Title:

Effects of membrane orientation on fouling characteristics of forward osmosis
membrane in concentration of microalgae culture

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Abstract:

Application of forward osmosis (FO) membrane to microalgae cultivation processes enables concentration of microalgae and nutrients with low energy consumption. To understand fouling characteristics of FO membrane in concentration of microalgae culture, we studied flux decline, flux recovery by cleaning, and foulants characteristics, in different membrane orientation of active-layer-facing-feed-solution (AL-FS) and active-layer-facing-draw-solution (AL-DS) modes. Batch concentration of *Chlorella vulgaris* was conducted with a cellulose-triacetate FO membrane. Rapid flux decline and lower flux recovery was observed in AL-DS mode because of inner-membrane fouling including internal pore clogging, adsorption and internal concentration polarization in the support layer. A proportion of polysaccharides in extracellular polymeric substances to soluble microbial products were larger in chemical cleaning effluent than physical one in AL-DS mode, although those were not significantly different in AL-FS mode. Excitation-emission matrix analysis revealed that proteins and humic-like substances were also possible irreversible foulants both in AL-DS and AL-FS modes.

Keywords: forward osmosis; microalgae; membrane fouling; extracellular polymeric substances (EPS)

1. Introduction

Recently, carbon dioxide capture by microalgae cultivation and harvesting has been spotlighted as one of the mitigation processes of global warming. The produced microalgae biomass could be utilized as carbon-neutral energy, by combination with methane fermentation, lipid extraction or other bioenergy conversion process, and for carbon capture and storage, by converting into petrochemical materials such as carbon fiber, resins, etc. Application of membrane processes is one promising unit operation to enhance microalgae productivity (Bilad et al. 2014). Various application of microfiltration and ultrafiltration has been studied to concentration of microalgae culture (Bhave et al. 2012; Zhang et al. 2010), and submerged filtration in a photobioreactor to utilize treated wastewater (Honda et al., 2012; Marbelia et al. 2014) and to recycle nutrients in cultivation media (Discart et al. 2013).

Forward osmosis (FO) membrane processes are recognized as emerging technology for wastewater reclamation, osmotic power generation, dewatering processes etc. (Hoover et al. 2011; McGinnis et al. 2008). An FO process utilizes water transportation through a semipermeable membrane driven by osmotic pressure difference between a relatively low concentration solution (feed) to a relatively high concentration solution (draw).

Therefore, the FO process enables concentration of feed solution with low energy consumption. Application of the FO membrane to microalgae cultivation and harvesting is also studied in dewatering of microalgae (Buckwalter et al. 2013; Hoover et al. 2011)- and concentration of nutrients in treated wastewater (Xue et al. 2015). Among these FO studies, fouling studies by microalgae are limited except Zou et al. (2011), which reported that Mg^{2+} enhances algal fouling of FO membrane.

A typical FO membrane can be used in either orientation of AL-DS mode, in which the membrane active layer faces the draw solution, or AL-FS mode, in which the membrane active layer facing the feed solution. It is known that fouling characteristics of the FO membrane depends on membrane orientation (Cornelissen et al. 2008; Motsa et al. 2014). However, the major fouling mechanisms and foulants characteristics have not been investigated in dewatering of microalgae culture with FO membrane. Moreover, difference of foulants characteristics by membrane orientation is unveiled yet. The objective of this study was to investigate effects of membrane orientation on fouling characteristics in concentration of microalgae culture using FO membrane. Characteristics of foulants and effects of membrane cleaning in different membrane orientation were also studied.

