

## Influence of calcium on the evolution of irreversible fouling in microfiltration/ultrafiltration membranes

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### ABSTRACT

Water treatment using microfiltration (MF)/ultrafiltration (UF) membranes is gaining in popularity all over the world but the problem of membrane fouling needs to be addressed. In this study, the influence of calcium on irreversible fouling in MF/UF membrane filtering natural organic matter (NOM) was investigated on the basis of a series of bench-scale filtration tests. Two types of feed water, solution of commercially available humic acid and surface water used for drinking water source, were filtered with four different MF/UF membranes. It was found that the influence of calcium on the evolution of irreversible fouling would differ depending on the feed water characteristics. Calcium facilitated the aggregation of small molecules with hydrophobic nature contained in commercially available humic acid and the aggregate probably plugged the micropores, resulting in severe irreversible fouling. The effect of calcium was not obvious in the case of the surface water used in this study. This result implies that the use of commercial humic acid for the examination of membrane fouling would be inappropriate.

**Key words** | calcium, irreversible fouling, microfiltration, natural organic matter, ultrafiltration

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### INTRODUCTION

Application of membrane technology to drinking water treatment offers many advantages such as strict removal of pathogens (e.g., *Cryptosporidium*) (Jacangelo 1991; Jacangelo *et al.* 1995). Many microfiltration (MF)/ultrafiltration (UF) membranes, which can be operated at relatively low pressure, have been installed at full-scale all over the world. The main limitation to the use of membranes in drinking water treatment is, however, high energy consumption that can mainly be attributed to membrane fouling occurring over a long period of operation. Much effort has been made to control membrane fouling. Several physical membrane cleaning methods such as backwashing were developed and used routinely in many existing low-pressure membrane plants to minimize membrane fouling. In a continuous operation, membrane filtration resistance gradually increases and is not totally reduced by the physical cleaning mentioned above. Such filtration resistance, defined here as irreversible membrane fouling, can only be overcome by the use of chemical reagents (Crozes *et al.* 1997; Kimura *et al.* 2004). Chemical cleaning of a membrane to cancel

irreversible fouling should be limited to a minimum frequency because repeated chemical cleaning may shorten membrane life, and disposal of spent chemical reagents poses another problem (Committee Report 2003). Thus, the control of the irreversible fouling is of importance for more efficient use of membranes. Information on the constituents causing irreversible fouling and understanding of the fouling mechanism are indispensable. In a number of studies, natural organic matter (NOM) has been demonstrated to be the major foulant which causes membrane fouling (Jucker & Clark 1994; Kaiya *et al.* 1996; Crozes *et al.* 1997; Khatib *et al.* 1997; Ruohomäki *et al.* 1998; Korbutowicz *et al.* 1999; Yuan & Zydny 1999; Fan *et al.* 2001; Lee *et al.* 2001; Committee Report 2003; Batsch *et al.* 2004; Her *et al.* 2004; Kimura *et al.* 2004; Lee *et al.* 2004; Müller *et al.* 2004; Schäfer *et al.* 2004; Jarusutthirak & Amy 2006). NOM represents a very wide range of macro-molecular compounds (Fan *et al.* 2001). It is still not clear which fraction of NOM causes the irreversible fouling. Also, lack of information on the mechanism of irreversible fouling caused by NOM is obvious.

Several researchers pointed out that calcium in the feed water would play an important role in the evolution of membrane fouling caused by NOM (Korbutowicz *et al.* 1999; Yuan & Zydney 1999; Schäfer *et al.* 2004). Jucker & Clark (1994) reported that calcium acted as a “bridge” between the membrane and the carboxylic group contained in humic acid. Yuan & Zydney (1999) claimed that a rapid decline of water flux could be attributed to pore blocking by aggregates of humic acid generated by the addition of calcium. In their studies, however, reversible fouling and irreversible fouling were not distinguished and it is consequently not clear which type of fouling might be influenced by calcium. In a pilot-scale study using surface water, it was reported that calcium did not contribute to the evolution of irreversible fouling (Kimura *et al.* 2004). The objectives of this study were to investigate (1) the influence of calcium on irreversible fouling in MF/UF membranes filtering NOM and (2) relationships between the degree of fouling induced by calcium and the properties of NOM.

## METHODS

### Membrane filtration

Four different hollow-fiber membranes were used in this study. Two of them were UF membranes and the other two were MF membranes. The two UF membranes had the same molecular weight cut-off (MWCO) of 100,000 but were made of different polymer, polyacrylonitrile (PAN) and polyethersulphone (PES). The two MF membranes had the same nominal pore size of 0.1  $\mu\text{m}$ . One was made of polyethylene (PE) and the other was made of polyvinylidene-fluoride (PVDF). Tiny membrane modules of 40  $\text{cm}^2$  in membrane area were assembled with the four types of membrane strings and were used in filtration experiments.

