



## Effect of metal ions on humic acid fouling of hollow fiber ultrafiltration membrane

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### ABSTRACT

Ultrafiltration using a hollow fiber membrane is increasingly used in water treatment for the removal of particles, turbidity and microorganisms to meet stringent water quality requirements. Fouling by natural organic matter (e.g. humic acid and fulvic acid) is a critical problem in membrane processes. In this work, experiments were performed to evaluate the effects of metal ions on humic acid fouling of a hollow fiber ultrafiltration membrane. Fouling was severe in the presence of metal ions, especially at high concentration of  $\text{Ca}^{2+}$  or  $\text{Fe}^{3+}$ . The accelerated fouling is considered to be due to the formation of intermolecular crosslinking between humic acid molecules, because the humic acid aggregate size increased in the presence of  $\text{Ca}^{2+}$ . Addition of ethylenediaminetetraacetic acid (EDTA) decomposed the aggregates and prevented metal ion-induced acceleration of fouling. Scanning electron micrograph images clearly revealed deposition of humic acid on the membrane after filtration, and that the presence of metal ions increased humic acid deposition, which led to accelerated fouling.

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### 1. Introduction

As water demand increases in the world, membrane processes for water purification have attracted increasing attention. During the past few decades a variety of membrane systems have been developed [1], and have greatly improved water flux, solute rejection, chemical tolerance, and especially the ability to maintain high performance levels at substantially lower operating pressures [2]. Microfiltration (MF) and ultrafiltration (UF) hollow fiber membranes are used for drinking water production and for waste water reclamation, because of their multiple advantages, including superior water quality, easy control of operation, low cost and easy maintenance. Despite the expansion of membrane applications, a decline in membrane performance over a period of time, i.e. membrane fouling, is still a critical problem in industry. Membrane fouling greatly decreases water permeate flux and affects separation properties [3,4]. Membrane fouling is usually caused by adsorption, deposition or cake-layer formation of solutes and colloids (termed foulants) onto a membrane. In general, the foulants can be classified into inorganic (clays, silica, salts and metal oxides), organic (aggregated natural and synthetic organics), and biological (bacteria and other micro-organisms) foulant types [5–7]. Among them, natural organic matter (NOM) is considered to be a major

membrane foulant in drinking water production. Several mechanisms for NOM fouling, including size exclusion and electrostatic repulsion, have been proposed [8]. For example, Van Houtte, et al. [9] showed that organic matter, including humic acid, serves as a “cement” for inorganic clays in the cake layer formed on a membrane surface. Lahoussine-Turcaud et al. [10] found that the flux decline during UF operation with Seine River water was primarily caused by the deposition of natural organic macromolecules, in particular humic substances, on membrane surfaces.

Comparison of experimental results with theoretical studies indicates that there is still major uncertainty concerning NOM fouling in membrane filtration. A more detailed picture of molecular interactions between membrane surfaces and NOM is required to better understand and prevent fouling phenomena. In the natural waters of Japan the presence of different kinds of metal ions, for example 20 ppm calcium, 0.5 ppm aluminum, and a trace amount of iron in suspension form has been reported [11]. The metal ions can increase the ionic strength, and crosslinking between the humic substances, which may affect fouling. Consequently, the combined influences of multiple substances on membrane fouling should be considered in the real water treatment process.

There have been a number of studies on membrane fouling. Although many studies of fouling employed only a single type of foulant, various types of foulants coexist in actual feed solutions. Moreover, the presence of minor substances, such as metal ions, in actual feed solutions may accelerate membrane fouling in practical water treatment. The metal ion contents of sea water and river water vary according to location, and show seasonal variations as

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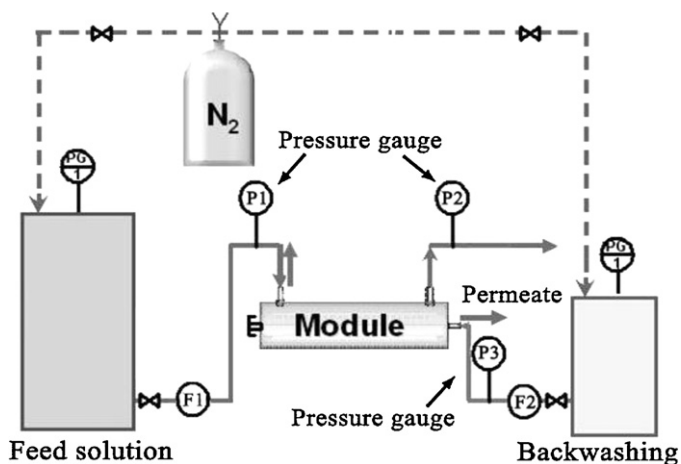


Fig. 1. Schematic diagram of minimodule laboratory scale apparatus employed for membrane filtration and backwashing.

well. Zydney and Yuan [12] first studied the effect of metal ions on humic acid fouling of flat MF membranes, and showed that the ionic environment of solutions remarkably affected the fouling of the membranes. Fouling of a hollow fiber membrane might be different from that of a flat sheet membrane, mainly due to the difference of flow direction [13]. The lateral fluid flow associated with a hollow fiber membrane has the potential to sweep foulant deposits off the membrane surface. There is a report describing a quite difference in fouling behaviors of MBR between a hollow fiber membrane and a flat sheet membrane [14]. Therefore, we considered that fouling by natural organic matter of a hollow fiber membrane might also lead to different results. In the present study we investigated the fouling of a hollow fiber membrane, and the effect of coexisting metal ions on the fouling.

