Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20559

78 (2017) 12–18
June

Effect of the addition of fine bubbles on reversible and irreversible membrane fouling in surface water treatment

Tomoichi Watabe, Tomoki Takahashi, Kazufumi Matsuyama, Hideto Matsuyama*

Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodaicho, Nada-ku, Kobe 657-8501, Japan, Tel./Fax: +81-78-803-6180; emails: matuyama@kobe-u.ac.jp (H. Matsuyama), tm_watabe@daicen.daicel.com (T. Watabe), t.takahashi@crystal.kobe-u.ac.jp (T. Takahashi), budouhitotsubudou@gmail.com (K. Matsuyama)

Received 9 February 2016; Accepted 3 February 2017

ABSTRACT

Membrane processes have been used in numerous applications such as drinking water production from surface water. However, in the water treatment processes with membrane, a membrane fouling is a major problem. In this paper, we investigated the effect of microbubbles (MBs) and ultrafine bubbles (UFBs) on reversible and irreversible fouling in a river water treatment with ultrafiltration process to make a drinking water. The fouling was evaluated by fouling indexes. The relation between a fouling property and a content of dissolved organic matter was also discussed. As a result, it was found that the fouling was mainly a reversible fouling due to biopolymers in feedwater. It was also confirmed that MBs and UFBs prevented sedimentation of foulants on membrane surface for both irreversible and reversible foulings. MBs were more effective to reduce the fouling than UFBs.

Keywords: Ultrafine bubbles; Microbubbles; Membrane fouling; Fouling indexes; River waters

1. Introduction

In recent years, membrane processes have attracted the worldwide attention of both scientific and industrial communities, and have been used in numerous applications such as drinking water production from surface water, wastewater treatment, and desalination of seawater. Particularly, the ultrafiltration (UF) membrane is usually used for the drinking water production from river water. In the water treatment processes with membrane such as reverse osmosis, nanofiltration, and UF, a membrane fouling due to a deposition of various foulants on membrane surface and a pore blocking is a major problem. Membrane fouling reduces a product quality and a permeation flux, and then increases energy consumption. In addition, it results in the frequent chemical cleaning of membranes and membrane module replacement. Thus, the fouling results in an increase of water production costs. Therefore, it is essential to prevent the fouling for reducing water production costs.

Membrane fouling is classified as a reversible and an irreversible fouling. The reversible fouling is recovered by physical cleaning such as a strong shear force or a backwashing, while the irreversible fouling is not recovered by physical cleaning. When the irreversible fouling occurred, a chemical cleaning of membrane is necessary to recover a water flux, and it is a serious problem for membrane processes. Therefore, numerous studies have been reported to reduce the irreversible fouling [1–4].

Natural organic matter (NOM) such as humic substances (HS), proteins, and polysaccharides is widely recognized as the major foulants in low-pressure membrane processes of surface water [5,6]. Generally, NOM is classified as a dissolved organic matter (DOM) and a particulate organic matter (POM). POM is the components filtered by 0.45 μm membrane. Recently, a high-performance liquid

* Corresponding author.

chromatography with liquid chromatography-organic carbon detection (LC-OCD) analysis is used to analyze DOM which causes membrane fouling. Excitation–emission matrix (EEM) fluorescence spectroscopy is also used to analyze components of DOM in water and soil [7,8]. The hydrophobic HS have been considered as the dominant foulants in UF membrane process [9]. Shang et al. [10] reported that the adsorption of HS on membrane is a major cause of the irreversible fouling. On the other hand, it is also reported that the polysaccharides and proteins are problematic foulants in UF process in spite of their relatively hydrophilic characters [5,6]. Kimura et al. [3] demonstrated that polysaccharide-like organic matter was responsible for the irreversible fouling in surface water filtration. The mechanism of membrane fouling due to NOM has been reported by Yamamura et al. [1,2]. First, the hydrophobic NOM such as HS adsorb on the membrane, and then hydrophilic NOM such as polysaccharides and proteins block the membrane pores.

One of the possible ways to reduce the irreversible fouling is the reduction of NOM content of raw water. A pretreatment of raw water is a highly potential way. Coagulation/sedimentation through the addition of chemicals is the most common pretreatment not only for improving the quality of treated water but also for reducing membrane fouling [11,12]. However, coagulation/sedimentation has various problems, such as a high flocculant cost and a subsequent membrane fouling by residual flocculants [13,14]. Recently, some chemical-free processes have been reported for membrane fouling reduction. Hallé et al. [15] reported the chemical-free rapid biological filtration for surface water treatment. Although the contact time with the biofilter was long, the membrane fouling was reduced [15]. Muthukumaran et al. [16] studied the use of ultrasonic cleaning for membrane fouling reduction in whey treatment.