### Feed water

Two types of the feed water were examined in this study. One commercially available humic acid (Aldrich, Milwaukee, USA) and surface water used as a drinking water source were used for the preparation of the feed water. Aldrich humic acid (HA) was dissolved in Milli-Q water to a concentration of 3.0  $\text{mg-C/L}$ .  $\text{Na}_2\text{CO}_3$  was also added to the

solution at a concentration of 0.5  $\text{mM}$ , resulting in approximately neutral pH of the solution. Surface water was collected from Chitose river (Kimura *et al.* 2004). Collected water was filtered with cartridge filters (10  $\mu\text{m}$ , 2  $\mu\text{m}$  and 0.45  $\mu\text{m}$ ) to remove suspended matter and then treated with cation exchange softener to remove hardness (calcium). With both types of the feed water, experiments with and without calcium were carried out to investigate the influence of calcium on irreversible fouling. In the experiments with calcium,  $\text{CaCl}_2$  was added to the feed water at a concentration of 8.0  $\text{mg-Ca/L}$ . Addition of calcium was done by the same manner as Yuan & Zydney (1999) tested.

### Filtration protocol

The four membranes were submerged in one filtration basin at the same time. Filtration was carried out by water level difference of 3 m. Filtration was continued for 11 hours and the change in permeate flux was monitored by electric balances. Following the 11 hours of filtration, the membrane modules were taken out from the basin and were physically cleaned. The physical cleaning performed in this study was backwashing (50 kPa, 3 minutes) using Milli-Q water followed by gentle wiping with a sponge. Following the physical cleaning, the tiny modules were placed back in the filtration basin and the filtration was re-started. The 11-hour filtration was repeated 6 times. At the time of each physical cleaning, the feed water remaining in the filtration basin was discarded to avoid excessive accumulation of rejected organic matter in the system. At the end of the filtration experiment, the tiny modules were disassembled and divided into two specimens. Each specimen was immersed into the solution of sodium hydroxide (pH 12) or hydrochloric acid (pH 2) to extract the foulant.

### Analytical methods

Concentrations of total dissolved organic carbon (DOC) were determined by a TOC analyzer (TOC-5000, Shimadzu, Kyoto, Japan). UV absorbance was measured by a spectrophotometer (U-2000, Hitachi, Tokyo, Japan). Prior to these analyses, samples were filtered with 0.45  $\mu\text{m}$  PTFE membrane filters. Fractionation of organic matter contained in the isolates was achieved by using the hydrophobic/hydrophilic

fractionation method described by Croué *et al.* (2003) to obtain three different fractions (i.e., hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI) fractions). Concentrations of metals were determined by ICP-AES (ICPS-7500, Shimadzu, Kyoto, Japan). To obtain information on organic matter from different aspects, fluorescence excitation-emission matrices (EEMs) of the samples were generated by using a fluorescence spectrophotometer equipped with a 150 W ozone-free xenon lamp (RF-5300PC, Shimadzu, Kyoto, Japan). In the measurement of fluorescence, wavelength of both emission and excitation was varied stepwise by 5 nm. Prior to the measurements of UV and fluorescence, pH of the samples was adjusted to ~7. Molecular weight distribution of organic matter was measured by using a high performance size exclusion chromatography with a UV detector (254 nm of wavelength). Two columns, TSK-gel G3000SW (TOSOH, Tokyo, Japan) and TOYOPEARL HW-65S (TOSOH, Tokyo, Japan), connected in series were used to cover a wide molecular weight range of 200–1 MDa. The mobile phase (phosphate buffer, pH 6.8) flow rate was 1.0 ml/min.