## 2. Experimental

### 2.1. Materials

Polyethersulfone (PES) hollow-fiber membrane (MWCO 300 kDa) was purchased from Daicel Chemical Industries, Japan. The pure water flux of the membrane was  $850 \pm 50 \text{ L}/(\text{m}^2 \text{ h atm})$ .

Humic acid and EDTA (disodium salt) were purchased from Aldrich Chemical Co. (Milwaukee, WI). All other chemicals were purchased from Wako Pure Chemical Industries, Japan. The water used was high-quality deionized water (DI water,  $>15 \text{ M}\Omega \text{ cm}^{-1}$ ) produced by an Elix-5 system (Millipore).

### 2.2. Membrane filtration of humic acid solution

Humic acid was used as a typical NOM foulant in filtration experiments. Fresh humic acid solutions (50 ppm) were prepared by dissolving humic acid in 0.5 mM  $\text{NaHCO}_3$  solution, which was used without further purification. Salts or EDTA were dissolved in homogeneous humic acid solutions to match given concentrations of metal ions. The pH of the solutions was adjusted to  $6.75 \pm 0.05$ , which is the pH value of natural water in Japan, using small amounts of 0.1 M HCl or NaOH solution [4]. DI water was passed through the PES membrane for 10 min at a flow rate of  $15 \text{ ml min}^{-1}$  at 0.5 atm prior to use, to remove coating and wetting agents from the membrane.

Filtration experiments were performed with a laboratory scale apparatus developed in our laboratory (Fig. 1) [15]. The apparatus consisted of a minimodule device that contained a single hollow fiber membrane 10.6 cm in length with an outer diameter of around

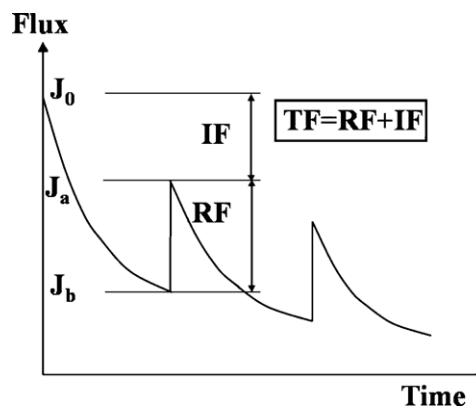


Fig. 2. Model profile of permeate flux in relation to irreversible and reversible fouling, through backwashing.

12.8 mm and an inner diameter of around 10.3 mm. The transmembrane pressure was controlled by nitrogen gas. Each filtration experiment was carried out by forcing a feed solution to permeate from the outside to the inside of the hollow fiber membrane at a flow rate of  $15 \text{ ml min}^{-1}$  at 0.5 atm transmembrane pressure. Prior to filtration experiments, DI water was passed through the membrane to measure the pure water permeability  $J_0$ . Then filtration of humic acid solutions was carried out to measure permeability  $J$ . The rejection  $R$  of humic acid by the membrane was determined by measuring the concentration of humic acid in permeate solutions. The humic acid concentration was measured from the absorbance at 254 nm using a UV spectrophotometer (GE-Healthcare) [12]. During the filtration experiments, backwashing was periodically carried out for 1 min at hourly intervals. For backwashing, DI water was passed from the inside to the outside of the membrane at 1 atm transmembrane pressure, and the flux that was used for the filtration process.

The fractionation method developed by Aiken [16] was used to determine the apparent molecular size distributions of foulants. Humic acid samples were fractionated using three ultrafiltration centrifugal filters (Amicon Ultra-4 centrifugal Filter Devices, Millipore) with nominal molecular weight cutoffs 10, 50 and 100 kDa, and two cellulose microfiltration membranes with pore sizes 0.1 and  $0.45 \mu\text{m}$  (DURAPORE membrane filters, Millipore). The pore size of three ultrafiltration membranes was calculated from their nominal molecular weight (MW) cutoffs by:

$$D = 0.1516 \text{MW}^{0.3371} \quad (1)$$

where  $D$  is the pore size [17]. Based on the equation, the molecular weights of 10, 50 and 100 kDa were transformed to 3.4 nm, 5.8 nm and 7.3 nm.