We have also reported that the microbubbles (MBs) are effective for reducing membrane fouling in the UF process of real surface water [17]. In a pilot-scale experiment, the stable membrane filtration was achieved under a high membrane flux of 3.0 $m^3/m^2/d$ by adding MBs to feedwater. MBs were also effective for chemical-free cleaning of the fouled membrane module. On the other hand, the lab-scale experiments using river water and model foulant solutions revealed that the effect of MBs on reduction of membrane fouling depended on the characteristics of raw water [18]. However, in these papers, the fouling behavior analysis such as reversible fouling and irreversible fouling was not investigated. In addition, only MBs were used in these papers, and the evaluation of water quality was insufficient since it was done by the only total organic carbon.

In this paper, we investigated the effect of two types of fine bubbles (FBs), MBs, and ultrafine bubbles (UFBs). In addition, the effect of FBs on reversible and irreversible fouling in UF process was analyzed separately. Three different river waters were used as a feedwater and the water quality was evaluated with EEM and LC-OCD. The fouling behaviors were evaluated by the fouling indexes [4,19–21]. The relation between the fouling indexes and component of DOM was also discussed.

2. Experimental setup

2.1. River waters and water quality

The water samples were obtained from three rivers in Japan (Toga River, Sumiyoshi River, and Muko River). They were used as feedwater in a lab-scale membrane filtration test. The river water samples were filtered through a 0.45 μm polytetrafluoroethylene filter before water quality analyses to remove POM. The DOM analysis of water samples was subjected to the LC-OCD system (Model 8, DOC-Labor, Karlsruhe, Germany). The dissolved organic carbon (DOC) content of DOM such as biopolymers, HS, building blocks, low-molecular-weight (LMW) acid, and LMW neutrals were measured by LC-OCD. The components of DOM were analyzed with the EEMs spectroscopy (Aqualog, Horiba, Kyoto, Japan) between 250 and 610 nm at intervals of 5 nm.

2.2. FBs generation and size distribution

A pressurized dissolution-type apparatus (OM4-MDG-045, AuraTec Co., Ltd., Fukuoka, Japan) was used as a FBs generator. The mixture of water and air supplied to the internal tank of FBs generator was pressurized by internal gear pump, where dissolved air was supersaturated. Highly pressurized water was released into a supply pipe through a reducing valve and nozzle, and then FBs were generated by discharging the pressure. In this study, two nozzles with different orifice diameter were used for generating MBs and UFBs. The MBs and UFBs size distributions were measured using SALD-7500nano (Shimadzu Co., Kyoto, Japan) and NanoSight (Quantum Design Japan, Inc., Tokyo, Japan) nanoparticle size analyzers, respectively. To measure the bubbles size distributions, the FBs generator was separated with the filtration equipment. Size of MBs changes every second. Therefore, MBs size distribution was measured with a low pressure flow cell connected with MBs generator. The flow rate was 1.5 L/min and the pressure was 0.1 bar. On the other hand, size of UFBs does not change for several minutes. In addition, NanoSight cannot be connected with UFBs generator. Therefore, UFBs size distribution was measured in other tank.

2.3. Filtration experiments

Cellulose acetate UF hollow fiber membranes (Daicen Membrane-Systems Ltd., Tokyo, Japan) were used for filtration. The membrane (inner/outer fiber diameters: 0.80/1.30 mm) was hydrophilic and showed low foulant adsorption. The nominal molecular weight cut-off (as determined by protein rejection) was 150,000 Da. One fiber was cut to 110 mm (effective membrane area: 0.00028 m^2) and used for filtration. The hydraulic permeability of the membrane, determined by using pure water, was 320 $L/m^2{\cdot}h$ at 0.5 bar.

Fig. 1 shows a schematic diagram of the lab-scale filtration equipment with the FBs generator. The filtration system consisted of two parts: an internal pressure type cross-flow unit with a circulation loop, and a pure water backwashing unit. The circulation loop comprised a membrane module, an FBs generator, and a feed tank. At first, a pure water was used as a feedwater and put into a feed tank kept at 25°C. Then, the cross-flow filtration was carried out under a constant

pressure of 0.5 bar (flow velocity was almost 0.06 m/s). The retentate was circulated to the feed tank. The FBs do not influence the filtration fluxes at all in the filtration of pure water containing FBs.