## RESULTS AND DISCUSSION

### Characteristics of the feed water

NOM is composed of a variety of organic molecules, which are complex products of chemical and biological degradation of plant and animal residues (Krasner *et al.* 1996). There might be a great difference in characteristics between commercially available HA and organic matter contained in specific natural water. The difference between Aldrich HA

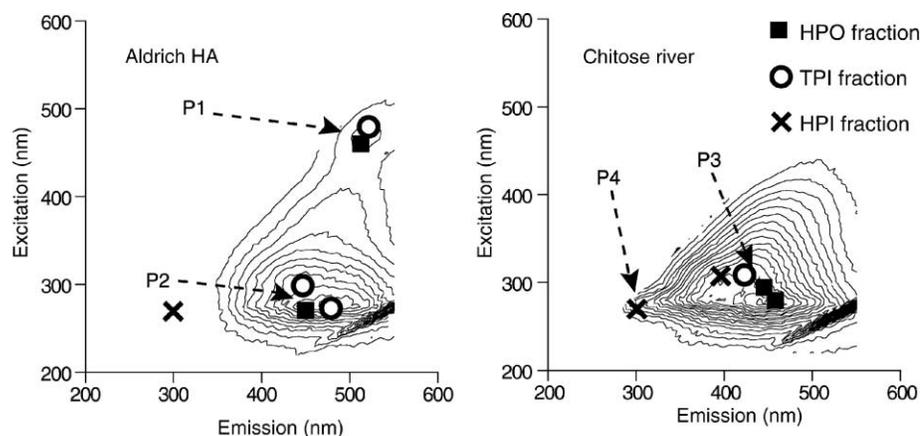
and organic matter in Chitose river surface water was therefore investigated by using various analytical methods.

Table 1 summarizes the concentrations of organic and inorganic matters in the two feed waters used in this study. The results of hydrophobic/hydrophilic fractionation were also shown in Table 1. The fractionation method used definitely divides organic matter into three fractions: hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI). Based on the definition given by Thurman and Malcom (1981), the HPO fraction is referred to humic substances. A value of specific ultraviolet absorbance (SUVA) is considered as a surrogate measurement for aromaticity of organic matter (Weishaar *et al.* 2003). It can be seen from Table 1 that SUVA of Aldrich HA was much higher than that of organic matter in Chitose river surface water, demonstrating that Aldrich HA was more aromatic than organic matter in Chitose river surface water. This was in accordance with the result of hydrophobic/hydrophilic fractionation. Aldrich HA contained more HPO fraction than the organic matter collected from the surface water.

EEMs of the feed water are shown in Figure 1. EEMs of HPO, TPI and HPI fractions in each organic matter were separately generated and major peak locations found in EEMs of each fraction are also indicated in Figure 1. Significant differences can be seen between EEMs of Aldrich HA and Chitose river water. In EEM of Aldrich HA, two large peaks are seen near 510/490 (emission/excitation) nm (P1) and 470/270 nm (P2). These two peaks were dominant in EEM of HPO fraction of Aldrich HA as well, implying that Aldrich HA was mainly composed of hydrophobic organic matter. In EEM of Chitose river water, two major peaks (P3 and P4) were seen at locations that were different from those of P1 and P2.

**Table 1** | Characteristics of the feed water used in this study

	DOC	UV	SUVA	XAD fractionation (%)			Ca	Fe
	(mg/L)	(1/cm)	(1/m/mg/L)	HPO	TPI	HPI	(mg/L)	(mg/L)
Aldrich HA	2.8	0.22	8.0	55	12	33	0.23	0.09
Aldrich HA + Ca	2.8	0.22	8.0	–	–	–	8.01	0.09
Chitose river	2.2	0.094	4.3	41	19	40	0.07	0.18
Chitose river + Ca	2.2	0.094	4.3	–	–	–	8.30	0.17



**Figure 1** | Fluorescence EEMs of the organic matters used in this study.

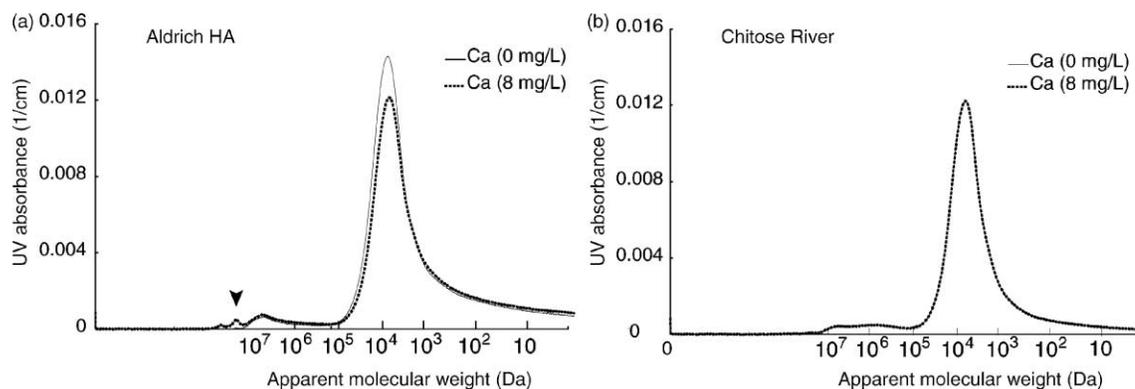
The location of P4 (300/270 nm) corresponded well with the location of the major peak found in EEM of HPI fraction of the organic matter in Chitose river water. Coble *et al.* (1993) reported that protein-like substance exhibited a peak in EEM at this location. The result of EEM analysis was in accordance with the SUVA analysis and the fractionation analysis: hydrophobic feature in Aldrich HA was obvious whereas the organic matter in Chitose river water was relatively hydrophilic.