The apparent molecular weight distributions were calculated from the difference in the humic acid concentrations between adjacent filtrate fractions.

The restorable flux decline was defined as reversible flux decline (RF), the non-restorable flux decline as irreversible flux decline (IF), and the sum of both as the total flux decline (TF). RF, IF and TF are illustrated in Fig. 2.

$$\text{RF} = \frac{J_a}{J_0} - \frac{J_b}{J_0} \quad (2)$$

$$\text{IF} = 1 - \frac{J_a}{J_0} \quad (3)$$

$$\text{TF} = \text{RF} + \text{IF} = 1 - \frac{J_b}{J_0} \quad (4)$$

where  $J_a$  and  $J_b$  indicate permeate flux after and before backwashing, respectively, and  $J_0$  indicates the initial permeate flux. The

backwashing efficiency (nRF) and normalized irreversible (nIF) flux decline were calculated by the following equations:

$$\text{nRF} = \frac{\text{RF}}{\text{TF}} \times 100 = \frac{J_a - J_b}{J_0 - J_b} \times 100 \quad (5)$$

$$\text{nIF} = \frac{\text{IF}}{\text{TF}} \times 100 = \frac{J_0 - J_a}{J_0 - J_b} \times 100 \quad (6)$$

### 2.3. Microscopic observation of fouled membranes

To obtain dry membranes, the hollow fiber membranes were frozen in liquid nitrogen and dried with a freeze dryer (FD-1000, EYELA, Tokyo). The dry membranes were fractured in liquid nitrogen and sputter coated with Au/Pd for field emission-scanning electron microscope (FE-SEM) observation, while samples for EDS (energy dispersive X-ray spectrometry) analysis were sputter coated with carbon. The cross-sections and the surfaces of the hollow fiber membranes were examined using FE-SEM (JSM-7500F JEOL, Tokyo). Elemental compositions of the fouled layers were determined by EDS.

Metal contents in humic acid were measured using the inductive coupled plasma (ICP) technique (ICP-AES, SII, Tokyo). The samples for ICP measurements were prepared by dissolving humic acid in DI water without using buffer solutions.

## 3. Results and discussion

### 3.1. Effect of metal ions on humic acid fouling

Some multivalent metal ions can form a complex with, primarily, the carboxylic groups of humic acid, resulting in larger aggregates of humic acid in the deposit on a flat membrane surface [12]. To study the effects of various metal ions on humic acid fouling of a hollow fiber membrane, cross-flow filtration of 50 ppm humic acid solutions using a polyethersulfone hollow fiber membrane at 0.5 atm were carried out for 2 h with periodic backwashing (1 min) after 1 h filtration. The relative permeability ( $J/J_0$ ) and rejection coefficient ( $R$ ) data are shown in Fig. 3a and b, respectively. In each case, at least two experiments were carried out to confirm reproducibility. The initial flux of water was  $850 \pm 50 \text{ L} (\text{m}^2 \text{ h atm})^{-1}$ . The flux of humic acid solution (no additive, solid circles in Fig. 3a) decreased with time due to the membrane fouling. The flux decline was more rapid in the presence of additive metal ions (0.025 mM) than in the case of pure humic acid solution. In particular, the presence of  $\text{Fe}^{3+}$  immediately reduced the flux to nearly one fifth within 1 h. The addition of  $\text{Ca}^{2+}$  reduced the flux more rapidly than without metal ions, but less rapidly than the addition of  $\text{Fe}^{3+}$ . The presence of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  also resulted in rapid decline of the flux, however in both cases the rate of decrease was smaller than for  $\text{Fe}^{3+}$ . Thus all of the metal ions that were added enhanced humic acid fouling during ultrafiltration using the hollow fiber membrane. Compared to a similar study on a flat sheet membrane [18], we observed similar effects of the ionic environment on the fouling in a hollow fiber membrane. However, cross-flow type filtration of humic acid using a hollow fiber membrane showed much lower fouling extent than that for a flat sheet membrane.

These results and reported data suggest that membrane fouling was accelerated by formation of large aggregates of humic acid due to the addition of metal ions. Multivalent metal ions tend to form complexes with carboxylic acid groups to produce intermolecular bonds between organic compounds [12,19]. This is one of the possible reasons for the presence of  $\text{Fe}^{3+}$  remarkably accelerating humic acid fouling.  $\text{Na}^+$ , on the other hand, is a monovalent cation that does not have a strong ability to combine with carboxylic groups [19]. However, the presence of the monovalent cation would increase ionic strength, and thus decrease the