FBs size, MBs, and UFBs were changed by changing nozzles equipped at the outlet of the generator. During the filtration, MBs or UFBs were kept being supplied to the water sample. The volumetric flow rate (mL/min) was determined by measuring the volume of permeate with time. After the pure water filtration, a river water sample was filtered through the same hollow fiber membrane and the volumetric flow rate was measured. The river water was filtrated for 1 h and then the membrane was backwashed for 10 min with pure water. The backwashing pressure was 1.0 bar. This procedure was repeated four times.

2.4. Fouling indexes

The fouling index is a conventional parameter to evaluate the fouling potential in membrane filtration. Standardized total fouling index (TFI), hydraulic reversible fouling index (HRFI), and hydraulic irreversible fouling index (HIFI) are generally used [4,19–21]. The definitions of indexes are indicated in Fig. 2. These indexes are obtained from the time course of water flux. The specific flux J_s (L/m²/h/bar) is expressed as follows:

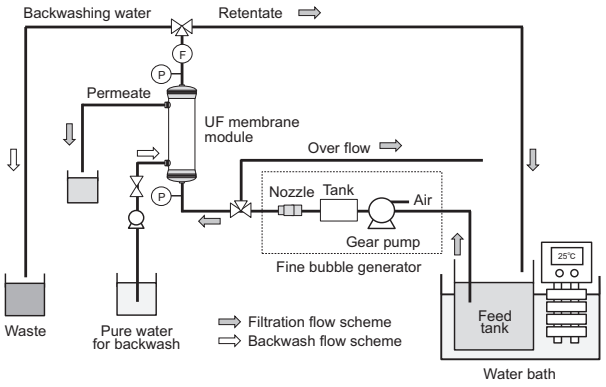

Fig. 1. Schematic diagram of membrane filtration equipment with fine bubbles.

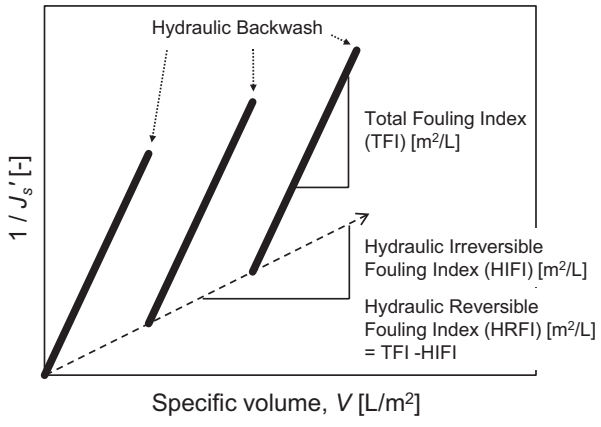

Fig. 2. Concept of membrane fouling progress during filtration.

$$J_s = \frac{J}{\Delta P} = \frac{1}{\mu\left(K_{\text{mem}} + k_{\text{total}} V\right)} \tag{1}$$

where J is the water flux (L/m²/h), ΔP is the transmembrane pressure (bar), μ is the viscosity of water (bar·h), K_{mem} is the resistance of a clean membrane (m²/L), k_{total} is the sum of rate constants for resistances (m⁴/L²) due to reversible fouling and irreversible fouling, and V is the specific permeate volume (L/m²). The normalized specific flux (J_s') was obtained by dividing $J/\Delta P$ at any specific volume, $(J/\Delta P)_V$ by the initial condition (clean membrane, $V = 0$), $(J/\Delta P)_0$ as follows:

$$J_s' = \frac{\left(J/\Delta P\right)_V}{\left(J/\Delta P\right)_0} = \frac{1}{1 + \dfrac{k_{\text{total}}}{K_{\text{mem}}} V} \tag{2}$$

$$\frac{1}{J_s'} = 1 + \frac{k_{\text{total}}}{K_{\text{mem}}} V \tag{3}$$

In Eqs. (2) and (3), $k_{\text{total}}/K_{\text{mem}}$ corresponds to TFI and is obtained from the gradient of $1/J_s'$ vs. V curve.

The concept of the linear relationship between $1/J_s'$ and V is shown in Fig. 2.

The increase in $1/J_s'$ just after backwashing indicates the amount of irreversible fouling which is evaluated as HIFI as shown in Fig. 2. HRFI is defined as the difference between the TFI and HIFI.

