicellular green algae, *Chlorella vulgaris* (average cell diameter: 5 μm) was used. Since *Chlorella vulgaris* is a species with high protein, carbohydrate, and fat content, it is widely used in the biofuel (Al-lwayzy *et al.* 2014), food, cosmetic, and pharmaceutical (Yeh *et al.* 2010) industries. The process of cultivation was performed in a 200 L pilot-scale tubular photo bioreactor (PBR) (Varicon Biofence). The treated waste leachate from the İSTAÇ A.Ş. Odayeri Solid Waste Storage Facility was used as the nutrient medium in the cultivation process. The waste leachate was obtained from the output of the nanofiltration membrane. The characterization of the nutrient medium was performed in our previous study (Elcik *et al.* 2016). The microalgal cells were cultivated until they reached sufficient density during the 30-day cultivation period. The pH of the medium was maintained at 7.5±1 using 0.1 N HCl and NaOH. Prior to the study procedure, all glassware items were sterilized in an autoclave (121℃ for 15 minutes).

2.2 Determination of the algal biomass concentration

To compare the harvesting performances of the different membranes, microalgal harvesting experiments were performed at 0.5 g /L dry biomass concentration. The calculation of the algal biomass dry weight was performed according to the method described in our previous study (Elcik *et al.* 2016).

2.3 Membrane

In this study, two ceramic and one polymeric microfiltration membranes with different

Table 1 The characteristics of microfiltration membranes

Membrane	Material	Pore size (μm)	Effective area (cm^2)	Manufacturer
Ceramic	Silica	1	113	Dumlupinar University Department of Materials Science and Engineering
SiCFM-00145	Silicon karbide	0.2	93	Cembrane A/S
MV020	PVDF	0.2	53.8	Microdyn-Nadir

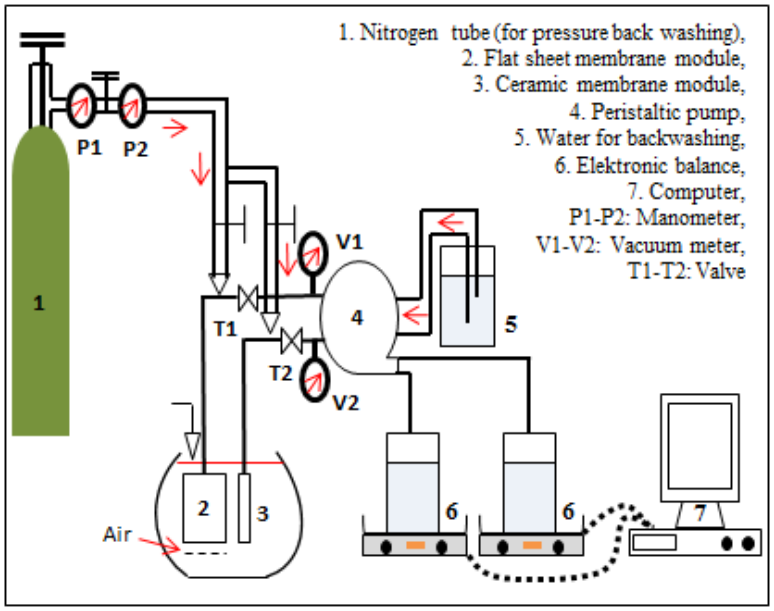


Fig. 1 Schematic diagram of the submerged membrane system

properties were used. Information on the membrane properties is provided in Table 1. Prior to the experiments, chemical residues were removed from the membrane surfaces by flushing pure water through the clean membranes for 30 minutes.

2.4 Experimental procedures

2.4.1 Membrane test unit

The experiments were performed using a laboratory-scale submerged membrane system. The experimental setup of the membrane system is shown in Fig. 1. The microalgae harvesting process was carried out through vacuum pressure created using a peristaltic pump. The membrane modules, submerged in an approximately 10-litre glass reactor, were operated at the specified vacuum rates. To reduce the fouling effect in the polymeric flat sheet membrane module, air with a flow rate of 3.5 L/min was blown through the whole effective filtration area by using diffusers positioned close to the membrane surface in front of the membrane module. In addition, pressure fluctuations were monitored with a vacuum gauge located in the membrane system. To calculate the membrane flux, the amount of permeation was calculated using an electronic balance connected to the computer.

Cleaning was performed with water and air in order to test the reusability of membranes. The cleaning process with air was performed with nitrogen gas, applied for 5 minutes at a pressure of 0.5 bar. Cleaning with water was performed by applying pure water from a separately prepared backwashing tank for 5 minutes at a pressure of 0.3 bar.