### Changes in the feed water characteristics associated with calcium addition

It was expected that the addition of calcium to the feed water would induce changes in the characteristics of organic matter to some extent. Figure 2 shows changes in molecular weight distribution of organic matter in the feed water associated with the addition of calcium. When calcium was absent in the feed water, there were two peaks in the chromatograms regardless

of the type of water: one big peak around molecular weight of 10 kDa and one small peak around molecular weight of  $6 \times 10^6$  kDa. When calcium was added, in the case of Aldrich HA, a tiny peak appeared near molecular weight of  $> 1$  MDa while the intensity of the peak of 10 kDa declined. Shift of molecular weight of organic matter found with Aldrich HA would probably be explained by aggregation of organic matter promoted by the added calcium. Calcium ions have ability for charge neutralization. In contrast, the addition of calcium did not cause significant change in molecular weight distribution of the organic matter in Chitose river water. It seemed that the extent of aggregation of organic matter induced by calcium was dependent on characteristics of the organic matter: hydrophobic organic matter such as the one contained in Aldrich HA was likely to aggregate in the presence of calcium ions.

The size distributions of calcium and iron in the feed water are shown in Table 2. As shown in Table 2, most of calcium added to the feed water existed in small sizes. In the case of



**Figure 2** | Apparent molecular weight distributions of organic matter contained in (a) Aldrich HA and (b) Chitose river surface water.

**Table 2** | Size distribution of calcium and iron in the feed water

	Size	0.45 $\mu\text{m}$ –0.1 $\mu\text{m}$	0.1 $\mu\text{m}$ –0.025 $\mu\text{m}$	0.025 $\mu\text{m}$ –100 kDa	<100 kDa
Aldrich HA	Ca (mg/L)	0.053	0.014	0.035	0.14
	Fe (mg/L)	0.023	0.018	0.041	0.008
Aldrich HA + Ca	Ca (mg/L)	0.222	0.249	0	8.7
	Fe (mg/L)	0.037	0.040	0.007	0.002
Chitose river	Ca (mg/L)	0	0	0	0.29
	Fe (mg/L)	0.046	0.12	0.001	0
Chitose river + Ca	Ca (mg/L)	0.027	0.09	0	8.7
	Fe (mg/L)	0.046	0.12	0.001	0

Aldrich HA, however, more than 5% of the added calcium existed in relatively large sizes ( $>0.025\ \mu\text{m}$ ). This was probably caused by the formation of complexes between calcium and organic matter. With respect to iron, most of the iron originally existed in large sizes ( $>100\ \text{kDa}$ ). Most of the iron in the feed solution was likely to exist as a complex with organic matter, which allowed the iron to exist in relatively large sizes. As a result of the addition of calcium, size distribution of the iron in HA solution was also shifted toward larger sizes. Such changes in size distribution of calcium and iron associated with the calcium addition were not seen with Chitose river water. The shift of size distribution found with iron in Aldrich HA could also be caused by the aggregation of organic matter by calcium. Changes in size distribution of iron caused by the addition of calcium corresponded very well with the finding for changes in molecular weight distribution of organic matter (Figure 2): only Aldrich HA aggregate as a result of the calcium addition.

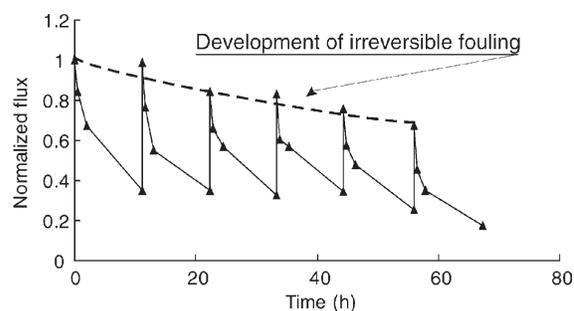
### Membrane filtration driven by a constant pressure difference