3. Results and discussion

3.1. Size distribution of FBs

Fig. 3 shows the size distributions of MBs and UFBs generated in the river water samples. The distribution of MBs was similar in all samples, and their diameters ranged from 0.5 to 2.0 μm and were mainly 0.75 μm, as shown in Fig. 3(a). Although the distributions of UFBs were slightly different in each sample, their diameters were mainly 100 nm, as shown in Fig. 3(b). Thus, it is clear that the size distribution of FBs scarcely depends on the river waters.

3.2. Water quality of river waters

Fig. 4 shows the LC-OCD chromatograms of the river water samples. According to Huber et al. [22], fractions A, B, C, D, and E are attributable to the biopolymers, HS, building blocks, LMW acids, and LMW neutrals, respectively. Approximately, molecular weight of the biopolymers is >20,000 g/mol, the HS is >1,000 g/mol, building blocks is 300–500 g/mol, and LMW acid and LMW neutrals are <350 g/mol. The results are summarized in Table 1, including the specific ultraviolet absorbance (SUVA). SUVA indicates the existence of the hydrophobic aromatic substances such as HS in dissolved organic compounds [23]. It was clearly from Table 1 that the content of each component in Muko River

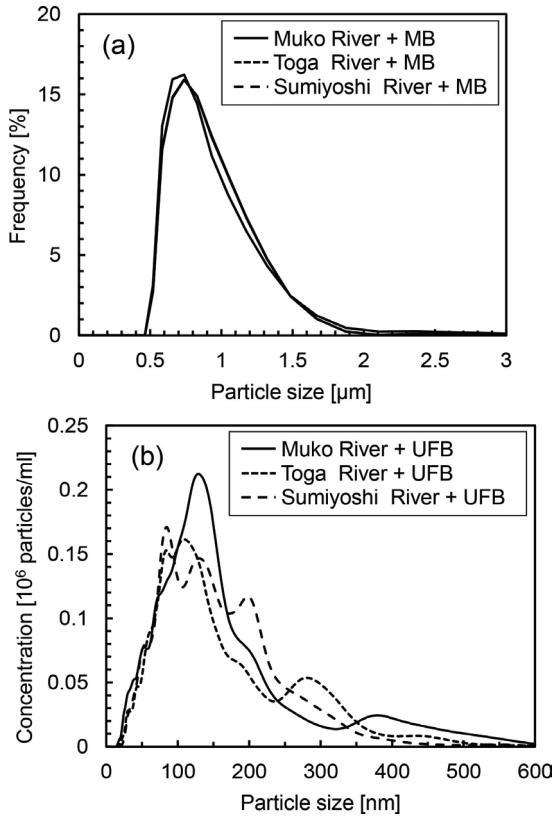

Fig. 3. Size distributions of: (a) microbubbles and (b) ultrafine bubbles in the river water samples.

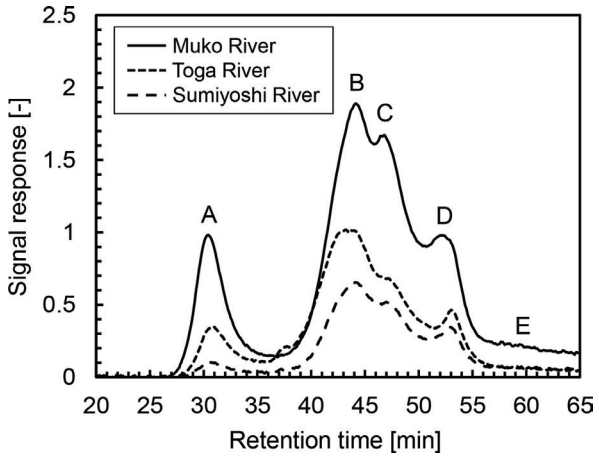

Fig. 4. LC-OCD chromatogram of river water samples.

Table 1
The water quality of three rivers by LC-OCD measurement

Samples	DOC [ppb-C]	Biopolymers [ppb-C]	Humic substance (HS) [ppb-C]	Building blocks + HS [ppb-C]	LMW acids [ppb-C]	LMW neutrals [ppb-C]	SUVA [1/m/mg/L] [ppb-C]
Muko River	1,737	261	851	273	59	293	1.46
Toga River	802	99	487	127	26	63	3.21
Sumiyoshi River	554	36	268	110	23	117	2.87

sample was the highest, and that of Sumiyoshi River sample was the lowest. In all samples, the main substance of DOC was HS. As for the SUVA value, Toga River sample showed the highest value. It indicates that the proportion of hydrophobic aromatic substances in DOM of Toga River sample is highest in three river waters.