2. Materials and Methods

2.1. Batch concentration of microalgae by FO membrane

Batch concentration of microalgae culture was conducted using a cross-flow membrane filtration module with a cellulose-triacetate FO membrane (CTA-ES, Hydration Technology Innovations, USA) (**Figure 1**). The cellulose-triacetate FO membrane has the asymmetric structure of the membrane with a tight layer (active layer) to reject salts, and a porous layer (support layer) to enable high water penetration. Contact angles of surface of the active and support layers were 75.1° and 72.5°, respectively. Zeta potential of the active and support layers were -69.4 mV and -70.4 mV (pH=6.3), respectively. The membrane module had $1.935 \times 10^{-3} \text{ m}^2$ (2.54 cm wide x 7.62 cm long) of effective membrane surface area, and the filtration chamber had 1 mm of height on both side of membrane. The FO membrane was placed either in active-layer-facing-feed-solution (AL-FS) mode or active-layer-facing-draw-solution (AL-DS) mode. As draw solution, 3.5% NaCl solution was used to simulate osmotic pressure of seawater. In feed solution, *Chlorella vulgaris* NIES-2170 was suspended to contain 70 mgC/L of a total organic carbon (TOC) concentration. One-liter each of feed and draw solutions were prepared and circulated at 400mL/min of flow rate for 48 hours,

until the feed solution was concentrated approximately double. Water temperature was kept at 21 ± 3 °C by water bath. Weight of the draw solution was monitored and recorded every 3 minutes to calculate flux. Conductivity of the feed solution was monitored with a conductivity meter (DM-32P, TOA-DKK, Japan) and recorded every 3 minutes.

2.2. Membrane cleaning

After each batch concentration test, physical cleaning was conducted by flushing with the deionized water for 1 hour at 400ml/min after replacing feed and draw solutions with the water. After physical cleaning, chemical cleaning was conducted in following manner: (i) flushing with a cleaning agent for 20 minutes at 400ml/min, (ii) soaking for 10 minutes, and (iii) flushing with the cleaning agent for 20 minutes at 400ml/min again. The NaOH solution with pH=11 was used as the cleaning agent. Pure water flux was measured after each cleaning. Permeability was calculated from the pure water flux and the estimated osmotic pressure difference between feed and draw solutions, as described below in 2.4.

2.3. Analysis of foulants

Soluble microbial products (SMP) and extracellular polymeric substances (EPS) was

fractionated from effluent of physical cleaning and chemical cleaning. A fraction of SMP was obtained as filtrate of a sample with 0.45 μ m cellulose-acetate membrane filter (DISMIC 25CS045AN, Advantec-Toyo, Japan). A fraction of EPS was extracted by heating with NaOH according to McSwain et al. (2005). After a sample was centrifuged at 8,000 rpm for 10 min, the pellet was suspended in 50 mL of physiological saline solution, which was adjusted to pH 11 by 1N NaOH solution. The suspended sample was heated at 80°C for 30 min, and then centrifuged at 12,000 x g for 1 min. The supernatant was taken for the further analysis after centrifuged again for 10 min.

Carbohydrates and proteins in each fraction were analyzed by the phenol-sulfate method using glucose as the standard, and modified Lowry method using bovine serum albumin (BSA) as the standard, respectively. Composition of organic substances in the sample was also analyzed by excitation-emission matrix (EEM) with a fluorescence spectrophotometer (FP-8200, Jasco, Japan). Excitation wavelengths were incrementally increased from 200 nm to 500 nm at 5 nm steps. For each excitation wavelength, the emission spectra were obtained by scanning from 210 to 600 nm at 5 nm steps. A fraction of organic matter which relates to each peak in the obtained matrix was identified according to Chen et al. (2003).

2.4. Calculation of water permeability

The water flux (J_w) was determined from increase in weight of the draw solution. The relationship of the water flux and the osmotic pressure difference between feed and draw solution ($\Delta\pi$) is given by

$$A = \frac{J_w}{\Delta\pi} \quad (1)$$

where A is the water permeability, and $\Delta\pi$ is osmotic pressure difference between feed and draw solutions. The water permeability here is defined as the apparent water permeability which accounts for the concentration polarization effects, because the osmotic pressure difference ($\Delta\pi$) is attributed to the occurrence of external and internal concentration polarization in FO membrane (Cornelissen et al. 2008; Wong et al. 2012). In this experiment, osmotic pressure difference changed dependent on dilution of draw solution by water permeation from feed to draw solution and salt intrusion from draw to feed solution. Osmotic pressure in feed solution ($\Delta\pi_F$) and salt intrusion from draw to feed solutions were determined from the measured conductivity in feed solution and correlation of NaCl concentration with conductivity. Osmotic pressure in draw solution ($\Delta\pi_D$) was determined from the calculated salt intrusion from feed solution and volume increased by water permeation from feed solutions.