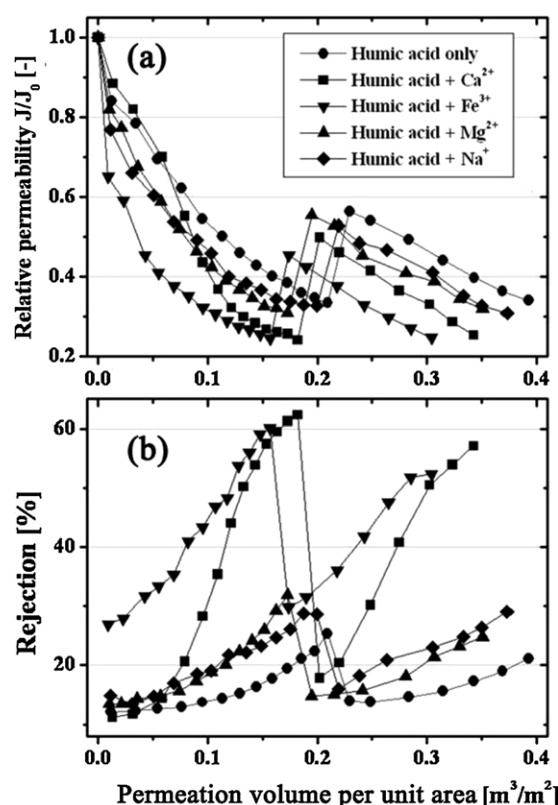


Fig. 3. Effect of various additive metal ions (0.025 mM) on the water flux and the rejection during filtration. (a) Relative permeability  $J/J_0$ , and (b) rejection.

repulsive force between negatively charged humic acid molecules, resulting in compaction of the humic acid deposit. Furthermore, the similar backwashing efficiency in all cases implies that the metal ions did not affect the interaction between the humic acid deposit and the membrane material.

The rejection of humic acid in the presence of  $\text{Fe}^{3+}$  was higher at the beginning of filtration than that without metal ions, and the rejection rapidly increased with filtration time (Fig. 3b). After backwashing the rejection decreased to the initial level. These results suggest that large aggregates of humic acid initially formed in the feed solution due to  $\text{Fe}^{3+}$  and that fouling occurred mainly on the membrane surface. That is the reason that the rejection easily recovered simply by backwashing. In the case of humic acid solution with  $\text{Ca}^{2+}$ , the rejection started from a low value ( $\sim 15\%$ ) and suddenly increased to more than 60%. This indicates that the humic acid aggregates with  $\text{Ca}^{2+}$  were not as large as with  $\text{Fe}^{3+}$ . Backwashing also decreased the rejection to the initial value. Although the addition of  $\text{Fe}^{3+}$  and  $\text{Ca}^{2+}$  promoted membrane fouling, the rejection properties of the membrane could be easily restored by backwashing, probably due to the large cake layer of humic acid (discussed later) on the membrane surface that affected the rejection and was easily detached by backwashing. The presence of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  also resulted in slightly higher rejection than in the absence of metal ions. The difference in the fouling phenomena for different metal ions might be due to the different ability and different manner of metal ions to form a complex with humic acid. It should be noted that backwashing did not recover the flux completely in any cases, because irreversible fouling occurred [15].

Fig. 4 shows the effect of  $\text{Ca}^{2+}$  concentration on humic acid fouling. The flux decline became steeper as the  $\text{Ca}^{2+}$  concentration increased from 0.025 mM to 0.5 mM, and the rejection of humic acid also increased with the increase of  $\text{Ca}^{2+}$  concentration. The difference of the initial rejections of the solutions with

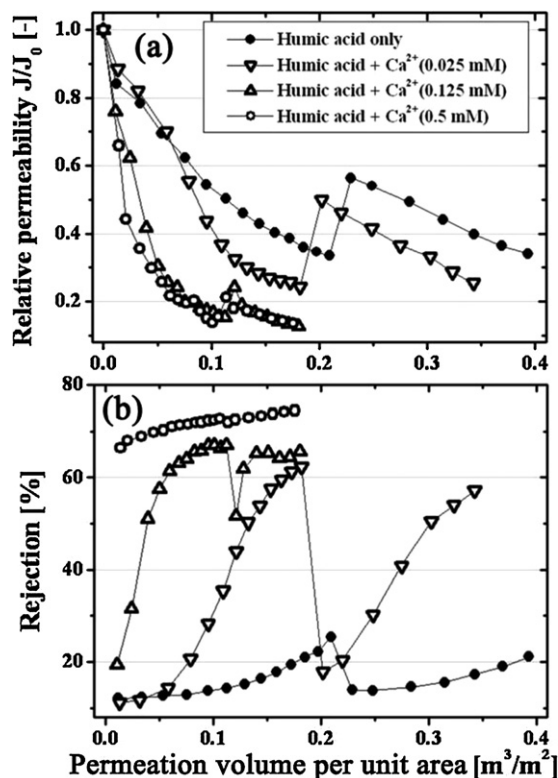


Fig. 4. Effect of different  $\text{Ca}^{2+}$  concentrations on the water flux and the rejection during filtration. (a) Relative permeability  $J/J_0$ , and (b) rejection.

added  $\text{Ca}^{2+}$  is a reflection of the differences in physical size of the humic acid aggregates formed in the presence of  $\text{Ca}^{2+}$ . By increasing the  $\text{Ca}^{2+}$  concentration backwashing also became less effective for flux recovery. These results suggest that the concentration of metal ions is a critical factor for humic acid fouling, and that high  $\text{Ca}^{2+}$  concentration makes the fouling more irreversible.