2.4.2 Measurement of the reversible-irreversible fouling

Measurements were performed at a transmembrane pressure of 0.01 to 0.1 bar and pH of 7±0.1. Prior to each experiment, pure water flux of each membrane was measured for 30 minutes, and the

obtained value was designated as $J_{(0)}$. Each filtration experiment consisted of four continuous filtration cycles. In each cycle, 0.5 g/L concentration of microalgal culture was filtered for 30 minutes. Each filtration cycle consisted of three steps: (1) filtration of microalgal culture; (2a) cleaning with air=nitrogen, applied for 5 minutes at a pressure of 0.5 bar, (2b) backwashing with water=pure water, applied for 5 minutes at a pressure of 0.3 bar; and (3) filtration with pure water for 30 minutes. The subsequent flux value of each filtration process was labelled $J_{X(n)}$ (n:cycle number). The subsequent pure water flux after cleaning was labeled J_n. Following this, reversible fouling, cumulative irreversible fouling, and total fouling for each filtration cycle were calculated according to Jermann *et al.* (Jermann *et al.* 2008) by using the Eqs. (1)-(3)

$$Irreversible\ fouling\ (IF)_n = \frac{J_0 - J_n}{J_0} \tag{1}$$

$$Total\ fouling\ (TF)_n = \frac{J_0 - J_{x(n)}}{J_0} \tag{2}$$

$$Reversible\ fouling\ (RF)_n = TF_n - IF_n \tag{3}$$

2.4.3 Characterization of the fouled membrane

Contact angles were measured by the sessile drop technique for MV020 polymeric membrane hydrophobicity/hydrophilicity analysis. Measurements were performed 30 seconds after the contact of 10 μl pure water drop with the membrane surface (this time is sufficient to stabilize the angle value). At least three measurements were taken for each membrane.

To understand the effects of microalgal contaminants on the membrane surface, the scanning electron microscope (SEM) images of the polymeric MF membrane were taken with a JSM-7001F brand thermal field SEM device. The membranes were first dried at 24±1℃ and then coated with gold.

To define the functional groups of microalgal pollutants deposited on the membrane surface, an Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy (Cary 630, Agilent) device was used. All spectra were measured by performing an average of 10 scans at 4 cm^{-1} spectral resolutions within a range of 4000-400 cm^{-1} and at intervals of 1 cm^{-1}. Prior to each analysis, background correction scans were performed for the ambient air. The scans were recorded with Agilent Microlab (version 5.0.98.0) spectroscopic software. Prior to each analysis, the diamond ATR was cleaned with hexane.

3. Results and discussion

The images (both clean and used) of the membrane modules used in microalgal culture harvesting processes performed with submerged membrane systems are shown in Fig. 2.

3.1 Critical flux determination

In this study, we determined the critical flux values of the membranes in order to ensure the operation of the microalgal culture filtration process at an optimum flux value. By operating the membranes at their critical flux values, we intended to minimize irreversible fouling. The critical flux studies performed by increasing the transmembrane pressure in steps were performed at a

(a) (b) (c)

Fig. 2 Images of clean (above) and fouled (below) membranes: (a)=1 μm ceramic membrane, (b)=0.2 μm ceramic membrane, (c)=0.2 μm polymeric membrane

transmembrane pressure of 50-150 mbar and with a 5-step increase in pressure. Fig. 3 shows the flux changes in 30-minute intervals according to the gradual increase of pressure with the MV020 membrane.

An evaluation in Fig. 3(a) of the effect of transmembrane pressure on flux reveals that an increase in pressure leads to a more rapid decrease in flux. The flux values by the end of the 30 minute filtration experiments decreased with an increase in pressure. The permeate flux decreased 16.5% at a transmembrane pressure of 50 mbar, while the rate of decrease was 32.8% at a pressure of 100 mbar, and 44% at a pressure of 150 mbar. This was due to the fact that the microalgal culture fouls the membrane pores more severely with increasing vacuum pressures. An evaluation in Fig. 3(b) of the flux values at the end of the pressure-dependent 30 minute filtration process indicates that the area of critical flux was $\leq$95 L/m^{2}hour. The permeate flux decreased further with an increase in pressure. Based on these results, it was determined that the transmembrane pressure should be kept below 50 mbar for the filtration of microalgal culture with the MV020 membrane. It was observed that membrane fouling increases above 50 mbar, and that this leads to more irreversible fouling over time. The effect of transmembrane pressure on the permeate flux with the 1 μm ceramic membrane is shown in Fig. 3.3.