3. Results and Discussion

3.1. Characteristics of membrane orientation in flux decline

Flux decline was more rapid in AL-DS mode until 36 hours of concentration, during which 0.4 L of water was permeated. Afterward, the flux and its decline rate became comparable between the two modes (**Figure 2a**). Since initial flux was 1.5 times larger in AL-DS mode, rapid flux decline is expected in AL-DS mode due to foulants accumulation and dilution of draw solution. However, decrease of water permeability vs. permeate volume was also larger in AL-DS mode until 0.4 L of permeate volume (**Figure 2b**). This indicates that not only larger flux but also surface characteristics of the support layer affected fouling progress in AL-DS mode. A cellulose-triacetate FO membrane has gradient density of membrane materials, which is high in active layer side and low in the support layer (Wei et al. 2011). This gradient density composes the asymmetric structure of the membrane with a tight layer (active layer) to reject salts, and a porous layer (support layer) to enable high water penetration. Therefore, inner-membrane fouling, i.e. internal pore clogging and adsorption of solutes occurred in AL-DS mode in the initial stage because organic foulants could enter and remain in internal pores of the loose support layer, which is away from cross-flow turbulence. Not only loose pore but also surface roughness of the support layer also probably

contributed in rapid accumulation of foulants in AL-DS mode. The rougher surface of the support layer was reported to allow foulant molecules to attach easily compared to the smooth surface of the active layer (Parida et al. 2013) by providing more surface area for the foulant molecules to attach (Li et al. 2007). Another possible reason is enhanced internal concentration polarization (ICP) in the support layer. Soluble microbial products, which probably consist of polysaccharides and proteins etc., could enter the loose support layer (as described in detail in Section 3.3). When these soluble organic matters were concentrated in the support layer, concentrative ICP on the feed solution side is enhanced. The enhanced concentrative ICP decreases differential osmotic pressure across the active layer and results in the flux decline. Moreover, cake-enhanced osmotic pressure (CEOP) was also possibly caused further enhancement of concentrative ICP. The CEOP phenomenon is explained that cake hinders diffusion of salts which intruded through osmotic membrane from draw solution and leads to reduction of differential osmotic pressure across the membrane (Hoek and Elimelech 2003). In this study, polysaccharides and proteins were detected in EPS in chemical cleaning effluent (as described in detail in Section 3.3). Although cake formation was not expected inside of the support layer, concentration of these EPS possibly resulted in gel formation and led to hinder diffusion of salts which intruded from draw solution.

Therefore, the possible reasons of the rapid flux decline in initial stage in AL-DS mode were (i) inner-membrane fouling by internal pore clogging and adsorption of solutes, (ii) rough surface of the support layer, (iii) concentrative ICP by SMP, and (iv) CEOP caused by EPS gel formation. Meanwhile, in the later stage after 0.4 L of permeation or 36 hours of concentration, the decrease rate of water permeability in AL-DS mode became smaller and comparable to that in AL-FS mode. This implies the major fouling mechanism shifted from inner-membrane fouling in the support layer to cake deposition on the membrane surface. Such shift of flux decline was also observed in concentration of RO brine water dosed with calcium ion (Parida et al. 2013) and humic acids (Tang et al. 2010).

In AL-FS mode, cake deposition on the membrane surface probably dominated fouling phenomenon because organic foulants hardly enter in the tight active layer. In cake deposition, accumulation of foulants is determined by balance between adhesion on membrane surface and lift off by cross-flow turbulence. Smooth surface of the active layer allowed cross-flow turbulence to reach close to membrane surface and resulted in less cake deposition as well as reduction of external concentration polarization. Due to less cake deposition, less CEOP occurred in AL-FS mode. These resulted in less flux

decline than in AL-DS mode. Moreover, self-compensation ICP also contributed flux stability in AL-FS mode. In AL-FS mode, severe dilutive ICP in the support layer dominates differential osmotic pressure across the active layer (Wong et al. 2012). However, since the dilutive ICP is eased when flux drops, the flux is maintained stable. Consequently, in AL-FS mode, flux was maintained more stable than in AL-DS mode due to smooth surface of the active layer and self-compensation ICP phenomenon.