Fig. 5 shows photographic and FE-SEM images of a clean membrane and membranes fouled with humic acid (50 ppm, with and without additives, for 2 h permeation). The membrane fouled with humic acid became yellowish (Fig. 5-2(a)) and the membrane fouled with humic acid plus  $\text{Ca}^{2+}$  became dark brown (Fig. 5-3(a)), while the original clean membrane was white (Fig. 5-1(a)). The fouling promoted by  $\text{Ca}^{2+}$  could be observed with the naked eye, and FE-SEM observation also revealed the deposits of foulants on the membrane. There were foulant deposits (cake layer) 1  $\mu\text{m}$  thick on the outer surface after the pure humic acid fouling, but the foulant deposit did not cover the whole outer surface under those experimental conditions. In the case of humic acid fouling in the presence of  $\text{Ca}^{2+}$ , a 5  $\mu\text{m}$  thick cake layer spread over the membrane surface. Thus the presence of  $\text{Ca}^{2+}$  strongly expanded the foulant cake layer.

### 3.2. Metal ions in humic acid and fouling layer

The metal content of the humic acid used in this study was measured using ICP-AES. The results shown in Table 1 confirmed the presence of various metals in the humic acid, which could cause the initial aggregation of humic acid and affect the humic acid fouling to some extent in the absence of added metal ions.

Table 1  
Metal contents of humic acid.

|                            | Ca | Fe  | Mg  | Al  | Na  | Cu    |
|----------------------------|----|-----|-----|-----|-----|-------|
| Amount in humic acid (wt%) | 2  | 0.4 | 0.3 | 1.1 | 0.5 | <0.01 |

Elemental analysis of the cake layer on the fouled membrane was carried out by EDS. Fig. 6 shows the presence of Ca, Fe and Mg in the surface of the cake layer, which is consistent with the original metal composition in the humic acid.

According to the above investigations, metal ions seem to play important roles in the humic acid fouling. In the practical water purification process, metal ions present in raw water would enhance NOM fouling by complexing with humic substances. Contamination of metal ions leached from plant equipment should also be avoided.

### 3.3. Effects of EDTA on humic acid fouling in the presence of metal ions

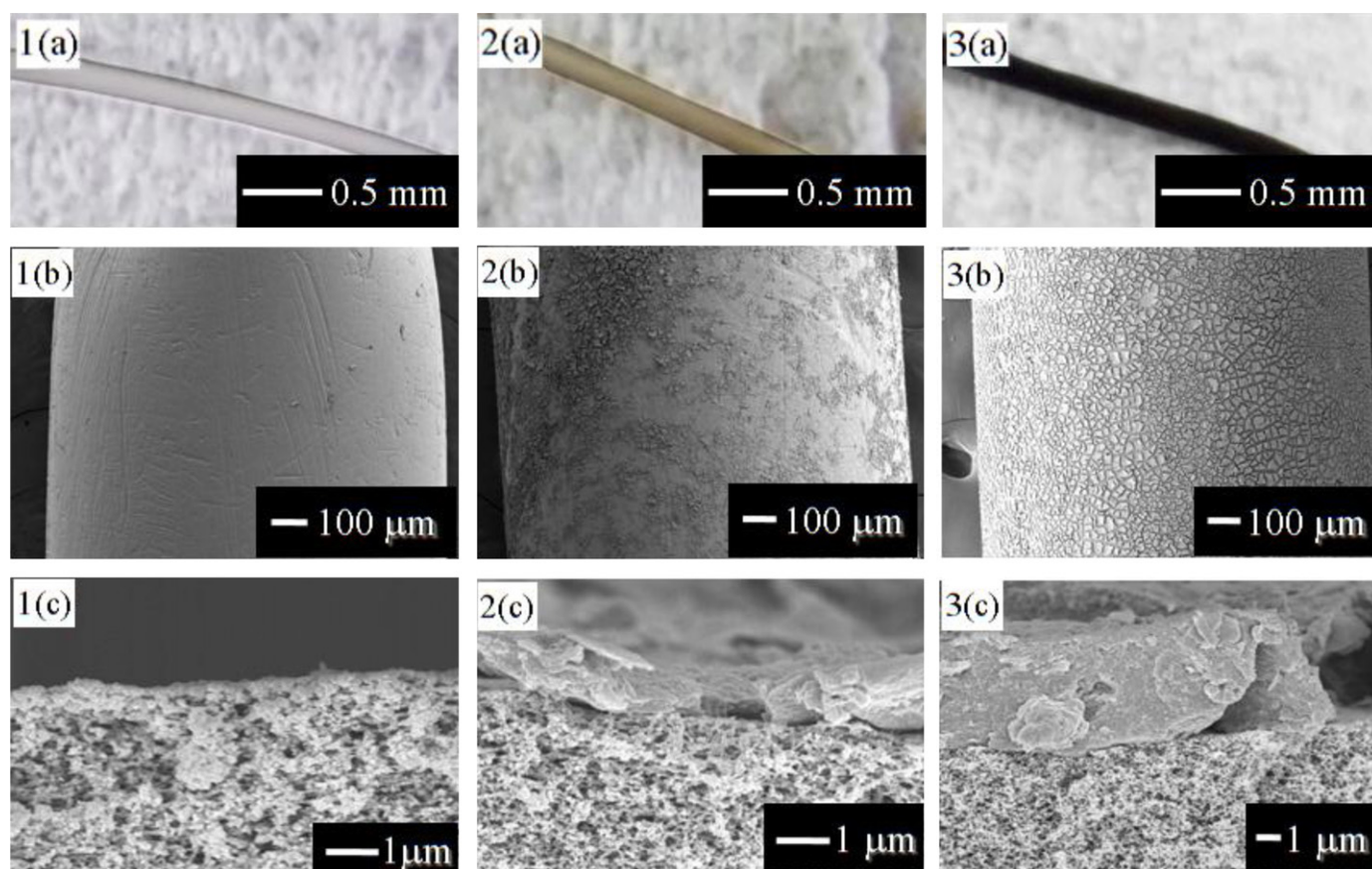
The usefulness of EDTA in preventing fouling could arise because of its role as a chelating agent [20,21], i.e. its ability to sequester metal ions such as  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$ . After complexation with EDTA, metal ions were expected to have reduced reactivity to humic acid.