When a membrane filtration is carried out under a constant pressure difference, permeate flux gradually decreases over time. By applying physical cleaning (e.g., backwash), permeate flux can be increased but membrane permeability can never be restored to the initial state due to deposition of foulant on/in the membrane that cannot be removed by physical cleaning. Figure 3 shows representative data obtained in filtration of

Aldrich HA by the PVDF membrane under a constant pressure difference. In Figure 3, permeate flux was normalized to the flux observed at the initiation of the experiment. All data regarding permeate flux shown in this paper were treated in this manner. As was expected, permeate flux decreased with elapse of time and was partially restored by physical cleaning. Membrane fouling can be divided into two categories: reversible fouling, which can be eliminated by physical cleaning, and irreversible fouling, which requires a chemical reagent(s) to be eliminated. In Figure 3, evolution of irreversible fouling can be evaluated by connecting points recorded just after the physical cleaning (dashed line).

### Influence of calcium on irreversible membrane fouling

Figures 4 and 5 show the changes in permeate fluxes during the filtration experiments with the Aldrich HA solution and



**Figure 3** | Change in normalized flux in the filtration of Aldrich HA with the PVDF membrane.

Chitose river surface water, respectively. In these figures, it is clearly demonstrated that the degree of irreversible fouling was different depending on the combination of membrane and organic matter. As stated before, Aldrich HA had a more hydrophobic feature than the organic matter in Chitose river water. Although hydrophobic humic acid has been pointed out to cause severe membrane fouling in previous studies, the degree of irreversible fouling caused by Aldrich HA was lower than that caused by Chitose river surface water in the cases of the PVDF and PE membranes. In spite of the fact that the two UF membranes used in this study had the same MWCO, the degree of fouling was considerably different in the two membranes regardless of the type of the feed water: evolution of the irreversible fouling was not apparent with any of the tested solutions in the experiments using the PAN membrane while severe irreversible fouling was observed with all of the cases in the experiments using the PES membrane. These results demonstrated that the material of the membrane had a great influence on the degree of irreversible fouling resistance (Kimura *et al.* 2006). In Figures 4 and 5, the influence of calcium on irreversible fouling are represented by the difference between the solid lines (without calcium) and the

dashed line (with calcium). When Aldrich HA was examined, except for the case of the PAN membrane, the addition of calcium apparently influenced the evolution of irreversible membrane fouling. Previous studies using Aldrich HA (Kaiya *et al.* 1996; Ruohomäki *et al.* 1998) also reported that membrane fouling was promoted by the addition of calcium but reversible fouling and irreversible fouling were not distinguished in those studies. In the experiments using Chitose river water, as can be seen from Figure 5, the influence of calcium on membrane fouling was not obvious with all of the tested membranes. As stated above, the influence of calcium on membrane fouling was apparent with Aldrich HA, but not with a surface water (Chitose river water). This difference can be attributed to the differences in properties of constituents contained in Aldrich HA and Chitose river water, which was described in the previous section. There was a difference in properties of a small molecular weight fraction between Aldrich HA and organic matter contained in Chitose river water: the former tends to aggregate in the presence of calcium while the latter does not (see Figure 2). Aggregated particles would have sizes comparable to the membrane pores and be more likely to

