Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1165738

57 (2016) 26383–26391
November

Taylor & Francis
Taylor & Francis Group

Characteristics of foulants of forward osmosis membranes used in municipal wastewater concentration processes

Sosuke Onoda[a,b], Yuta Masumori[a], Taro Miyoshi[a,*], Masahiro Yasukawa[a], Tomoki Takahashi[a], Hideto Matsuyama[a,*]

[a]*Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada-ku, Kobe 657-8501, Japan, emails: s.onoda@kobelco-eco.co.jp (S. Onoda), yuta.mas1024@gmail.com (Y. Masumori), t-miyoshi@pegasus.kobe-u.ac.jp (T. Miyoshi), myasukawa@people.kobe-u.ac.jp (M. Yasukawa), t.takahashi@crystal.kobe-u.ac.jp (T. Takahashi), matuyama@kobe-u.ac.jp (H. Matsuyama)*

[b]*Research and Development Planning Department, Technical Development Division, Technical Research Center, Kobelco Eco-Solutions Co., Ltd., 1-1-4 Murotani, Nishi, Kobe 651-2241, Japan*

Received 27 October 2015; Accepted 8 March 2016

ABSTRACT

This study investigated the organic matter that causes fouling in the forward osmosis (FO) membrane filtration system used in wastewater concentration processes. The development of the fouling of FO membranes caused by actual municipal wastewater was compared with that of the fouling caused by solutions containing artificial foulants (i.e. Aldrich humic acid, bovine serum albumin, and sodium alginate). This comparison shows that the development of the fouling was underestimated when using the artificial foulants. The characteristics of the foulants were investigated using fluorescence excitation-emission matrix spectra and liquid chromatography-organic carbon detection analyses. The results obtained by these advanced analytical methods indicated that the so-called biopolymers (i.e. organic macromolecules mainly comprising polysaccharides and proteins) were the major components of the foulants. In contrast, hydrophobic organic matter, such as humic substances, was not a dominant component.

Keywords: Concentration of wastewater; Forward osmosis; Membrane fouling; Characteristics of foulants

1. Introduction

Wastewater treatment systems are generally energy intensive; however, municipal wastewater contains significant amounts of valuable resources, such as organic matter, that can be used for producing methane gas (an energy source) and nitrogen and phosphorus (nutrients). If we could successfully recover these valuable resources, wastewater treatment could be transformed from an energy-consuming system to a resource-recovery system.

Anaerobic treatment is considered a core technology in the development of wastewater treatment systems. In such treatment, the organic matter contained in the wastewater can be converted to methane through the activities of micro-organisms during anaerobic treatment. Recently, anaerobic membrane bioreactors (AnMBRs) have been attracting significant

---

*Corresponding authors.

attention in both research and industry. Because particulate matter, including micro-organisms, can be completely retained by the membrane (i.e. the micro-organisms are not washed out from the reactor), it is expected that the reactor can achieve stable operation even under relatively high biomass concentrations [1]. However, the relatively low concentration of organic matter in municipal wastewater may prevent the operation of an AnMBR at its optimal temperature (i.e. approximately 38℃), decreasing the treatment efficiency. In addition, because AnMBRs do not include a pathway for removing nutrients, such as nitrogen and phosphorus, post-treatment is needed to recover such nutrients.

The forward osmosis (FO) membrane filtration process might be a suitable means of overcoming the aforementioned problems with AnMBRs [2,3]. In this process, the water to be treated is spontaneously transferred across a semipermeable membrane by the osmotic pressure gradient between the feed water and draw solution (DS). In the context of AnMBR, an FO membrane could be utilized to up-concentrate municipal wastewater prior to AnMBR or post-treatment for removing nutrients. Lateef et al. reported that the chemical oxygen demand (COD) could be increased to more than 6,000 mg/L by applying direct membrane filtration using a microfiltration (MF) membrane [4]. However, the dissolved organic matter, which cannot be retained by an MF membrane, remaining in the MF membrane effluent poses an operational issue, resulting in a loss of organic matter (i.e. a source of methane) and requiring intensive post-treatment to remove the organic matter contained in the effluent. Because FO membranes have a similar rejection capability as reverse osmosis (RO) membranes, applying FO membranes to concentrate municipal wastewater prior to anaerobic treatment may solve the problems associated with the release of organic matter into the effluent of the membrane-based concentration process. Zhang et al. achieved an approximately sixfold concentration of municipal wastewater (the final concentration of COD in the concentrated wastewater was approximately 1,600 mg/L) using FO membrane filtration [5], which may be suitable for application in anaerobic treatment without extensive heating [6]. With regard to its application in post-treatment for removing nutrients, it has been reported that FO membranes can achieve the moderate ammonium nitrogen removal and almost complete phosphorus removal [7]. If these nutrients could be effectively retained by an FO membrane, the recovery of the concentrated nutrients would then be possible (e.g. by applying the magnesium ammonium phosphate crystallization process) [8].