Fig. 7 shows the effect of EDTA on the relative permeability ( $J/J_0$ ) and the rejection ( $R$ ) of 50 ppm humic acid, with and without  $\text{Ca}^{2+}$ , for 2 h permeation. Addition of EDTA to the humic acid solution without  $\text{Ca}^{2+}$  slightly improved the permeability of the humic acid solution (open circles in Fig. 7), probably due to chelation of the metal ions originally present in the humic acid. The addition of EDTA to the humic acid solution with  $\text{Ca}^{2+}$  markedly improved the permeability. The color of the fouled membrane was yellowish in the presence of  $\text{Ca}^{2+}$  and EDTA, which was similar to that of the membrane fouled with humic acid only. However, EDTA did not restore the permeability of the solution containing  $\text{Ca}^{2+}$  to that of the pure humic acid solution. Although EDTA readily forms a complex with  $\text{Ca}^{2+}$  ion, there would be competitive complex formation between  $\text{Ca}^{2+}$ -EDTA and  $\text{Ca}^{2+}$ -humic acid. That is one possible major reason why the addition of EDTA did not entirely restore the permeability of the solution containing  $\text{Ca}^{2+}$ . The rejection measurements revealed that the addition of EDTA to the  $\text{Ca}^{2+}$ -humic acid solution decomposed the  $\text{Ca}^{2+}$ -humic acid complex, resulting in a rejection profile similar to that of the humic acid solution. It should be noted that there was also a difference in the rejection profile between the  $\text{Ca}^{2+}$ -humic acid solution with EDTA and the humic acid solution. This difference also indicates that a small proportion of humic acid formed a complex with  $\text{Ca}^{2+}$  even in the presence of EDTA.

Backwashing is one of the practical methods to recover a fouled membrane, and backwashing with DI water was carried out for membranes fouled under various conditions. In the present study, the recovery of flux induced by backwashing was considered as reversible fouling, and the unrecovered flux was regarded as irreversible fouling [15]. The backwashing efficiency (nRF) under various filtration conditions is summarized in Fig. 8. The nRF values for the humic acid solution with 0.025 mM metal ions were almost the same as for the pure humic acid solution, which has two possible implications. One is that the compactivity of the cake layer on the membrane surface was similar; the other is that metal ions used at this concentration did not affect the interaction between the humic acid aggregate and the membrane material. The presence of  $\text{Ca}^{2+}$  at high concentration (0.5 mM) drastically decreased nRF. The high  $\text{Ca}^{2+}$  concentration might contribute to the connection between the humic acid aggregates in the cake layer, promoting irreversible fouling. The addition of EDTA to the feed solutions, except for the case of humic acid with  $\text{Fe}^{3+}$ , increased the nRF. That effect was possibly due to EDTA making the fouling layer less compacted and hence much easier to wash off by backwashing.