3.2. Flux recovery by cleaning

Flux recovery was higher in AL-FS mode both in physical and chemical cleaning (**Table 1**). In AL-DS mode, 30% of fouling was irreversible after physical cleaning, and approximately 15% of fouling was irreversible even after chemical cleaning. This indicates that inner-membrane fouling in the support layer, i.e. internal pore clogging and adsorption, is the possible reasons of irreversible fouling. In this study, physical cleaning was conducted by cross-flow flushing, in which the fouling layer is broken into smaller species by shear force of cross-flow turbulence and removed. Because foulants in internal pores are away from the cross-flow turbulence, they could not be removed and remained as irreversible foulants. Another possible reason of the larger irreversible fouling in AL-DS mode was morphology of membrane surface on the support layer side.

The membrane used in this study had embedded woven support. Bumps by the woven fiber material appear on the support layer, while the active layer has smoother surface (**Figure S1**). In AL-DS mode, SEM observation showed that some foulants remained on the edge of bumps (**Figure S1c**). The bumps on the support layer possibly cause a drift of foulants and hinder the removal of foulants in cleaning by cross-flow cleaning. Consequently, inner-membrane fouling and uneven surface of the support layer caused low flux recovery by physical cleaning in AL-DS mode. Moreover, low recovery after chemical cleaning shows that some of the internally clogged foulants could not be removed even by chemical cleaning. Osmotic backwash would be a more preferable as a cleaning method in AL-DS mode. In osmotic backwash, water moves from draw solution side to feed solution side by replacing draw solution to ultrapure water. That reverse water movement not only loosens the foulants gel layer and flush them back to bulk solution but also generate a reverse ICP profile to restore membrane charge. It showed better flux recovery than flushing in cleaning of FO membrane fouled with alginic acid (Motsa et al. 2014).

In AL-FS mode, flux recovery by physical cleaning was almost 90%, which agreed with past studies on FO membrane fouled with wastewater (Valladares Linares et al. 2012)

and alginic acid (Motsa et al. 2014). Better recovery than AL-DS mode was probably because foulants did not cause internal pore clogging but accumulated as cake on the surface of the tight active layer. Moreover, smoother surface of the active layer resulted in better removal of the cake layer by allowing cross-flow turbulence reach close to the membrane surface and leading to more efficient lift off of the cake from the membrane. Flux recovery in this study was comparable or better than past studies on concentration of microalgae with UF membrane (Qu et al. 2012a, 2012b). Babel and Takizawa (2010) suggested that EPS of microalgae causes significant increase of filtration resistance when compressed by filtration pressure. However, such compression of EPS did not occur with FO membrane due to no operational filtration pressure. No filtration pressure also resulted in the less compression of cake and led to easier removal of the microalgal cake by cross-flow turbulence. Better flux recovery is reported with FO membrane than RO membrane, because there is no operational pressure to compress cake on the membrane surface (Lee et al. 2010). Therefore, an FO membrane process is more appropriate for concentration of microalgae culture than MF or UF filtration due to better flux recovery by physical cleaning as well as lower energy consumption for filtration pressure.

3.3. Characterization of foulants

In AL-FS mode, proportions of carbohydrates in EPS to SMP were comparable between foulants removed by physical and chemical cleaning. However, in AL-DS mode, more carbohydrates were contained in EPS in chemical cleaning effluent (**Figure 3a**). This suggests that carbohydrates in EPS probably related to inner-membrane fouling of the support layer in AL-DS mode. Some studies reported that polysaccharides were one of the major foulants irreversible in physical cleaning in ultrafiltration (UF) and reverse osmosis (RO) membranes (Chiou et al. 2010; Herzberg et al. 2009; Qu et al. 2012a, 2012b). Carbohydrates in EPS are expected to have larger molecule size than those in soluble form. Because a large-molecule polysaccharide has many -OH groups, which have positive polarity, it tended to adhere to the membrane material of cellulose triacetate, which is supposed to have slight negative charges. Therefore, polysaccharides contained in EPS possibly tended to be captured in internal pores of the support layer, and found more in chemical cleaning effluent in AL-DS mode.