Composition of polysaccharides and proteins, which are similar size, is unidentified because these are analyzed as biopolymer in LC-OCD. Then, the components of DOM were analyzed by EEM. The measurement results are shown in Fig. 5. According to Chen et al. [7], the peak in region IV in this figure is attributable to the soluble microbial by-product-like material such as tryptophan and the peak in region V is humic-acid-like organics such as humic acid. As for the region IV, the Muko River sample showed the strongest peak although the samples from the Toga and Sumiyoshi Rivers did not show the clearly detectable EEM peaks. In addition, as for the region V, the Muko River sample showed the strongest peak and Sumiyoshi River sample showed the weakest peak. This tendency has good relation to the quantity of biopolymer and HS analyzed by LC-OCD. It indicated that the protein content in the biopolymer composition of Muko River sample was higher than other samples.

3.3. Effect of addition of FBs on fouling behavior

Fig. 6 shows the inverse of specific flux ($1/J_s'$) as a function of specific volume for the three river water samples. In all cases, four cycle (one cycle: filtration and backwashing) experiments were conducted. The addition of FBs decreased the gradient, which indicated that TFI was decreased and FBs was effective in the reduction of membrane fouling by all river water samples. This fouling-reduction effect depended on not only the river samples, but also the bubble size distribution (MBs or UFBs).

Fig. 7 shows the effect of FBs on the fouling indexes and the backwashing efficiency in three river samples. In Fig. 7(a), the order of the TFI values in each samples agreed with that of the DOC values of the river water samples shown in Table 1, regardless of the presence or absence of FBs. That is, the Muko River sample showed the largest TFI and the Sumiyoshi River sample showed the lowest. In all filtration tests, the HRFI was larger than the HIFI. Therefore, reversible fouling is a dominant factor to water flux reduction in this paper. In addition, the FBs were effective in reducing both the HRFI and HIFI, and the effect of MBs was greater than that of UFBs except Sumiyoshi River water. In the case of the Sumiyoshi River sample, the difference between the effects of MBs and UFBs was not clear, because the fouling indexes were too low.

In addition, the index of backwashing efficiency defined as 100 × (TFI – HIFI)/TFI was shown in Fig. 7(b). This index indicates the percentage of reversible fouling. Thus, if the flux recovery of fouled membrane is high this index is large. The backwashing efficiencies were >70% in each filtration test, and it was >85% in case of Muko River sample. From Fig. 7(b), the effect of FBs on the backwashing efficiency was not clear. It means that the percentage of reversible fouling is not clearly affected by FBs. On the other hand, TFI is decreased by FBs. Therefore, it is clear that the FBs prevented sedimentation of foulants on membrane surface for both irreversible and reversible foulings.

The large molecules such as the biopolymers and HS are the main compounds for membrane fouling, because the molecular weight cut-off of employed UF membrane was 150,000 Da. In addition, Kimura et al. [20] reported that the biopolymers were mainly responsible for membrane fouling in low-pressure membrane processes. The relationship between the fouling indexes and biopolymers concentration was shown in Fig. 8.

As shown in Fig. 8(a), HRFI increased with the increase in the biopolymers concentration. The MBs were effective