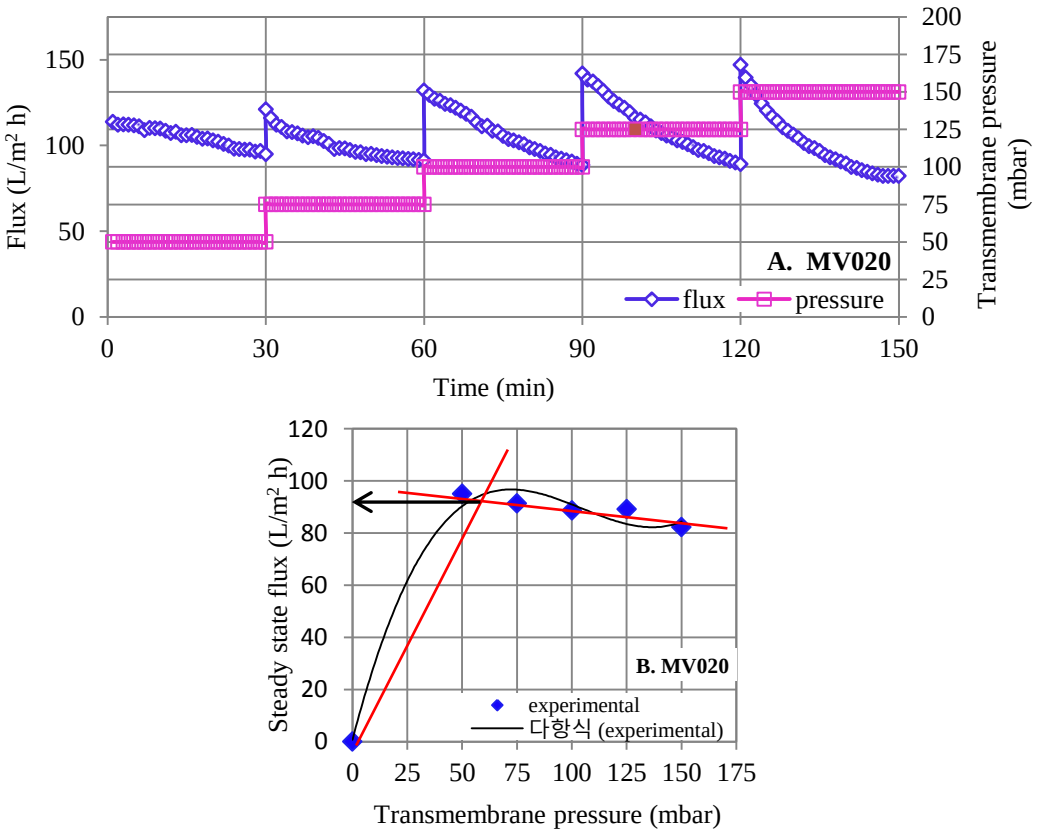


Fig. 3 Effect of transmembrane pressure on permeate flux, MV020 membrane (T=25℃)

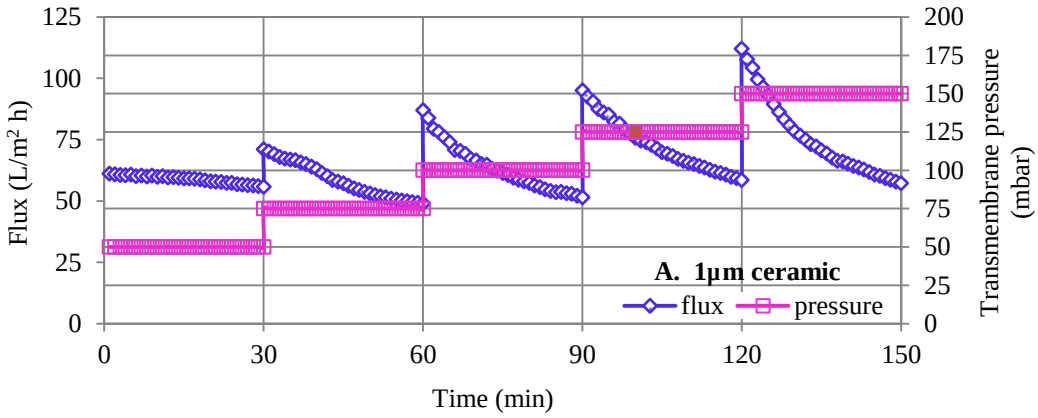


Fig. 4 Effect of transmembrane pressure on permeate flux, 1 μm ceramic membrane (T=25℃)

An evaluation in Fig. 4(a) of the effect of transmembrane pressure on flux for the 1 μm ceramic membrane reveals that, similarly to the MV020 membrane, an increase in pressure leads to a greater reduction in flux. The permeate flux decreased 8.7% at a transmembrane pressure of 50 mbar, while the reduction rate was 40.9% at a pressure of 100 mbar, and 48.9% at a pressure of