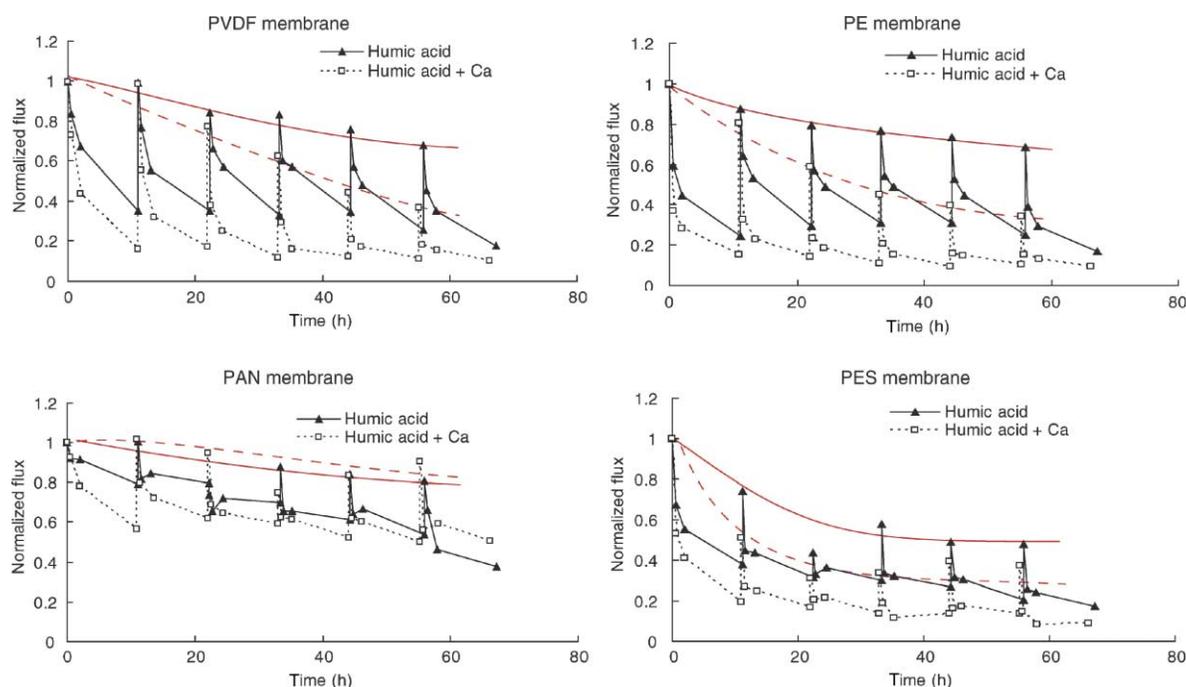
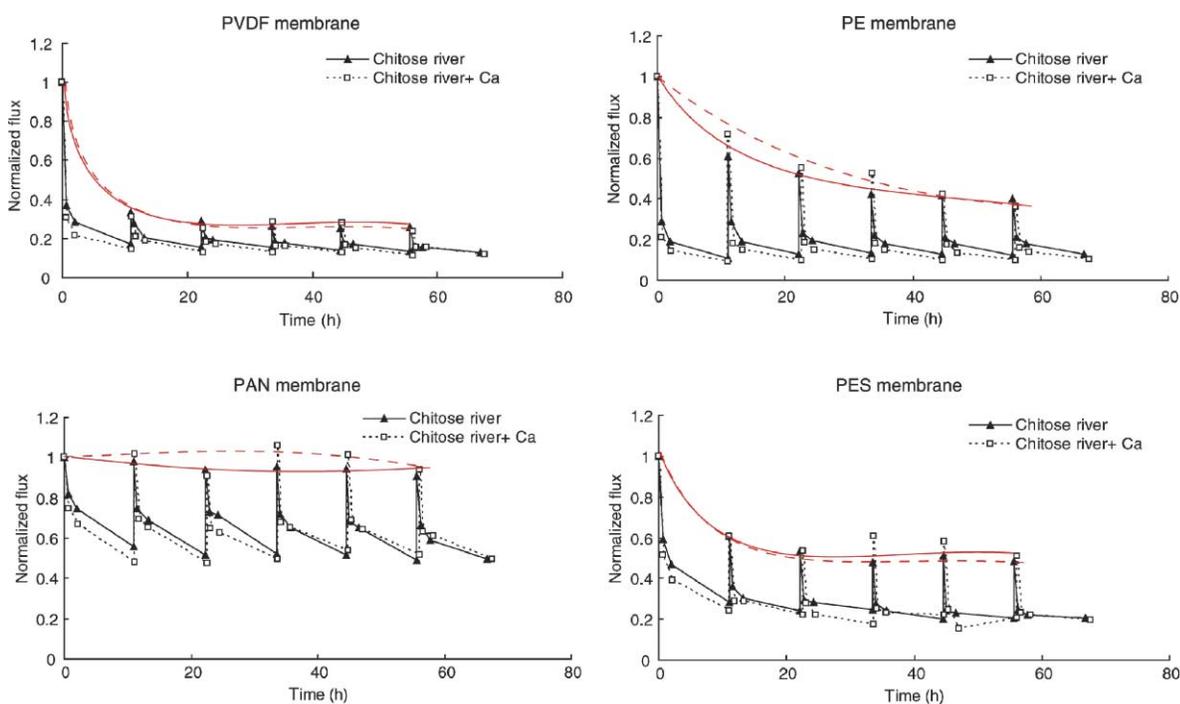


Figure 4 | Change in normalized flux in the filtration of Aldrich HA.



**Figure 5** | Change in normalized flux in the filtration of Chitose river water.

plug them, resulting in the evolution of irreversible fouling. The reason for the insignificant effect of calcium on membrane fouling in the PAN membrane is not clear at present. PAN might be a very good polymer material to prevent irreversible fouling caused by some types of organic matter. In our previous study examining various types of organic matter (Kimura *et al.* 2006), the PAN membrane exhibited less irreversible membrane than did other membranes made of different polymers.