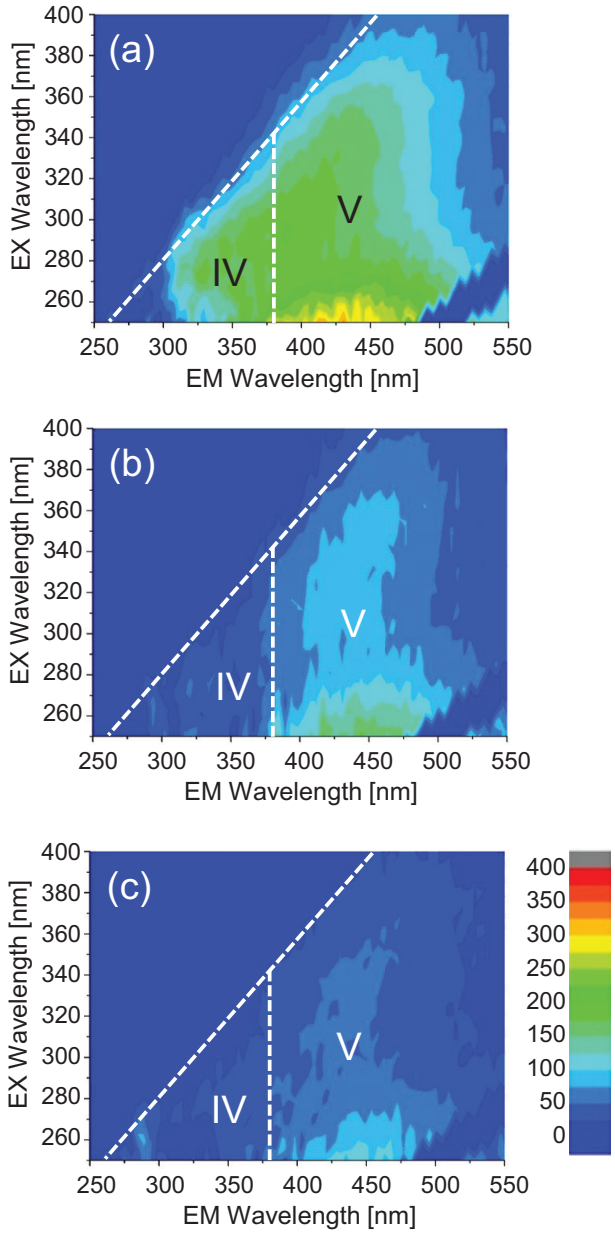

Fig. 5. EEM spectra of surface water samples: (a) Muko River, (b) Toga River, and (c) Sumiyoshi River.

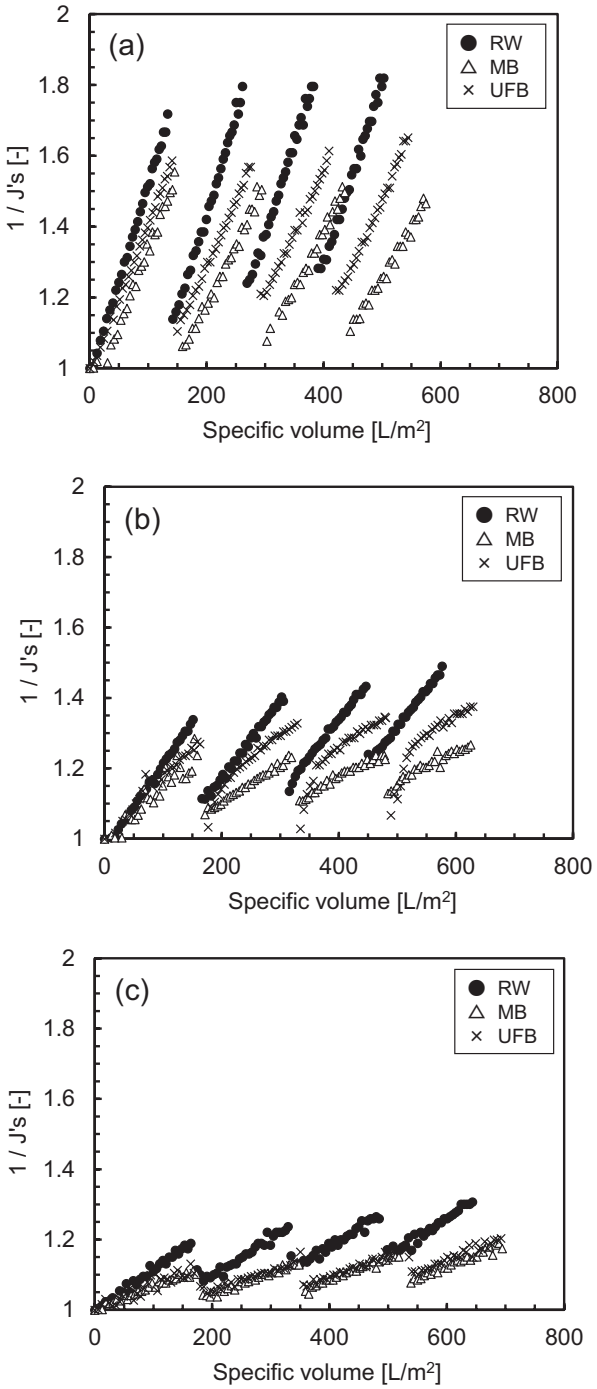

Fig. 6. Effect of addition of FBs on inverse of specific flux in the river water (RW) samples: (a) Toga River, (b) Sumiyoshi River, and (c) Muko River.