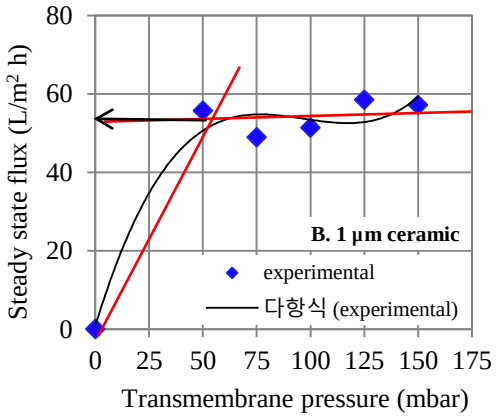


Fig. 4 Continued

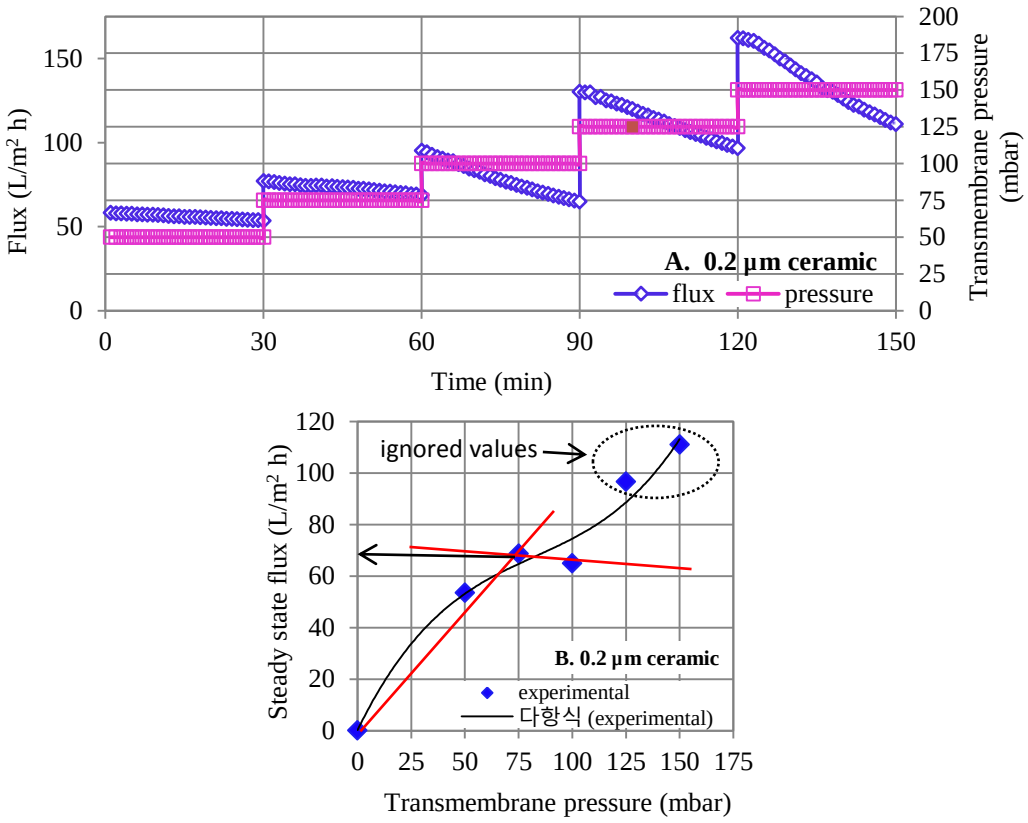


Fig. 5 Effect of transmembrane pressure on permeate flux, 0.2 μm ceramic membrane (T=25℃)

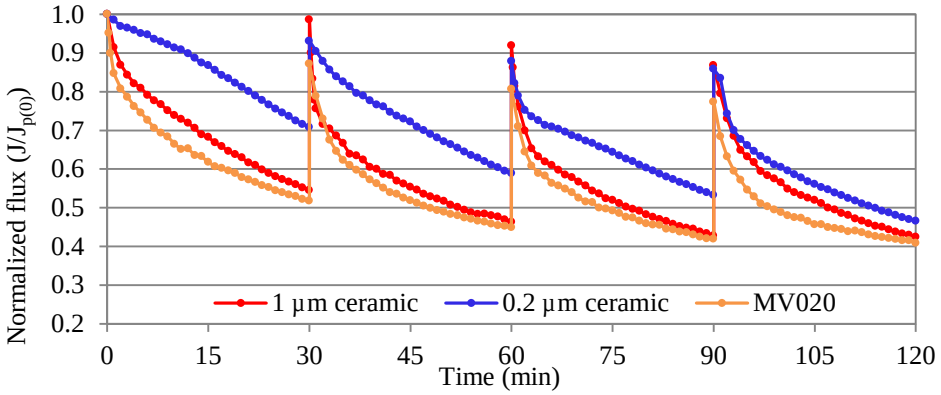
150 mbar. An evaluation in Fig. 4(b) of the transmembrane pressure dependent flux values for the 1 μm ceramic membrane indicates that the area of critical flux was ≤55 L/m^{2}hour. Depending on the critical flux value, keeping the operating pressure ≤50 mbar would be appropriate for minimizing fouling. Fig. 5 shows the effect of the transmembrane pressure on the permeate flux

for the 0.2 μm ceramic membrane.

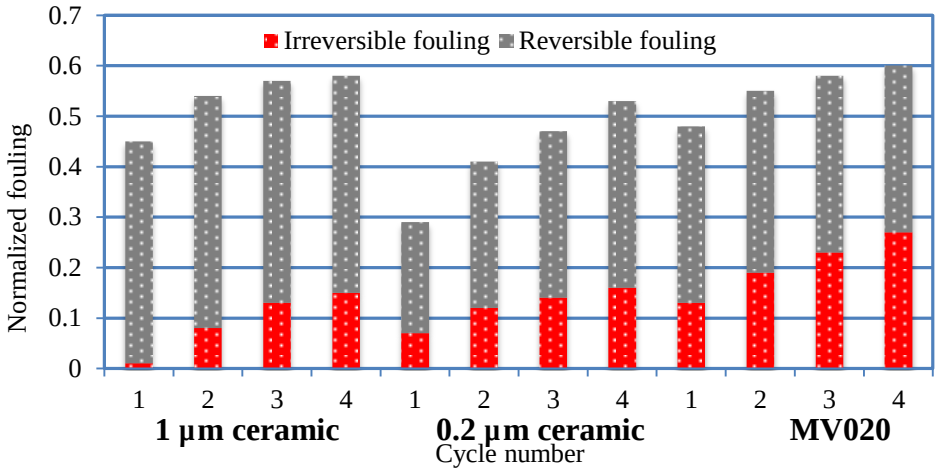
An evaluation of Fig. 5(a) of the effect of the transmembrane pressure on flux reveals that the permeate flux decreases rapidly at operating pressures of 100 mbar and above. The permeate flux decreased by 7.9% at a transmembrane pressure of 50 mbar, while the rate of reduction was 10.9% at a pressure of 75 mbar and 31.7% at 100 mbar and 150 mbar.

An evaluation in Fig. 5(b) of the transmembrane pressure dependent flux values for the 0.2 μm ceramic membrane indicates that the area of critical flux was ≤70 L/m^{2}hour. Depending on the critical flux value, keeping the operating pressure ≤75 mbar would be appropriate to minimize fouling.