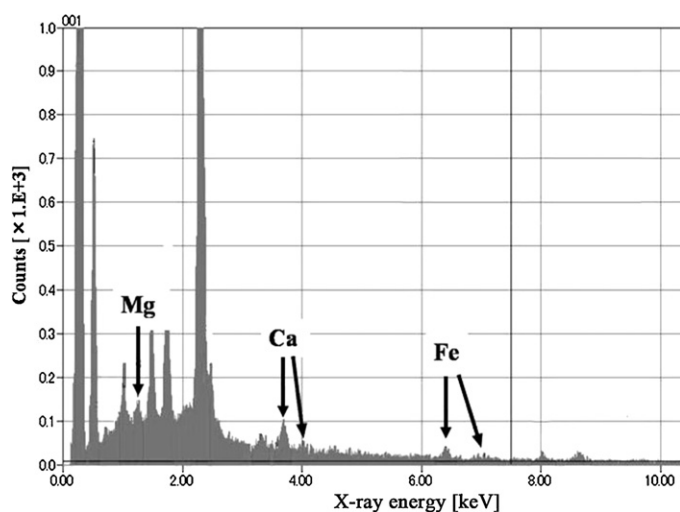
In the above discussion, we attributed the enhanced fouling to large aggregates of humic acid due to the additive metal ions. To determine the aggregation of humic acid, we measured the apparent molecular size distribution of pure humic acid and humic acid



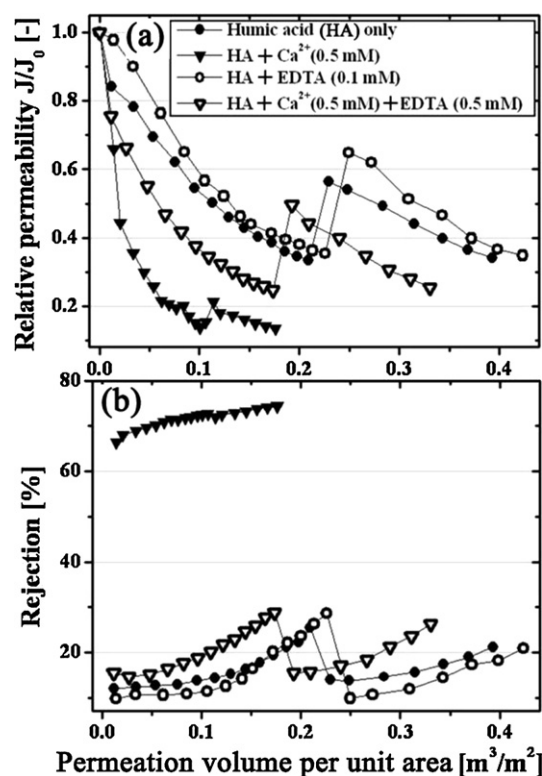


**Fig. 5.** Photographic images and FE-SEM images of the whole (a), the outer surface (b) and the cross section (c) of the membranes. (1) Clean membrane before use, (2) membrane fouled by a humic acid solution, and (3) membrane fouled by a humic acid solution with 0.5 mM  $\text{Ca}^{2+}$ .

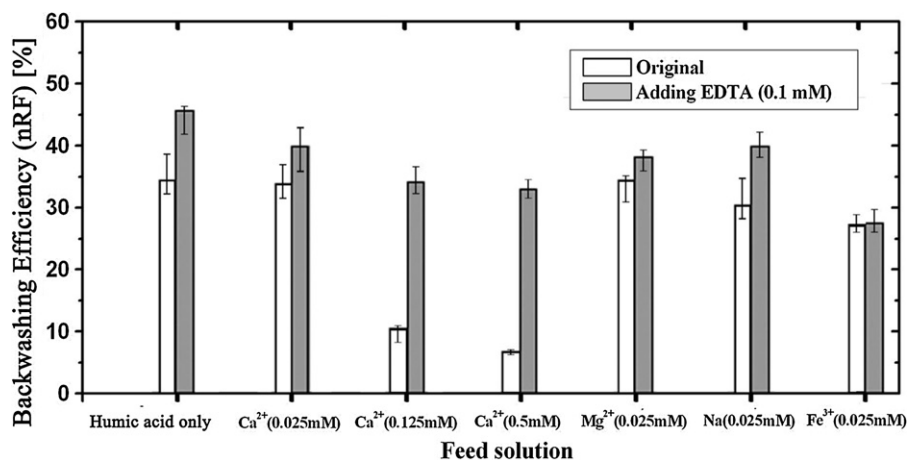
with additives (Fig. 9). In relation to the molecular size distribution of pure humic acid (Fig. 9a), the fractions of small ( $<3.4$  nm) and large ( $>0.1 \mu\text{m}$ ) molecules were under 10% (based on the absorbance). The major fractions of molecular size between 3.4 nm and  $0.1 \mu\text{m}$  contributed more than 80%. After adding 0.025 mM  $\text{Ca}^{2+}$  (Fig. 9b), only the fraction between 3.4 and 5.8 nm decreased, and the large molecular size ( $0.1$ – $0.45 \mu\text{m}$ ) fraction increased. This means that aggregation of humic acid was enhanced by adding  $\text{Ca}^{2+}$ .