The implementation of the wastewater pre-concentration and AnMBR effluent post-treatment processes depend critically on controlling membrane fouling. In all membrane-based water treatment processes, the reduction in water permeability due to membrane fouling is a serious problem. Membrane fouling is believed to be less important in FO membrane filtration processes than in pressure-driven membrane systems (e.g. RO membranes) due to the absence of extreme hydraulic pressures [9]. In addition, the fouling of FO membranes is reported to be highly reversible [10]. However, most of the previous investigations into the fouling of FO membranes were conducted using artificial foulants (Aldrich humic acid (AHA), bovine serum albumin (BSA), and sodium alginate) [10–12]. Because such artificial foulants cannot represent the entire range of membrane fouling caused by the organic matter contained in actual wastewater [13], the current understanding of the fouling of FO membranes is extremely limited. To understand this process properly, the analysis of fundamental data obtained from FO membrane filtration tests using actual feed water (e.g. actual municipal wastewater or AnMBR effluent) is of critical importance.

Based on this background, we investigated the fouling of FO membranes caused by actual municipal wastewater and an effluent obtained from a bench-scale AnMBR operated using the same municipal wastewater as feed water. Upon the conclusion of the FO membrane filtration tests, the foulants were detached from the membranes to characterize the dominant types present. In addition, the validity of evaluating FO membrane fouling using artificial foulants (i.e. AHA, BSA, and sodium alginate) was also investigated. Based on the data obtained from this study, the characteristics of organic matter that affect the development of the FO membrane fouling are discussed.

2. Materials and methods

2.1. Feed water and DS for FO membrane filtration

The water quality data for the feed waters used in this study are shown in Table 1. Municipal wastewater was collected from the Port Island wastewater treatment plant in Kobe, Japan. The effluent from the primary sedimentation basin was used as the feed water in the FO membrane filtration test. The wastewater was subjected to coarse mesh (approximately 2 mm) filtration prior to the test. The effluent of an AnMBR was obtained from a bench-scale bioreactor operated at the Port Island wastewater treatment plant. This AnMBR was also fed with the effluent from the

Table 1
Water quality data for municipal wastewater, AnMBR effluent, and water containing artificial foulant

		LC-OCD analysis				
Feed water	TOC (mg C/L)	Biopolymers (mg C/L)	Humics + building blocks (mg C/L)	LMW acids (mg C/L)	LMW neutrals (mg C/L)	Electrical conductivity (after adding Na_2SO_4) (mS/m)
Municipal wastewater	97.1	5.2	18.7	14.7	10.3	113
AnMBR effluent	37.6	0.85	6.0	0.7	2.0	No data
AHA (300 mg/L)	98.1	0.6	86.3	0.0	0.0	112
BSA (200 mg/L)	103.3	85.9	8.3	0.0	0.0	113
Sodium alginate (335 mg/L)	93.2	91.3	0.0	0.4	0.0	120
Mixture $\begin{bmatrix} \text{AHA}: & 240\ \text{mg/L} \\ \text{BSA}: & 20\ \text{mg/L} \\ \text{Alginate}: & 34\ \text{mg/L} \end{bmatrix}$	97.1	15.0	26.5	1.7	3.0	111

primary sedimentation basin. The hydraulic retention time and organic loading rate of the AnMBR were 30 h and 2.3×10^{-3} kg CODcr/m^3/d, respectively. During the continuous operation of the AnMBR, the mixed liquor suspension was not withdrawn from the reactor. The AnMBR was equipped with an ultrafiltration (UF) membrane made of hydrophilized polyvinyl chloride (PVC) with a nominal pore size of 0.04 μm (Sekisui Chemical, Osaka, Japan). The osmotic pressures of the municipal wastewater and AnMBR effluent were approximately 0.05 MPa. The osmotic pressure was measured using a Wescor 5600 vapor pressure osmometer (Wescor Inc., Logan, UT, USA).