A comparison of critical flux values between the different membranes showed that the polymeric membrane provided higher flux values than the ceramic membranes. Furthermore, compared to the ceramic membranes with pore sizes of 0.2 μm and 1 µm, the ceramic membrane with smaller pore size provided higher critical flux values. In general, membranes with larger pore diameters had higher flux values. The underlying reasons for both of these observations are



(a)



(b)

Fig. 6 Flux decline (a) and reversibility (b) of fouling during filtration experiment with different membrane, cleaning with water, (TMP=0.01-0.1 bar, T=25℃)

possibly associated with differences in membrane materials and pore sizes.

3.2 Reversible and irreversible fouling

The physical cleaning process has a significant effect on reversible and irreversible membrane fouling caused by microalgal culture. It is possible to reduce irreversible fouling, extend the membrane lifespan and increase filtration efficiency by optimizing the cleaning process.

In this study, reversible and irreversible membrane fouling potentials were investigated after cleaning was applied with water and air, which are widely used for cleaning submerged membrane systems.

3.2.1 The reversibility of fouling-cleaning with water

Fig. 6(a) shows the changes in normalized flux values in microalgal culture filtration processes performed with ceramic and polymeric membranes of different properties.

An analysis of the normalized flux values indicates that the tendency for fouling of the 0.2 μm ceramic membrane was lower than that of the 1 μm ceramic and 0.2 μm polymeric membranes. While the reduction in the permeate flux was more linear for the 0.2 μm ceramic membrane in the first two filtration process, the flux began to decrease rapidly at the start of third and fourth filtration experiments. The main reason for this is that microalgal culture initially fouls the membrane pores, and then accumulates on the membrane surface. Fouling in the pores that cannot be removed by backwashing causes a quick decrease in the flux in the next filtration cycles. A relatively similar trend was also observed in the fluxes of other membranes.

Fig. 6(b) shows the degrees of reversible and irreversible membrane fouling observed in microalgae harvesting performed with three different types of membranes. An evaluation of these results reveals that microalgal culture causes more irreversible fouling in the polymeric membrane. At the end of the fourth filtration cycle, the percentages of irreversible fouling for the 1 μm ceramic, 0.2 μm ceramic, and 0.2 μm polymeric membranes were 15%, 16%, and 27%, respectively.

In general, the extent of reversible fouling was greater in membranes with larger pore sizes. Similarly, in this study, the percentages of reversible fouling by the end of the fourth filtration cycle for the 1 μm ceramic, 0.2 μm ceramic, and 0.2 μm polymeric membranes were 43%, 37%, and 33%, respectively.

In microalgal culture filtration performed with membranes of different properties, Sun *et al.* (2014) reported achieving 67.74% - 96.15% recovery in the permeate flux through backwashing with water. They also reported that high membrane surface hydrophilicity and membrane intrinsic resistance increased the recovery rate (Sun *et al.* 2014).

For membranes fouled by microalgal culture filtration, Liang *et al.* (2008) reported that it is possible to achieve up to 80% flux recovery by backwashing the membranes with water for 20 minutes. In this study, after four filtration cycles, flux recovery rate of polymeric membrane stayed 55% while maximum flux recovery was obtained by 1 µm ceramic membrane as 74%. Also results showed that irreversible membrane fouling caused by microalgal culture increased with time for all of the membranes.

3.2.2 The reversibility of fouling-cleaning with air

Fig. 7(a) shows the changes in normalized flux values in microalgal culture filtration performed with ceramic and polymeric membranes of different properties.

An evaluation of the membrane filtration fluxes revealed a decreasing trend, independent of the