### Constituents responsible for irreversible membrane fouling

As described above, the addition of calcium had an influence on the evolution of irreversible membrane fouling when Aldrich HA was filtered. It was found that the characteristics of components that were responsible for the irreversible fouling apparently changed depending on the presence of calcium, as shown in this section. This was revealed by analyses of the foulant desorbed from the fouled membranes by chemical reagents. Table 3 summarizes the results of principal analyses carried out for the foulants desorbed from the fouled membranes.

In Table 3, data for the PAN membrane are not included because irreversible fouling was not obvious in the experiments using the PAN membrane regardless of the feed water or presence of calcium. Also, values of SUVA were not determined for the foulant desorbed with HCl. This was because the iron extracted by acid would interfere with the measurement of UV absorbance.

Values of SUVA determined for the foulants in the experiments without calcium addition were much lower than those of the feed water (Table 1). This implies that a relatively hydrophilic fraction of each organic matter, which is likely to exhibit a lower SUVA, was responsible for the evolution of the irreversible fouling. Similar results were obtained in previous studies (Kimura *et al.* 2004, 2006). In the experiments where calcium was added, values of SUVA determined for the desorbed foulants apparently increased from the values found in the experiment without calcium. As a result of calcium addition, the nature of the foulant causing irreversible fouling might become more hydrophobic. It should be noted here that the presence of calcium in the feed water increased the amount of organic matter that could be desorbed from the fouled membranes in the case of Aldrich HA, except for the PE membrane. Such an

**Table 3** | Characteristics of desorbed components from fouled membranes

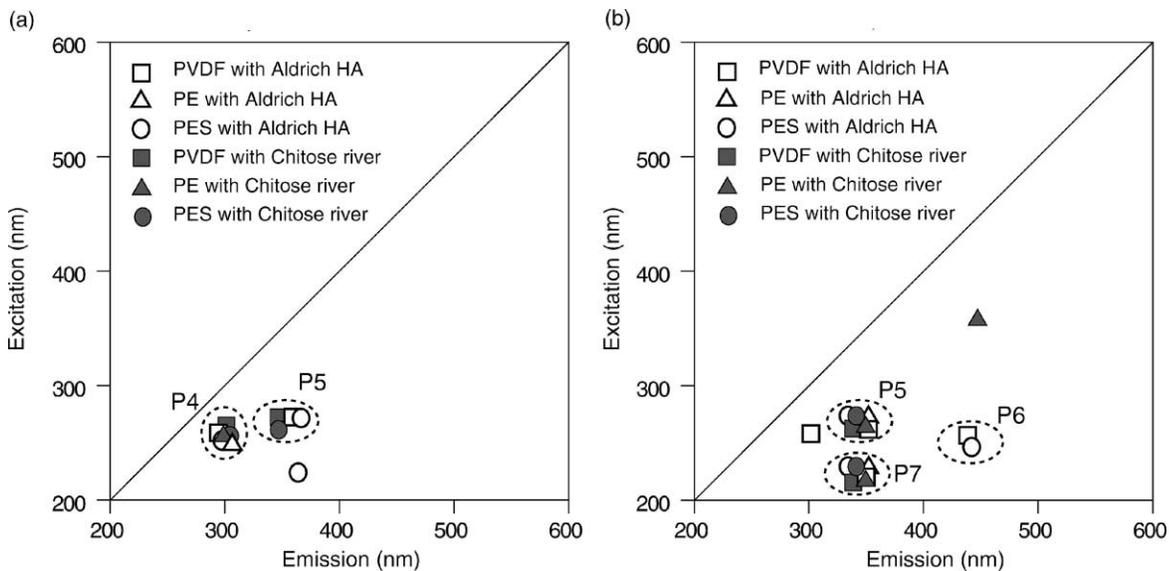
			Aldrich HA			Aldrich HA + Ca		
			PVDF	PE	PES	PVDF	PE	PES
NaOH	TOC	(mg/m <sup>2</sup> )	51	34	113	102	30	248
	SUVA	(1/m/mg/L)	2.0	1.7	2.8	2.8	2.3	6.4
	Ca	(mg/m <sup>2</sup> )	5.3	4.7	3.4	9.9	2.7	30.2
	Fe	(mg/m <sup>2</sup> )	1.1	1.1	5.3	2.3	0.8	10.3
HCl	TOC	(mg/m <sup>2</sup> )	23	14	21	12	26	11
	Ca	(mg/m <sup>2</sup> )	10	0.4	7.6	16	5	30
	Fe	(mg/m <sup>2</sup> )	1.6	0.4	3.0	3.1	0.6	4.9
			Chitose river			Chitose river + Ca		
			PVDF	PE	PES	PVDF	PE	PES
NaOH	TOC	(mg/m <sup>2</sup> )	52	13	51	45	15	47
	SUVA	(1/m/mg/L)	1.0	1.2	1.2	1.7	1.6	7.5
	Ca	(mg/m <sup>2</sup> )	5.1	2.6	5.4	6.2	1.9	2.5
	Fe	(mg/m <sup>2</sup> )	1.6	1.2	1.7	1.9	0.9	1.8
HCl	TOC	(mg/m <sup>2</sup> )	20	11	24	17	5.8	12
	Ca	(mg/m <sup>2</sup> )	5.3	4.0	6.2	19	5.7	8.4
	Fe	(mg/m <sup>2</sup> )	7.6	3.4	5.4	10	5.1	5.0