In addition to the municipal wastewater, solutions containing artificial foulants (AHA (Sigma-Aldrich, Germany), BSA (Sigma-Aldrich, Germany), and sodium alginate (Wako Pure Chemical Industries, Japan) and a mixture of all three (hereinafter referred to as the "mixture") were also used in the investigation. The artificial feed waters were prepared by dissolving AHA, BSA, and sodium alginate in water at concentrations of 225, 500, and 200 mg/L, respectively. The "mixture" was prepared by dissolving the three artificial foulants in the same water so that the final concentration of AHA, BSA, and sodium alginate becomes 240, 20, and 34 mg/L, respectively. The experiment using the mixture was carried out to evaluate the extent of synergistic effects (i.e. the acceleration of membrane fouling caused by the interaction between multiple foulants) on the development of membrane fouling. All artificial feed waters had total organic carbon (TOC) concentrations of approximately 100 mg/L, which is almost equal to those of the municipal wastewater used. The TOC concentrations were determined using a TOC analyzer (TOC-V, Shimadzu, Kyoto, Japan). In the experiments using artificial feed waters, the osmotic pressure was adjusted to be equal to that of the municipal wastewater by adding Na_2SO_4. The LC-OCD chromatograms of each feed water are shown in Fig. S1.

A 0.6 M NaCl solution was used as the DS. The salt concentration of the DS was selected to be similar to the typical concentration found in sea water. During the FO filtration test, the NaCl concentration was maintained by adding saturated NaCl solution to the DS tank according to the change in salt concentration (evaluated by monitoring electrical conductivity).

2.2. Batch FO membrane filtration experiment

The development of membrane fouling was evaluated by batch FO membrane filtration experiments. The schematic illustration of this experiment system is shown in Fig. 1. This experiment was carried out using a lab-scale cross-flow FO membrane filtration apparatus having an effective membrane surface area of 29.75 cm^2. A commercial cellulose triacetate FO membrane with an embedded support (CTA-ES, Hydration Technologies Inc., Albany, OR) was used. Both feed water and DS were circulated to the apparatus using a peristaltic pump (MP-2000, EYELA, Tokyo, Japan) in a counter-current direction, and cross-flow velocities of both feed water and DS were 23.1 cm/min. Then, the water was recirculated to reservoir tanks. At the beginning of the experiment, the volumes of both feed water and DS were set at 2 L. All filtration tests were performed with the active layer of the membrane facing the feed solution

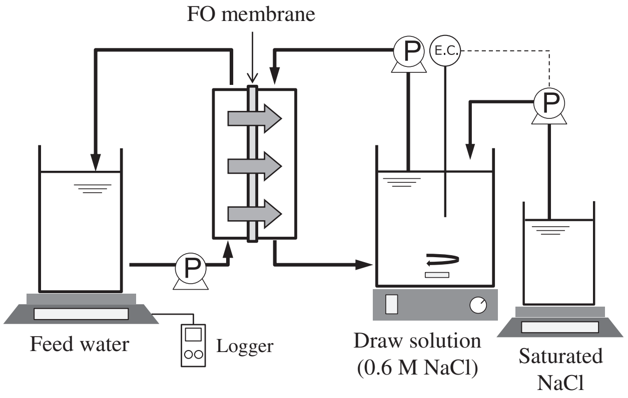

Fig. 1. Schematic illustration of the batch FO membrane filtration experiment system.

(AL-FS) flow direction. This arrangement is thought to be the best one when treating feed water with a high fouling potential [14]. The water flux (J_w, L/m^2 h) was determined by measuring the reduction in the weight of the feed water. The filtration tests were carried out at room temperature (approximately 25°C), and they were continued for 72 h.

2.3. *Evaluation of membrane fouling after the batch FO membrane filtration experiment*

To evaluate the degree of membrane fouling incurred in the batch FO membrane filtration experiment, the water permeability of the fouled FO membrane was measured using Milli-Q water as feed water. At this time, if the FO membrane is slightly dirty, the Milli-Q FS will also be dirty because of its circulation, and the fouling cannot be accurately evaluated. Therefore, before the water permeability measurement, the loosely adhered dirt was rinsed by circulating Milli-Q water at the same cross-flow velocity as used in the batch FO membrane filtration experiment (23.1 cm/min) (defined as the "Milli-Q rinse" procedure). The feed was then replaced with new Milli-Q water, and water permeability was measured. We regarded this measurement as the water permeability after the filtration. In addition, the cross-flow velocity of the feed water (Milli-Q) and DS were same as used in Section 2.2. Following this initial stage, the membrane was removed from the apparatus and immersed in Milli-Q water in a tightly sealed container. The container was then shaken at 180 rpm for 30 min in a thermostatic shaker (NTS-400AL, EYELA, Tokyo, Japan) to detach the remaining tightly attached foulant layer. The water permeability was measured in the same manner as described above and was regarded as the water permeability of the membrane after physical cleaning.