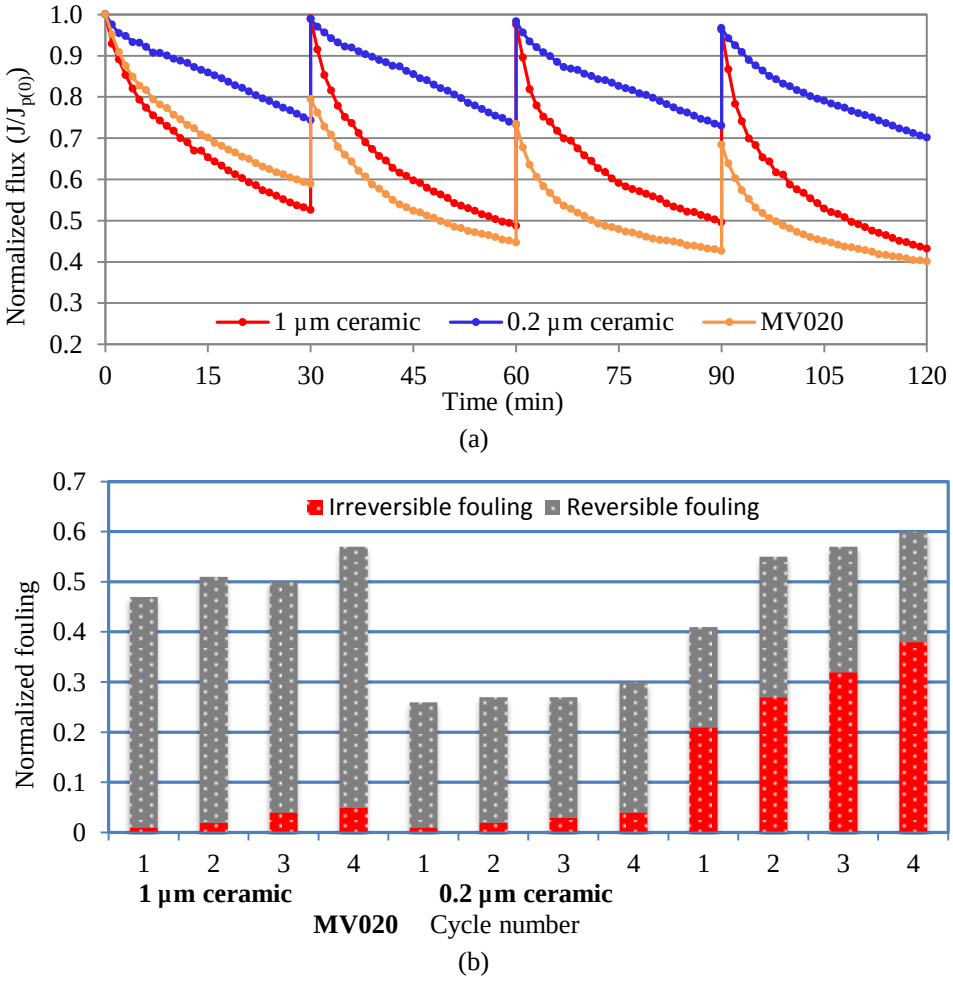


Fig. 7 Flux decline (a) and reversibility (b) of fouling during filtration experiment with different membrane, cleaning with air, (TMP=0.01-0.1 bar, *T*=25℃)

applied cleaning method, which was similar to the trend observed in other experiments on backwashing with water. Similarly to the backwashing with water in the 0.2 μm ceramic membrane, the reduction in the permeate flux was more linear in the first two filtration experiments, while the reduction in flux at the start of the third and fourth filtration experiments were relatively higher.

Fig. 7(b) shows the degrees of reversible and irreversible fouling caused by microalgal culture. An evaluation of the degrees of irreversible membrane fouling revealed a significant difference between ceramic and polymeric membranes. The level of irreversible fouling with the ceramic membranes was lower compared to the MV020 polymeric membrane. The percentages of irreversible fouling by the end of the fourth filtration cycle for the 1 μm ceramic, 0.2 μm ceramic, and 1 μm polymeric membranes were 5%, 4%, and 38%, respectively. This significant difference between irreversible fouling percentages indicates that cleaning with air is very effective for ceramic membranes. Cleaning with air removed most of the microalgal cells and extracellular

organic materials that had accumulated inside the pores.

Rios *et al.* (2011) previously used ceramic and polymeric membranes in microalgal culture filtration, and reported that ceramic membranes can be cleaned more easily than polymeric membranes due to their different pore structures (Rios *et al.* 2011).

In this study, maximum flux recovery rate achieved up to %90 by air cleaning of ceramic membrane having 1 μm pore size. Experimental results showed that membrane pore and manufacturing material may affect the recovery of filtration flux rate.

3.3 Characterization of the fouled polymeric MV020 membrane

3.3.1 SEM images of the membrane

Scanning electron microscopy (SEM) is widely used to obtain information about membrane morphology by taking images of membrane surfaces and cross-sections (Qu *et al.* 2012).

Rickman *et al.* (2012) studied membrane fouling caused by microalgal culture by using SEM. Based on an examination of the membrane SEM images, they reported that microalgal cells with diameters of approximately 10 μm tend to form a cake layer on the membrane surface, and this cake layer contains intracellular materials (Rickman *et al.* 2012). Zhang *et al.* (2010) performed the characterization of clean membranes and of membranes fouled by microalgal culture filtration using SEM. Based on their study results, they reported that the surfaces of clean membranes are quite smooth and clear, while fouled membrane surfaces are covered with a layer of algal cake (Zhang *et al.* 2010). They also reported that the cake layer was approximately 12.3 μm thick (Zhang *et al.* 2010). Qu *et al.* (2012) investigated membrane fouling caused by microalgal culture and extracellular organic materials (EOMs) released from microalgal cells by using SEM. According to their study results, microalgal cells and EOMs coated the membrane surface by the end of the filtration process (Qu *et al.* 2012). They also noted that microalgal cells that cannot be fully removed from the membrane through the cleaning process may subsequently lead to irreversible fouling (Qu *et al.* 2012).

Fig. 8 shows the detailed SEM images of a clean MV020 membrane and an MV020 membrane fouled during microalgal culture filtration.

An evaluation of the SEM image in Fig. 8(a) indicates that the clean membrane has a clean and relatively smooth surface. On the other hand, an evaluation of the SEM image in Fig. 8(b) shows that microalgal cells coat the surface of the used membrane. The fouled layer formed by microalgal cells is shown more clearly in Fig. 8(c). The thickness of the algal cake layer measured 3.56 µm and 5.21 µm at two different points, while the average thickness of the cake layer was approximately 4.38 μm. The thickness of the cake layer formed on the membrane surface by microalgal cells may vary depending on the operating principle of membrane system, the properties of the member, the operating conditions, and the microalgal culture. Yu *et al.* (2014) used SEM to measure the thickness of the cake layer formed on the membrane surface by extracellular organic materials (EOMs) released from microalgal cells. Based on the SEM images taken from the membrane cross-section, they reported that EOMs formed a layer of approximately 0.56 µm thick (Yu *et al.* 2014). An evaluation in Fig. 8(d) of the SEM image for the used membrane indicates that the microalgal culture does not foul the support layer.