increase in extractable organic matter associated with the addition of calcium was not seen in the case of Chitose river water.

Locations of major peaks in EEMs of the foulants desorbed from the fouled membrane are shown in Figure 6. Figures 6 (a) and (b) correspond to the experiments without and with calcium, respectively. According to Figure 6 (a), in the absence of calcium, foulants desorbed from the fouled membrane had two major peaks around 300/270 nm (P4) and 340/270 nm (P5) in EEMs, regardless of the types of membrane or feed water. The intensity of the peak of P4 was always much greater than that of P5. As stated before, the appearance of P4 in an EEM can be attributed to the

presence of protein-like substances (Coble 1996). Thus, in the absence of calcium, a similar hydrophilic organic matter (e.g., protein-like substance) was responsible for irreversible fouling regardless of types of membrane or feed water, despite the fact that the characteristics of Aldrich HA and the organic matter in the Chitose river water were considerably different.

In the EEMs of the foulant desorbed from the membranes examined with calcium, the peak P4 was not seen. Instead, the presence of peaks near 450/250 nm (P6) and near 350/220 nm (P7) became significant in the EEMs for the foulant desorbed in the experiments where calcium was added. Three peaks identified as P5, P6 and



**Figure 6** | Major EEM peak positions of the membrane foulant desorbed by NaOH solutions; (a) experiments without Ca; (b) experiments with Ca.

P7 in an EEM were reported to be indicators of the presence of humic substances (Coble *et al.* 1993; Coble 1996). Particularly, in the EEMs of the foulants desorbed from the PVDF and PES membranes examined with Aldrich HA and calcium, intensities of the peak of P6 (indication of humic acid) were very strong. These results clearly indicate that constituents that were responsible for irreversible fouling changed as a result of calcium addition in the case of Aldrich HA. Addition of calcium would facilitate irreversible fouling by hydrophobic fraction in Aldrich HA. Changes in constituents that were responsible for irreversible fouling were induced by the addition of calcium in the case of Chitose river water as well. Intensities of P5 and P7 became significant in the EEMs of the foulant as a result of calcium addition in the case of Chitose river water, while P4 was dominant in the absence of calcium. The foulant desorbed from the PE membrane examined with Chitose river water and calcium showed a significant peak near 450/350 nm in the EEM, which can be related to the presence of humic acid (Coble *et al.* 1993; Nagao *et al.* 1997). As shown above, the addition of calcium changed the characteristics of constituents causing irreversible fouling. Regardless of the type of organic matter, the addition of calcium made the foulant more hydrophobic. In the case of Aldrich HA,

this alternation was associated with the production of aggregates with sizes comparable to the membrane pores (Figure 2), and brought about an increase in irreversible fouling. In the case of the Chitose river, although the characteristics of the constituents causing irreversible fouling certainly changed (Table 3 and Figure 6), the apparent degree of irreversible fouling did not change (Figure 5).

## CONCLUSIONS

In this study, the influence of calcium on irreversible fouling in MF/UF membrane filtering NOM was investigated on the basis of a series of bench-scale filtration tests. It was found that the influence of calcium on the evolution of irreversible fouling would differ depending on the feed water properties. In the case of a commercially available humic acid (Aldrich HA), the influence of calcium was obvious. Calcium promotes the aggregation of small molecules with hydrophobic nature in Aldrich HA and the aggregates would plug the micropores, resulting in severe irreversible fouling. The effect of calcium was not obvious in the case of a surface water used for a drinking water source. This result implies that the use of

commercially available humic acid for the examination of membrane fouling would be inappropriate.

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First received 5 April 2007; accepted in revised form 19 June 2007