2.4. *Characterization of foulants detached from membranes*

By subjecting the Milli-Q used for the above-mentioned shaking cleaning to fluorescence excitation-emission matrix (EEM) and liquid chromatography with organic carbon detection (LC-OCD) analyses, foulant detached from the FO membrane was analyzed.

2.5. *Analytical methods*

Fluorescence EEMs were generated using a fluorescence spectrophotometer equipped with a 150-W ozone-free xenon arc lamp (Aqua log, Horiba, Kyoto, Japan). The interval of the excitation and emission wavelengths was 3 nm. The excitation and emission wavelengths between 220 and 880 nm were measured. The concentrations of biopolymers and humic substances were determined using an LC-OCD system (Model 8, DOC-LABOR, and Karlsruhe, Germany).

3. Results and discussion

3.1. *FO membrane fouling caused by each feed water*

Fig. 2 shows the changes in water flux during the batch FO membrane filtration tests using the municipal wastewater, effluent from the bench-scale AnMBR fed with the municipal wastewater, and the three solutions containing artificial foulants (i.e. AHA, BSA,

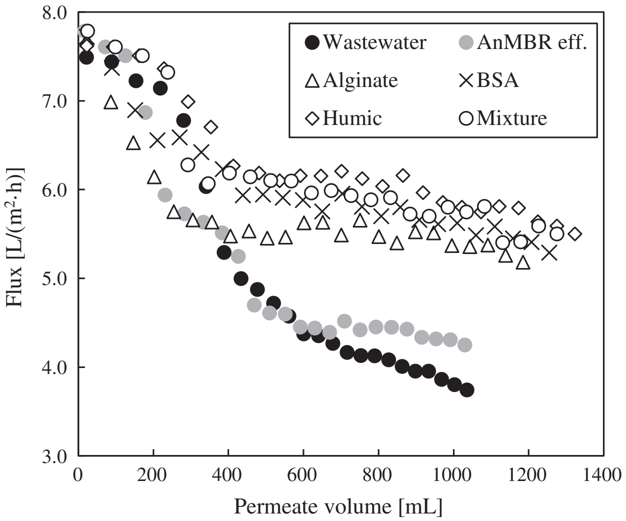

Fig. 2. Changes in water flux in the batch FO membrane filtration tests using various feed waters.

and sodium alginate) and their mixture. As mentioned above, the TOC concentrations of the feed waters containing artificial foulants were adjusted to be equal to those of the municipal wastewater (i.e. 100 mg C/L). Nevertheless, the flux decline caused by the municipal wastewater was apparently greater than that caused by the artificial feed solutions. The FO membrane filtration test using the artificial foulants mixture was carried out to evaluate the impact of the synergistic effect of several types of organic matter on the development of membrane fouling. In a previous investigation undertaken by Neemann et al., the occurrence of non-covalent interactions between BSA and sodium alginate resulted in an increase in the fouling potential of low-pressure membranes [15]. The results obtained from the present study indicate that such synergistic effects are not important in the fouling of FO membranes. In the case of the AnMBR effluent, the TOC concentration (37.6 mg/L) was lower than that of the other feed waters examined in this study. However, the development of membrane fouling in the FO filtration test using the AnMBR effluent was much more significant than in those tests in which the feed waters were comprised of artificial organic compounds. The degree of membrane fouling caused by the AnMBR effluent was almost the same as that developed in the test using the municipal wastewater, suggesting that the organic matter contained in the AnMBR effluent has a much higher potential for causing fouling of the FO membrane used in this study.

The degrees of recovery in membrane water permeability achieved by Milli-Q rinsing are described in Fig. 3. The vertical line in Fig. 3 is the normalized flux. This is the value obtained by dividing the water flux measured after the batch FO membrane filtration experiments, or after physical cleaning, by the water flux of a new FO membrane. Physically irreversible fouling was substantially developed in the FO filtration tests using the municipal wastewater, and the effluent obtained from the bench-scale MBR, as shown by the fact that water permeabilities could not be fully recovered by this method of cleaning. On the other hand, the water permeability of membranes was almost completely recovered by Milli-Q rinsing, where the solutions containing the artificial foulants (i.e. AHA, BSA, sodium alginate and their mixture) were used as the feed water. In many previous studies, the fouling of FO membranes has been reported to be highly reversible by physical cleaning, such as surface flushing [9,10,16]. However, in most previous studies, a feed water composed of artificial organic compounds was used [9,10]. The results obtained in this study clearly indicate that the trend in the reversibility of FO membrane fouling found in previous studies was only limited to membrane fouling caused by artificial foulants. As indicated by the results obtained in this study, artificial foulants such as AHA, BSA, and sodium alginate were not capable of reproducing the entire range of membrane fouling developed in tests using the municipal wastewater. This study has shown that investigations of FO membrane fouling with surrogate wastewater are unable to obtain reliable results unless a suitable composition is chosen. To accurately investigate the development of this type of fouling, an FO membrane filtration test using actual municipal wastewater should be performed.