3.3.2 The ATR-FTIR spectra of the membrane

The chemical structures of the materials deposited on the membrane after filtration can be identified by using ATR-FTIR spectroscopy (Howe *et al.* 2002). The spectra of the materials

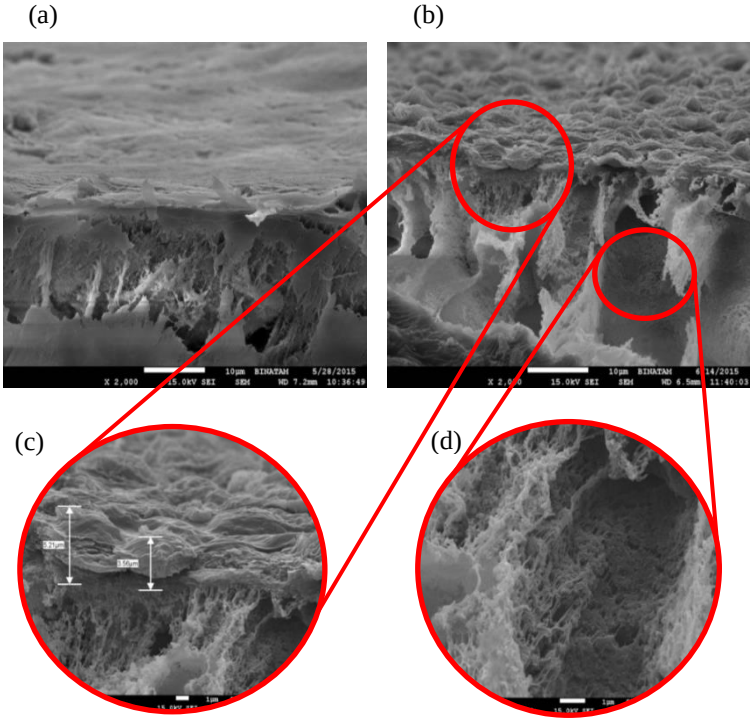


Fig. 8 Detailed SEM images of fouled MV020 membrane: (a)=clean membrane, (b)=fouled membrane, (c)=zoomed cross section of fouled membrane, (d)=support layer of fouled membrane, (TMP=0.01-0.1 bar, *T*=25℃)

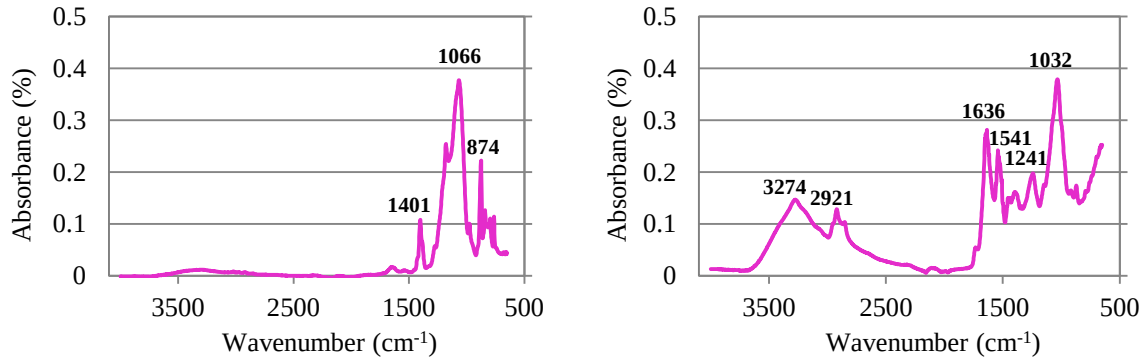


Fig. 9 FTIR analysis of MV020 membrane: Left and right panels are for clean and fouled membrane, respectively, (fouled membrane operation conditions: TMP=0.01-0.1 bar, *T*=25℃)

fouling the membrane can be easily distinguished from the spectrum of the membrane material (Howe *et al.* 2002). Delaunay *et al.* (2008) previously used ATR-FTIR to investigate membrane fouling caused by proteins. Ao *et al.* (2016) also used ATR-FTIR to analyze the polysaccharides that cause membrane fouling. Li *et al.* (2011) investigated the organic materials that cause membrane fouling by using ATR-FTIR.

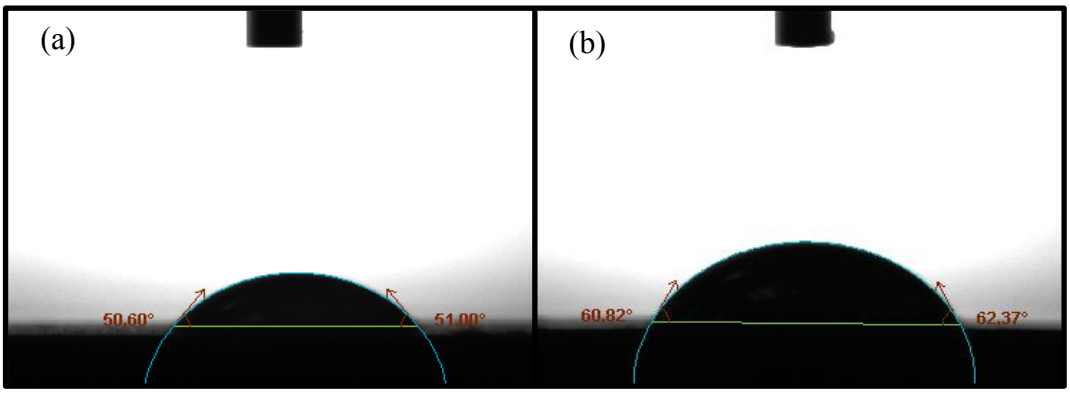


Fig. 10 Contact angles of clean (left) and fouled (right) MV020 membranes, (fouled membrane operation conditions: TMP=0.01-0.1 bar, *T*=25℃)