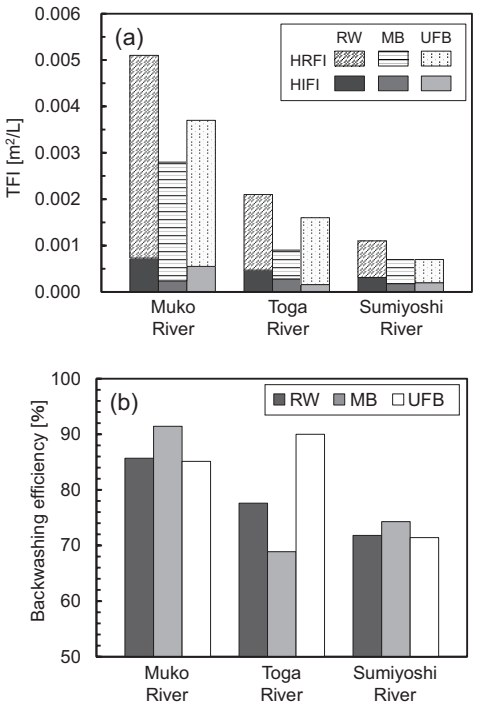

Fig. 7. Effect of FBs on: (a) the fouling indexes and (b) the backwashing efficiency in three river samples.

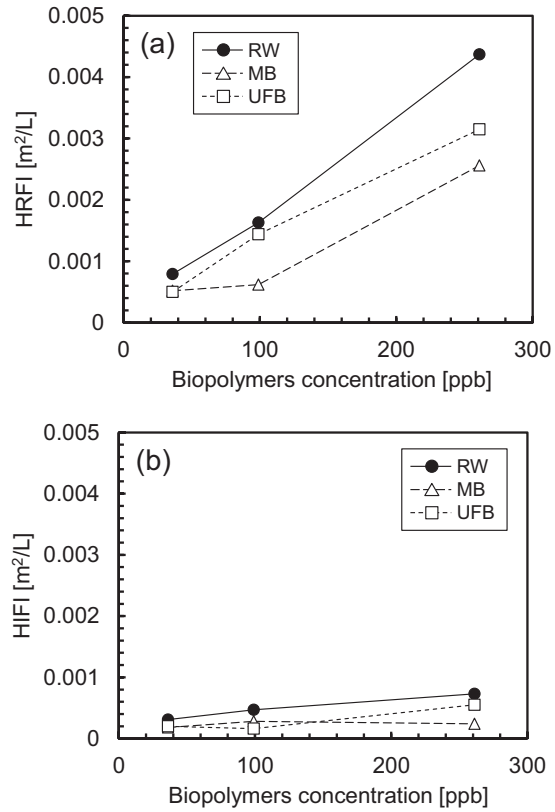

Fig. 8. Relationship between the fouling indexes and biopolymer concentration: (a) the effect of FBs on HRFI and (b) the effect of FBs on HIFI.

for HRFI reduction than that of UFBs. This indicates that the fouling reduction mechanisms may be different in the cases of the additions of MBs and UFBs. For example, the effect of MBs on shear rate at the membrane/water interface may be stronger than that of UFBs although the total surface area of UFBs is large than that of MBs. Moreover, the difference may be caused by the difference in a shrinkage characteristic of MBs and UFBs, but further study is necessary to confirm these.

On the other hand, the HIFI slightly increased with the increase in the biopolymers concentration as shown in Fig. 8(b). The clear difference of MBs and UFBs was not observed. However, it is clear from Fig. 8 that FBs are very effective to reduce the fouling in the UF of river water.

4. Conclusion

We investigated the effect of FBs, MBs, and UFBs, on reversible and irreversible foulings in UF process using three river waters. The fouling behaviors were evaluated by the fouling indexes. The relation between the fouling indexes and component of DOM was also discussed. HRFI was >70% of TFI. Thus, it was found that the fouling in river water treatment with UF membrane was mainly reversible fouling. In addition, the reversible fouling was mainly due to the biopolymer, since HRFI increased with the increase in the biopolymers concentration. On the other hand, HIFI slightly increased with the increase in the biopolymers concentration. The MBs were more effective for HRFI reduction than that of UFBs. TFI was reduced by FBs, but the percentage of HRFI in TFI was scarcely affected by FBs. Thus, it is clear that FBs prevented sedimentation of foulants on membrane surface for both irreversible and reversible foulings. Thus, FBs are very effective to reduce the fouling in UF process using river water. However, the mechanism of fouling reduction due to the addition of FBs and UFBs should be investigated in our future work.

Acknowledgments

This work was partly supported by Grants-in-Aid from the Special Coordination Fund for Promoting Science and Technology, Creation of Innovation Centers for Advanced Interdisciplinary Research Areas (Innovative Bioproduction, Kobe), and the Regional Innovation Strategy Support Program from the MEXT, Japan.