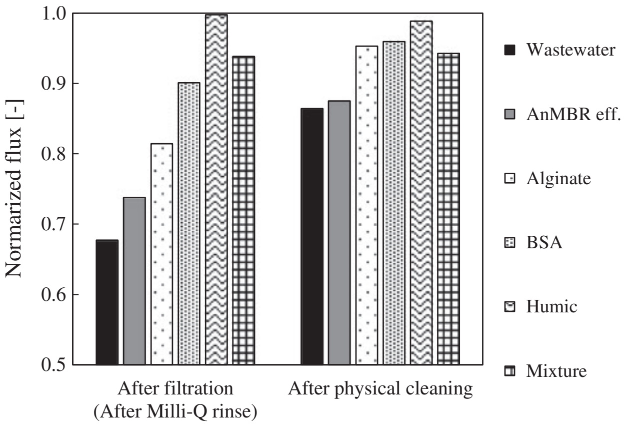

Fig. 3. Recoveries of membrane water permeabilities by physical cleaning (intensive shaking).

3.2. Characteristics of foulants in FO membranes

Based on the results presented in the previous section, it can be concluded that in evaluating the fouling mechanisms of FO membranes, information about the characteristics of the foulants in actual feed waters is of critical importance. In this study, the foulants accumulated on the FO membranes during the filtration tests using actual municipal wastewater were detached and characterized.

The important fractions of the organic matter causing the fouling were investigated using LC-OCD analysis. The biopolymer concentrations evaluated using this analysis have been recently considered to be one of the most important foulants in many types of membrane separation (e.g. river water filtration using low-pressure membranes) [17,18]. The results of the LC-OCD analysis of the organic matter contained in the feed water and the foulants detached from the membranes are presented in Fig. 4. As can be seen in the figure, the chromatogram obtained for the municipal wastewater and AnMBR effluent contained peaks associated with a broad range of organic matter,

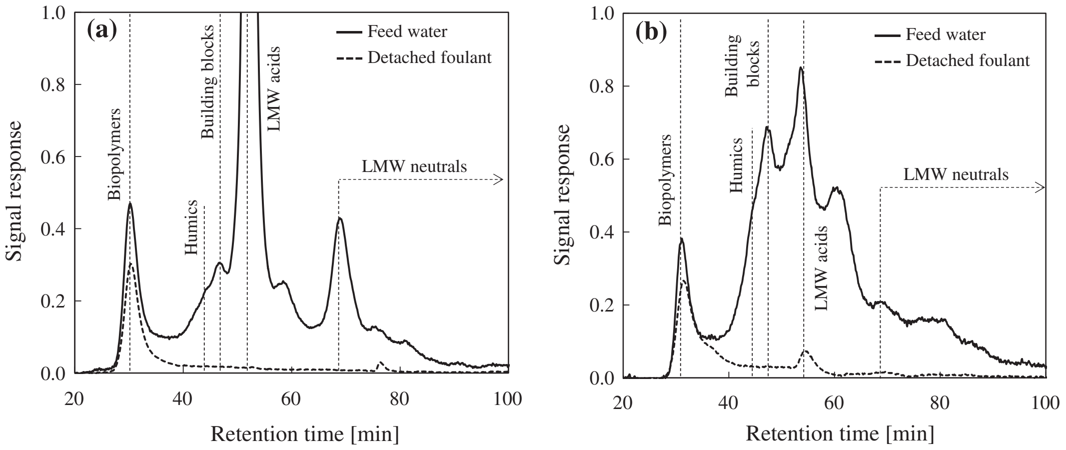

Fig. 4. Chromatograms obtained by the LC-OCD analysis of the organic matter contained in feed waters and foulants detached from membranes: (a) municipal wastewater and (b) AnMBR effluent.