In this study, the ATR-FTIR analysis of clean and used MV020 membranes was performed to gain a better understanding of the chemical structures of the materials that cause fouling. An evaluation of the ATR-FTIR results in Fig. 9 for the clean and used membranes indicated that a different spectra from each type of membrane. The absorption bands of the fouled MV020 membrane were 3274, 2921, 1636, 1541, 1241 and 1032 cm^{-1}. These bands respectively correspond to the Amide A *v*(N–H) bond of proteins (Duygu *et al.* 2012), the methylene v_{as} (CH2) stretching band of lipids (Mayers *et al.* 2013), the Amide I *v*(C=O) stretching band and the Amide II *v*(N-H) bending band of protein groups (Chiou *et al.* 2010), the v_{as} (>P=O) stretching band of phosphodiesterases, and the polysaccharides *v*(C-O-C) stretching band of carbohydrates (Dean *et al.* 2010). These absorption bands indicate that membrane fouling caused by microalgal culture results mainly from proteins, carbohydrates, and lipids.

Zhang *et al.* (2010) emphasized that the microalgal culture medium consisting of protein, polysaccharides, lipids, and similar substances is responsible for membrane fouling. Similarly, Qu *et al.* (2012) reported that microalgal cells and the organic materials they release contain proteins and polysaccharides that contribute to fouling.

3.3.3 The Hydrophobicity/Hydrophilicity of the membranes

The hydrophobicity/hydrophilicity of membranes can be analyzed by contact angle measurements (Ahmad *et al.* 2013). The contact angle measures the wetting property of the membrane surface (Jhaveri and Murthy 2016). If the membrane is hydrophilic, a hydration layer is formed on the membrane surface during filtration, which keeps foulants away (Jhaveri and Murthy 2016). Sun *et al.* (2013) reported that during microalgal harvesting, membranes with hydrophilic surfaces exhibit a lower tendency for fouling and can be cleaned without using chemicals, while hydrophobic membranes have a strong tendency to become fouled. Qu *et al.* (2014) described that membrane fouling caused by extracellular organic materials released from microalgal cells is further increased when of hydrophobic membranes are used. Sun *et al.* (2014) similarly reported that during the filtration of the microalgal culture with UF membranes, hydrophobic PP, and PVDF membranes show a higher tendency for fouling than hydrophilic cellulose acetate membranes.

While the contact angles of ceramic membranes with super hydrophilic surfaces were <10°, those of the polymeric MV020 membrane were measured as 50.66±1.39°. In microalgal culture

filtration, irreversible membrane fouling is significantly lower in polymeric MV020 membranes due to the hydrophilic nature of ceramic membranes, as shown in Fig. 6(b) and Fig. 7(b). In this study, a contact angle of 61.60±0.80° was measured for the fouled MV020 membrane.

An evaluation in Fig. 10 of the contact angle images for clean and used MV020 membrane indicated that microalgal culture increases the hydrophobicity of the membrane surface. This may be due to the microalgal cake layer formed by the depositing of microalgal cells on the membrane surface. The algal cake layer coating the membrane surface prevents the direct interaction of the membrane surface with the water droplet.

4. Conclusions

The current study investigated the feasibility of microalgal biomass harvesting by using a specific experiment procedure involving the submerged membrane method, as well as polymeric and ceramic membranes. The experimental results of the study are summarized below.

1) In the filtration experiments, the microalgal culture first fouled the membrane pores, and then deposited on the membrane, creating an algal cake layer on its surface.

2) The critical flux values of one polymeric (pore size: 0.2 μm) and two ceramic membranes (pore size: 0.2 μm and pore size: 1 μm) determined as ≤95 L/m^{2}hour, ≤70 L/m^{2}hour and ≤55 L/m^{2}hour, respectively. Results showed that the critical flux may vary depending on the membrane material and pore diameter.

3) Compared to ceramic membranes, polymeric membranes are more vulnerable to irreversible fouling. Irreversible membrane fouling for polymeric membrane was 27% with backwashing water and %38 with pressure air cleaning. For ceramic membranes these values were maximum 16% with backwashing water and %5 with pressure air cleaning. This lower tendency for irreversible fouling of ceramic membranes is due to the surface-liquid interactions associated with the hydrophilic structures on the ceramic membrane surfaces.

4) In terms of flux recovery during microalgal biomass harvesting, the backwashing method with water is more feasible for polymeric membranes (recovery rate: %55), while the cleaning method with air is more feasible for ceramic membranes (recovery rate: %87-91). In ceramic membranes, cleaning with air allows for substantial removal of microalgal cells and extracellular organic materials that have accumulated in the membrane pores. According to the results, ın the recovery of the filtration flux, cleaning method, membrane material and membrane pores size plays key role.

5) Results in this study showed that ceramic membrane having 0.2-1 μm pore size in the submerged membrane system could effectively be used with periodically cleaning via pressure air for microalgal culture harvesting.

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