References

[1] H. Yamamura, K. Kimura, Y. Watanabe, Mechanism involved in the evolution of physically irreversible fouling in microfiltration and ultrafiltration membranes used for drinking water treatment, Environ. Sci. Technol., 41 (2007) 6789–6794.
[2] H. Yamamura, K. Okimoto, K. Kimura, Y. Watanabe, Hydrophilic fraction of natural organic matter causing irreversible fouling of microfiltration and ultrafiltration membranes, Water Res., 54 (2014) 123–136.
[3] K. Kimura, Y. Hane, Y. Watanabe, G. Amy, N. Ohkuma, Irreversible membrane fouling during ultrafiltration of surface water, Water Res., 38 (2004) 3431–3441.
[4] A.H. Nguyen, J.E. Tobiason, K.J. Howe, Fouling indices for low pressure hollow fiber membrane performance assessment, Water Res., 45 (2011) 2627–2637.

[5] N. Lee, G. Amy, J.P. Croue, H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res., 38 (2004) 4511–4523.
[6] N. Lee, G. Amy, J.P. Croue, H. Buisson, Morphological analyses of natural organic matter (NOM) fouling of low-pressure membranes (MF/UF), J. Membr. Sci., 261 (2005) 7–16.
[7] 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 (2003) 5701–5710.
[8] 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 (2011) 5161–5170.
[9] C. Jucker, M.M. Clark, Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes, J. Membr. Sci., 97 (1994) 37–52.
[10] R. Shang, F. Vuong, J. Hu, S. Li, A.J.B. Kemperman, K. Nijmeijer, E.R. Cornelissen, S.G.J. Heijman, L.C. Rietveld, Hydraulically irreversible fouling on ceramic MF/UF membranes: comparison of fouling indices, foulant composition and irreversible pore narrowing, Sep. Purif. Technol., 147 (2015) 303–310.
[11] W. Gao, H. Liang, J. Ma, M. Han, Z.-L. Chen, Z.-S. Han, G.-B. Li, Membrane fouling control in ultrafiltration technology for drinking water production: a review, Desalination, 272 (2011) 1–8.
[12] H. Huang, K. Schwab, J.G. Jacangelo, Pretreatment for low pressure membranes in water treatment: a review, Environ. Sci. Technol., 43 (2009) 3011–3019.
[13] S.J. Judd, P. Hillis, Optimization of combined coagulation and microfiltration for water treatment, Water Res., 35 (2001) 2895–2904.
[14] Y. Soffer, J. Gilron, A. Adin, Streaming potential and SEM-EDX study of UF membranes fouled by colloidal iron, Desalination, 146 (2002) 115–121.
[15] C. Hallé, P.M. Huck, S. Peldszus, J. Haberkamp, M. Jekel, Assessing the performance of biological filtration as pretreatment to low pressure membranes for drinking water, Environ. Sci. Technol., 43 (2009) 3878–3884.
[16] S. Muthukumaran, K. Yang, A. Seuren, S. Kentish, M. Ashokkumar, G.W. Stevens, F. Grieser, The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry, Sep. Purif. Technol., 39 (2004) 99–107.
[17] T. Watabe, K. Matsuyama, T. Takahashi, H. Matsuyama, Use of microbubbles to reduce membrane fouling during water filtration, Desal. Wat. Treat., 57 (2016) 3820–3826.
[18] T. Watabe, K. Matsuyama, T. Takahashi, H. Matsuyama, The effect of microbubbles on membrane fouling caused by different foulants, Desal. Wat. Treat., 57 (2016) 9558–9568.
[19] H. Huang, T.A. Young, J.G. Jacangelo, Unified membrane fouling index for low pressure membrane filtration of natural waters: principles and methodology, Environ. Sci. Technol., 42 (2008) 714–720.
[20] 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 (2014) 434–443.
[21] D.T. Myat, M. Mergen, O. Zhao, M.B. Stewart, J.D. Orbell, S. Gray, Characterisation of organic matter in IX and PACl treated wastewater in relation to the fouling of a hydrophobic polypropylene membrane, Water Res., 46 (2012) 5151–5164.
[22] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterization of aquatic humic and non-humic matter with size-exclusion chromatography – organic carbon detection – organic nitrogen detection (LC-OCD-OND), Water Res., 45 (2011) 879–885.
[23] J.L. Weishaar, G.R. Aiken, B.A. Bergamaschi, M.S. Fram, R. Fujii, K. Mopper, Evaluation of specific 50 ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, Environ. Sci. Technol., 37 (2003) 4702–4708.