namely biopolymers (about 30 min), humic substances (about 45 min), building blocks (about 50 min), and low-molecular-weight (LMW) acids (about 58 min) and neutrals (about 70 min) [19]. In the chromatogram obtained for the feed water, the peak assigned to biopolymers was not prominent. In contrast, the peak assigned to biopolymers was predominant in the chromatogram obtained for the foulant detached from the membranes, irrespective of the feed water used (i.e. both municipal wastewater and AnMBR effluent). In the LC-OCD chromatogram for the detached foulant, the peak assigned to humic substances, i.e. a peak located at approximately 45 min [19] was not clearly seen, indicating that hydrophobic organic matter was a minor component in the foulant that caused physically irreversible fouling of the FO membrane used in filtering the municipal wastewater and AnMBR effluent.

Fig. 5 shows the fluorescence EEM spectra obtained for the feed water and the foulants detached from the membranes at the end of the FO filtration test using the municipal wastewater. In the fluorescence EEM spectra, a peak located at the area of Ex/Em = 275 nm/350 nm (Peak 1 in Fig. 5) can be attributed to protein-like substances contained in soluble microbial products (SMPs) [20]. Peaks that can be attributed to humic acid-like substances appear at the area of Ex/Em = 350 nm/425 nm (Peak 2 in Fig. 5) [20]. In the spectra obtained for the municipal wastewater, in addition to the peak that can be attributed to protein-like substances, peaks that can be attributed to humic acid-like substances were also clearly seen (Fig. 5(a)). On the other hand, only the peak that can be attributed to protein-like substances was prominently detected and the peaks that can be attributed to

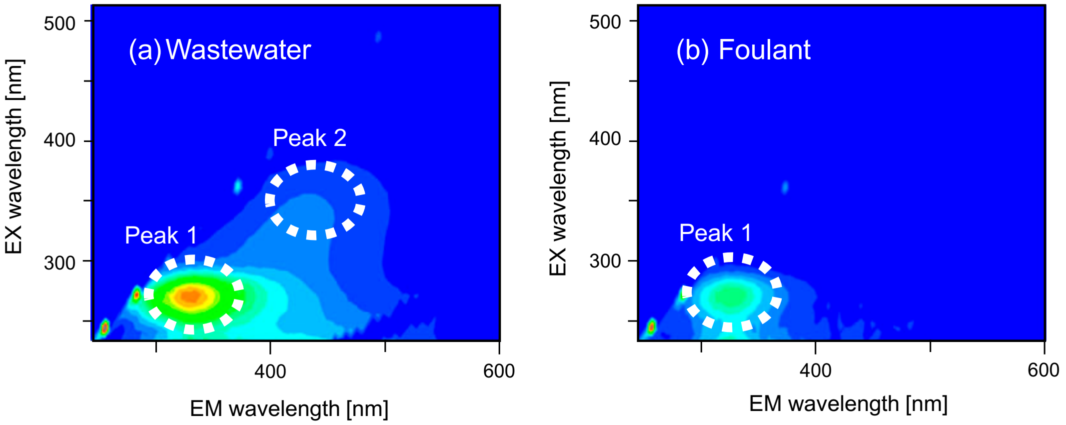

Fig. 5. Fluorescence EEM spectra obtained for municipal wastewater (a) and the foulant detached from the membrane (b).

humic acid-like substances were not seen in the spectra determined for the foulants detached from the FO membrane used in filtering the municipal wastewater (Fig. 5(b)). This result suggests that proteins contained in the SMP preferably attached to the FO membrane during the filtration tests. The importance of the protein-like substances in the development of membrane fouling has also been reported in other membrane filtration processes [21,22]. The results presented in Fig. 5 also indicate that the contribution of hydrophobic organic matter, such as humic substances, to the development of the fouling of the FO membrane was not pronounced. This result is generally in agreement with that obtained by LC-OCD analysis (Fig. 3), indicating that biopolymers are predominant in the foulants detached from the membranes since protein is one of the major components of biopolymers. Some researchers have used principal component analysis or the PARAFAC model to conduct a more detailed analysis of EEM data [23,24]. Although such advanced statistical analyses were not implemented in this study, the results presented in Fig. 5 strongly suggest that organic macromolecules produced through the activity of micro-organisms were the major contributors to membrane fouling during the FO membrane filtration tests.