In terms of mass, proteins were the major foulants in the both modes (**Figure 3b**).

However, proportions of proteins in EPS to SMP were not significantly different between in AL-DS and AL-FS mode. This is probably because affinity to the active and

support layers did not probably change between EPS-form and soluble proteins. Charge of a protein molecule depends more on pH and its isoelectric point rather than its size. Therefore, fractioning by EPS and SMP could not distinguish proteins with higher affinity to the membrane from those with lower affinity.

In addition to carbohydrates and proteins, humic-like substances were also found in foulants removed by chemical cleaning both in AL-DS and AL-FS modes. The EEM of the chemical cleaning effluent had two peaks of protein-like substances ($E_x/E_m = 250/340$ and $270/340$ nm) and two peaks of humic-like substances ($E_x/E_m = 250/420$ and $300/420$ nm), which are reported to be humic acid-like, fulvic acid-like, and/or hydrophobic substances (Chen et al. 2003). These humic-like substances contained not in physical cleaning effluent but in chemical cleaning effluent both as EPS and soluble forms (**Figures S2 and S3**). They were possibly originated from polymeric substances consisting of cell walls of *Chl. vulgaris*, such as cellulose, xylan, chitin, algaenan, etc. (Gerkin et al. 2013; Kodner et al. 2009; Popper and Tuohy 2010). Li et al. (2011) and Zhang et al. (2010) reported algogenic organic matter in microalgae is reported to cause substantial flux decline in UF membrane. In application of the cellulose triacetate FO membrane to microalgae concentration, these humic-like substances and

polysaccharides in EPS can be significant foulants.

4. Conclusions

Flux decline was initially rapid in AL-DS mode but became comparable to AL-FS mode later, probably because fouling mechanism shifted from inner-membrane fouling to cake deposition. Flux recovery was lower in AL-DS mode after both physical and chemical cleaning because of uneven surface characteristics of the support layer. In AL-DS mode, polysaccharides in EPS probably played an important role in irreversible fouling.

Proteins and humic-like substances were also found as possible irreversible foulants independent of membrane orientation. AL-FS mode is preferable in concentration of microalgae due to its flux stability and better flux recovery by physical cleaning.

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Figure Captions:

Figure 1 Schematic diagram of experimental setup.

Figure 2 Flux decline (a) and increase of apparent water permeability (b) in

concentration of microalgae culture in different membrane orientation.

Figure 3 Proportion of carbohydrates (a) and proteins (b) in extracellular polymeric substances (EPS) to soluble microbial products (SMP) in foulants removed by physical and chemical cleaning in different membrane orientation. The values in the bars are amount of carbohydrates/proteins per membrane surface area per permeate volume.

Table 1 Recovery of flux and permeability coefficients by cleaning

	Pure water flux (J_w) ^a [m/day]		Apparent water permeability (L_p) ^a [m/day/MPa]		Apparent filtration resistance (R_f) [10 ¹⁵ m ⁻¹]
<u>AL-DS mode</u>					
virgin	0.23		0.081		1.3
after physical cleaning	0.16	(70%)	0.057	(71%)	1.9
after chemical cleaning	0.20	(84%)	0.069	(86%)	1.4
<u>AL-FS mode</u>					
virgin	0.15		0.050		2.0
after physical cleaning	0.13	(88%)	0.044	(88%)	2.3
after chemical cleaning	0.15	(100%)	0.050	(100%)	2.0

^a The values in parentheses are % recovery by cleaning.

Figure 1

Figure 2 (a)

Figure 2 (b)

Figure 3 (a)

Figure 3 (b)