**Fig. 6.** EDS spectra of a membrane fouled by a humic acid solution. The x axis corresponds to X-ray energy (keV) and the y axis to counts.



**Fig. 7.** Effect of EDTA on humic acid fouling with and without  $\text{Ca}^{2+}$  during filtration. (a) Relative permeability  $J/J_0$ , and (b) rejection.



**Fig. 8.** Backwashing efficiency (nRF) of membranes fouled by humic acids with various additives. Backwashing was carried out using DI water for 1 min, after filtration for 1 h.

The addition of EDTA to a humic acid solution (Fig. 9c) decreased the fraction with molecular size between 7.3 nm and 0.1  $\mu$ m, while the number of molecules between 5.8 and 7.3 nm increased. In the case of a humic acid solution with Ca<sup>2+</sup>, the effect of EDTA (Fig. 9d) was more obvious. The fractions between 0.1  $\mu$ m and 0.45  $\mu$ m and between 7.3 nm and 0.1  $\mu$ m shifted to those between 5.8 and 7.3 nm, and 3.4 and 5.8 nm. The decrease of the apparent molecu-

lar size distribution of humic acid on addition of EDTA was due to inhibition of the interaction between the humic acid molecules and metal ions. The initial aggregation and metal ion-induced aggregation of humic acid are also of great importance in membrane fouling. That is one of the major reasons why the addition of EDTA was effective in inhibiting membrane fouling.

#### 4. Conclusions

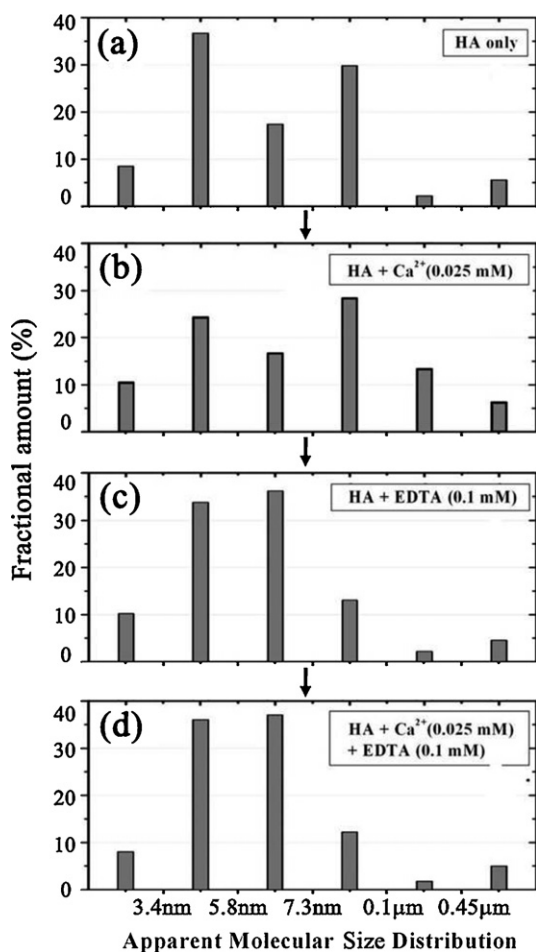
The important role of the ionic environment in humic acid fouling was investigated. Although there are reports on aggregation of humic acid induced by multivalent metal ions, there was still uncertainty about humic acid fouling of a hollow fiber membrane. Our investigation has revealed that the presence of various metal ions accelerated humic acid fouling of the hollow fiber ultrafiltration membrane, even though the lateral fluid flow associated with the hollow fiber membrane has the potential to sweep foulant deposits off the membrane surface. The humic acid aggregate size increased with addition of the metal ions, and the observed size was larger than the pore size of the membrane. The amount of humic acid deposition on the membrane surface increased to a remarkable extent in the presence of Ca<sup>2+</sup>, indicating that the foulant deposit could not be swept away by the lateral flow of the feed solution. Addition of the chelating agent EDTA inhibited, to a large extent, metal ion-induced aggregation of humic acid, resulting in inhibition of fouling. The results of the present study underline the importance of monitoring and controlling metal ion concentrations in the source water, and the necessity of preventing metal ion contamination from plant apparatus to reduce fouling. Backwashing fouled membranes using a chelating agent solution might be an effective strategy for restoring membrane permeability.

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**Fig. 9.** Apparent molecular size distribution for humic acid only, and humic acid with additives. (a) Humic acid only; (b–d) humic acid with (b) 0.025 mM Ca<sup>2+</sup>, (c) 0.1 mM EDTA, and (d) 0.025 mM Ca<sup>2+</sup> and 0.1 mM EDTA.

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