As mentioned above, organic macromolecules produced through microbial activities are thought to be responsible for the fouling of FO membranes. Many researchers have reported that these organic substances cause severe fouling in various types of membrane filtration processes used for drinking water and wastewater treatment processes [17,21–25]. Since the driving force in the FO membrane filtration process is completely different from that of other conventional membrane-based water treatment processes, where a gradient in hydraulic pressure is utilized, the characteristics of the dominant foulants in this process were also expected to be different. However, the dominant foulants in the FO membrane filtration process are likely to be similar to those of pressure-driven membrane filtration processes. To confirm this finding, investigations into the characteristics of the foulants obtained at the end of long-term continuous-operation FO membrane filtration processes, operating under conditions that simulate practical applications, should be an important area of research.

Among the feed waters used in this study, the solutions containing artificial foulants (excepting that containing AHA) had much higher biopolymer concentrations than the real municipal wastewater, as revealed by the LC-OCD results. Based on the aforementioned finding that biopolymers are the dominant contributors to FO membrane fouling, these artificial solutions would be likely to cause more severe membrane fouling than real municipal wastewater. However, the results of the FO membrane fouling test revealed that the membrane fouling caused by real municipal wastewater was more severe than the fouling caused by the artificial solutions, including the "mixture." This discrepancy suggests that the potential for causing membrane fouling differs depending on the types and characteristics of the polysaccharides or proteins present. In such cases, the detailed characteristics of the polysaccharides or proteins, which have high fouling potentials, need to be investigated. Recent advances in analytical techniques for investigating the detailed characteristics of polysaccharides and proteins [26–28] may give opportunities to identify those that cause severe fouling in FO membrane filtration processes. Further study regarding these points is needed.

4. Conclusions

The characteristics of organic compounds causing severe membrane fouling in the FO membrane filtration process were investigated. The comparison of FO membrane fouling by artificial foulants (i.e. AHA, BSA, and sodium alginate) and organic matter contained in actual municipal wastewater showed that the organic matter contained in the municipal wastewater had a much higher fouling potential than that of the artificial foulants. This suggests that the artificial foulants discussed above are not appropriate compounds for investigating the fouling of FO membranes. The foulants detached from the FO membranes used for filtering the municipal wastewater were characterized using fluorescence EEM and LC-OCD analyses. The results of these analyses clearly indicate that biopolymer-like organic matter (organic macromolecules generated by microbial activities) was the dominant component in the detached foulant. Based on the results of this study, it can be concluded that, as in the cases of conventional pressure-driven membranes, hydrophilic organic macromolecules are important organic fractions contributing to the fouling of FO membranes, despite the significant difference in the driving force between the two processes.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2016.1165738.

Acknowledgments

This work has been supported by the Regional Innovation Strategy Support Program, Ministry of Education, Cultures, Sports, Science and Technology, Japan, and the Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Young Scientists (B) (25820255), Japan. We are deeply grateful for the kind assistance given by the Public Construction Projects Bureau of Kobe City.

References

[1] G. Skouteris, D. Hermosilla, P. López, C. Negro, Á. Blanco, Anaerobic membrane bioreactors for wastewater treatment: A review, Chem. Eng. J. 198–199 (2012) 138–148.

[2] L. Chen, Y. Gu, C. Cao, J. Zhang, J.W. Ng, C. Tang, Performance of a submerged anaerobic membrane bioreactor with forward osmosis membrane for low-strength wastewater treatment, Water Res. 50 (2014) 114–123.

[3] Y. Ding, Y. Tian, Z. Li, F. Liu, H. You, Characterization of organic membrane foulants in a forward osmosis membrane bioreactor treating anaerobic membrane bioreactor effluent, Bioresour. Technol. 167 (2014) 137–143.

[4] S.K. Lateef, B.Z. Soh, K. Kimura, Direct membrane filtration of municipal wastewater with chemically enhanced backwash for recovery of organic matter, Bioresour. Technol. 150 (2013) 149–155.

[5] X. Zhang, Z. Ning, D.K. Wang, J.C.D. da Costa, Processing municipal wastewaters by forward osmosis using CTA membrane, J. Membr. Sci. 468 (2014) 269–275.

[6] P.L. McCarty, J. Bae, J. Kim, Domestic wastewater treatment as a net energy producer—Can this be achieved? Environ. Sci. Technol. 45(17) (2011) 7100–7106.

[7] S. Onoda, Y. Masumori, T. Miyoshi, M. Yasukawa, T. Takahashi, H. Matsuyama, Rejection of nutrients contained in an anaerobic digestion effluent using a forward osmosis membrane, Desalin. Water Treat. (2015) 1–11.

[8] Y. Song, P. Yuan, B. Zheng, J. Peng, F. Yuan, Y. Gao, Nutrients removal and recovery by crystallization of magnesium ammonium phosphate from synthetic swine wastewater, Chemosphere 69(2) (2007) 319–324.

[9] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), J. Membr. Sci. 365(1–2) (2010) 34–39.

[10] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, J. Membr. Sci. 348(1–2) (2010) 337–345.

[11] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, J. Membr. Sci. 354(1–2) (2010) 123–133.

[12] M.M. Motsa, B.B. Mamba, A. D'Haese, E.M.V. Hoek, A.R.D. Verliefde, Organic fouling in forward osmosis membranes: The role of feed solution chemistry and membrane structural properties, J. Membr. Sci. 460 (2014) 99–109.

[13] H. Yamamura, K. Okimoto, K. Kimura, Y. Watanabe, Influence of calcium on the evolution of irreversible fouling in microfiltration/ultrafiltration membranes, J. Water Sup.: Res. Technol.—AQUA, 56(6–7) (2007) 425–434.

[14] S. Zhao, L. Zou, D. Mulcahy, Effects of membrane orientation on process performance in forward osmosis applications, J. Membr. Sci. 382(1–2) (2011) 308–315.

[15] F. Neemann, S. Rosenberger, B. Jefferson, E.J. McAdam, Non-covalent protein–polysaccharide interactions and their influence on membrane fouling, J. Membr. Sci. 446 (2013) 310–317.

[16] Z.-Y. Li, V. Yangali-Quintanilla, R. Valladares-Linares, Q. Li, T. Zhan, G. Amy, Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis, Water Res. 46(1) (2012) 195–204.

[17] K. Kimura, K. Tanaka, Y. Watanabe, Microfiltration of different surface waters with/without coagulation: Clear correlations between membrane fouling and hydrophilic biopolymers, Water Res. 49(1) (2014) 434–443.

[18] F. Chen, S. Peldszus, R.H. Peiris, A.S. Ruhl, R. Mehrez, M. Jekel, R.L. Legge, P.M. Huck, Pilot-scale investigation of drinking water ultrafiltration membrane fouling rates using advanced data analysis techniques, Water Res. 48 (2014) 508–518.

[19] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography–organic carbon detection–organic nitrogen detection (LC–OCD–OND), Water Res. 45(2) (2011) 879–885.

[20] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, Fluorescence excitation−emission matrix regional integration to quantify spectra for dissolved organic matter, Environ. Sci. Technol. 37(24) (2003) 5701–5710.

[21] T. Miyoshi, T. Tsuyuhara, R. Ogyu, K. Kimura, Y. Watanabe, Seasonal variation in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater, Water Res. 43(20) (2009) 5109–5118.

[22] S. Peldszus, C. Hallé, R.H. Peiris, M. Hamouda, X. Jin, R.L. Legge, H. Budman, C. Moresoli, P.M. Huck, Reversible and irreversible low-pressure membrane foulants in drinking water treatment: Identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment, Water Res. 45(16) (2011) 5161–5170.

[23] R.H. Peiris, C. Hallé, H. Budman, C. Moresoli, S. Peldszus, P.M. Huck, R.L. Legge, Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices, Water Res. 44(1) (2010) 185–194.

[24] K.R. Murphy, A. Hambly, S. Singh, R.K. Henderson, A. Baker, R. Stuetz, S.J. Khan, Organic matter fluorescence in municipal water recycling schemes: Toward a unified PARAFAC model, Environ. Sci. Technol. 45(7) (2011) 2909–2916.

[25] Y. Zhao, L. Song, S.L. Ong, Fouling behavior and foulant characteristics of reverse osmosis membranes for treated secondary effluent reclamation, J. Membr. Sci. 349(1–2) (2010) 65–74.

[26] K. Kimura, I. Tanaka, S. Nishimura, R. Miyoshi, T. Miyoshi, Y. Watanabe, Further examination of polysaccharides causing membrane fouling in membrane bioreactors (MBRs): Application of lectin affinity chromatography and MALDI-TOF/MS, Water Res. 46(17) (2012) 5725–5734.

[27] T. Miyoshi, T. Aizawa, K. Kimura, Y. Watanabe, Identification of proteins involved in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater, Int. Biodeterior. Biodegrad. 75 (2012) 15–22.

[28] K. Kimura, S. Nishimura, R. Miyoshi, A. Hoque, T. Miyoshi, Y. Watanabe, Application of glyco-blotting for identification of structures of polysaccharides causing membrane fouling in a pilot-scale membrane bioreactor treating municipal wastewater, Bioresour. Technol. 179 (2014) 180–186.