



## Fouling characteristics of NOM during the ceramic membrane microfiltration process for water treatment

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### ABSTRACT

Ceramic membrane filtration is one of the most promising membrane technologies used for advanced water treatment. Many studies of the fouling behavior of natural organic matter (NOM) have been conducted, but membrane fouling due to dissolved organic matter remains a critical problem preventing the efficient operation of ceramic microfiltration (MF) in water treatment. The aim of this study was to evaluate the fouling characteristics of NOM during ceramic MF using pilot-scale ceramic membrane equipment. In experiments to characterize this fouling behavior, humic acid (HA), bovine serum albumin (BSA), and sodium alginate (SA) were used as representatives of humic substances, proteins, and polysaccharides, respectively. In particular, we evaluated the effects of several parameters on the fouling characteristics of NOM, including concentration, foulant mixture, and rate of flux recovery. The flux decline in the presence of SA showed that ceramic membrane fouling occurred immediately. The membrane fouling by HA was well explained by a linear regression equation. More interestingly, BSA was found to cause mainly irreversible fouling, which is significant because this mechanism involves internal pore adsorption through particle superposition due to foulant accumulation on the membrane surface. The results indicate that the different fouling behaviors of the three types of macromolecules are distinct due to their apparent physical–chemical characteristics.

*Keywords:* Ceramic membrane; Fouling; Microfiltration; Natural organic matter (NOM)

### 1. Introduction

Membrane filtration technology has been widely used for water and wastewater treatment in recent decades. It has been considered one of the most promising technologies because it has many advantages for water treatment, including a lower requirement for chemicals, easy automation, and a high

potential for integrating various processes [1,2]. Microfiltration (MF) and ultrafiltration (UF) membrane technology have been applied to treat various components of wastewater or surface water, such as particles, bacteria, and nonorganic matter (NOM) [3,4]. The most significant obstacle to the MF membrane in water treatment is membrane fouling, which generally leads to an increase in transmembrane pressure (TMP).

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In membrane filtration technology, one type of membrane fouling is physical reversible fouling, which can be controlled by physical washing, such as backwashing [5]. However, organic compounds cause physical irreversible fouling, especially on MF and UF membranes, because they are much smaller than the pore sizes of MF and UF membranes. Also, dissolved and colloidal organic compounds can adsorb to or block the pores. Different forms of organic compounds have different membrane fouling properties. For example, when an organic compound has hydrophilic fractions, physical irreversible fouling of membrane filtration technology can occur, regardless of the type of membrane [6]. In waste and wastewater treatment with membrane filtration technology, irreversible membrane fouling by carbohydrates has been observed [5], and hydrophilic organic compounds with very high-molecular weights, such as soluble microbial products and protein matter, have been the main causes of physical irreversible fouling at membranes [7]. Whereas physical reversible fouling refers to external fouling that leads to cake formation, which is the major reason for macro-solute or particle deposition during filtration [8].

Comparison of previous experimental research with theoretical studies indicates that there is still uncertainty about NOM fouling in MF technology. A further description of the interactions between the membrane surface and NOM is needed to elucidate how fouling can be reduced. Many of the previous membrane fouling studies used only a single type of organic foulant, while various types of organic foulants coexist in actual feed solutions. Although polymeric membranes have been used in many studies of MF and UF, it is well known that ceramic membranes can operate at higher feed pressures, permeate fluxes, and backwashing pressures than polymeric membranes [9].

In this study, therefore, pilot-scale ceramic MF equipment was used to study the complex phenomena of ceramic MF membrane fouling by NOM and to investigate the mechanisms of membrane fouling by NOM in order to verify the characteristics of NOM fouling on ceramic membranes.

## 2. Materials and methods

### 2.1. Membrane fouling

Membrane fouling can be described as reversible or irreversible fouling, the definitions of which are shown in Fig. S1. Reversible fouling can be removed by a strong shearing force or backwashing, but irreversible fouling involves the strong adsorption of particles and thus cannot be removed by physical

Table 1  
The recovery rate of flux in different operation cycles

	HA	BSA	SA
$J/J_0$	30.8	26.8	10.5
$J_{hw}/J_0$	45.9	37.8	43.9
$J_{cc}/J_0$	100	100	100

washing. The removal of irreversible fouling is influenced to various degrees by pressure, filtration time, and backwashing duration.

### 2.2. Membrane fouling mechanism

There are four theoretical membrane fouling models: complete blocking, standard blocking, intermediate blocking, and cake filtration. Complete blocking

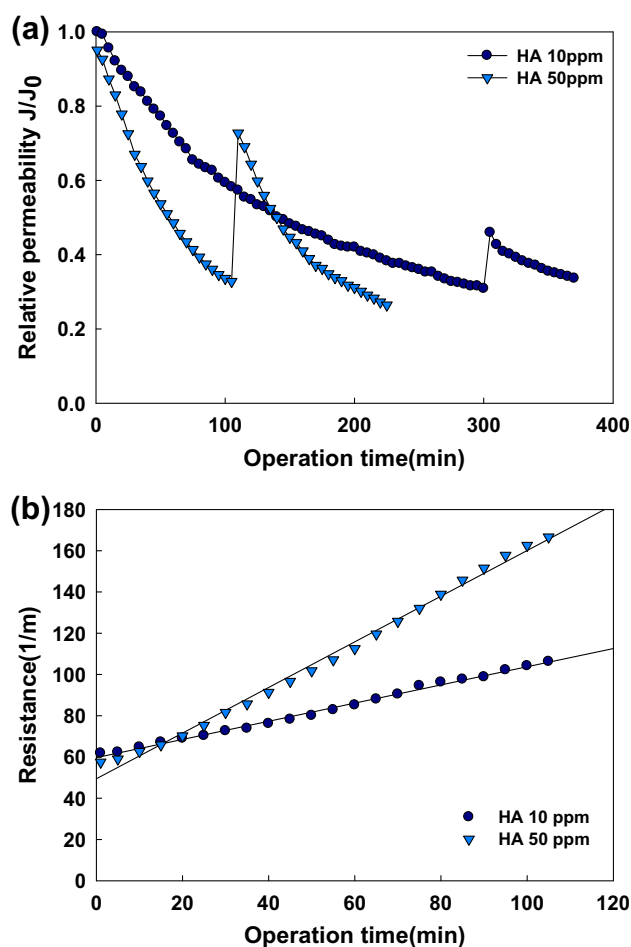


Fig. 1. The relative permeability vs. filtration time with clean water flux after hydraulic backwashing (a) and the resistance vs. filtration time of HA at 10 and 50 ppm (b).

occurs at the membrane surface when particles block the pores with no superposition. The flux variation as a function of time can be written as [1]:

$$J = J_0 e^{-At} \tag{1}$$

$$A = K_A u_0 \tag{2}$$

where  $K_A$  is the blocked membrane surface per unit of total volume permeated by the membrane,  $J_0$  is the pure water flux, and  $u_0$  is the mean initial velocity of the filtrate.

The standard blocking phenomenon occurs when particles are deposited onto the internal walls of the membrane, thus reducing the membrane pore volume. The flux variation with time can be presented as follows:

$$J = \frac{J_0}{(1 + Bt)^2} \tag{3}$$

$$B = K_B u_0 \tag{4}$$

where  $K_B$  is the decrease in cross-sectional area in the pores due to particles deposited on the walls per unit of total permeate volume.

The intermediate blocking phenomenon occurs due to the superposition of particles on the membrane. In this case, each particle directly blocks some membrane area or settles on already deposited particles. The measurement of flux variation with time is given by

$$J = \frac{J_0}{(1 + At)} \tag{5}$$

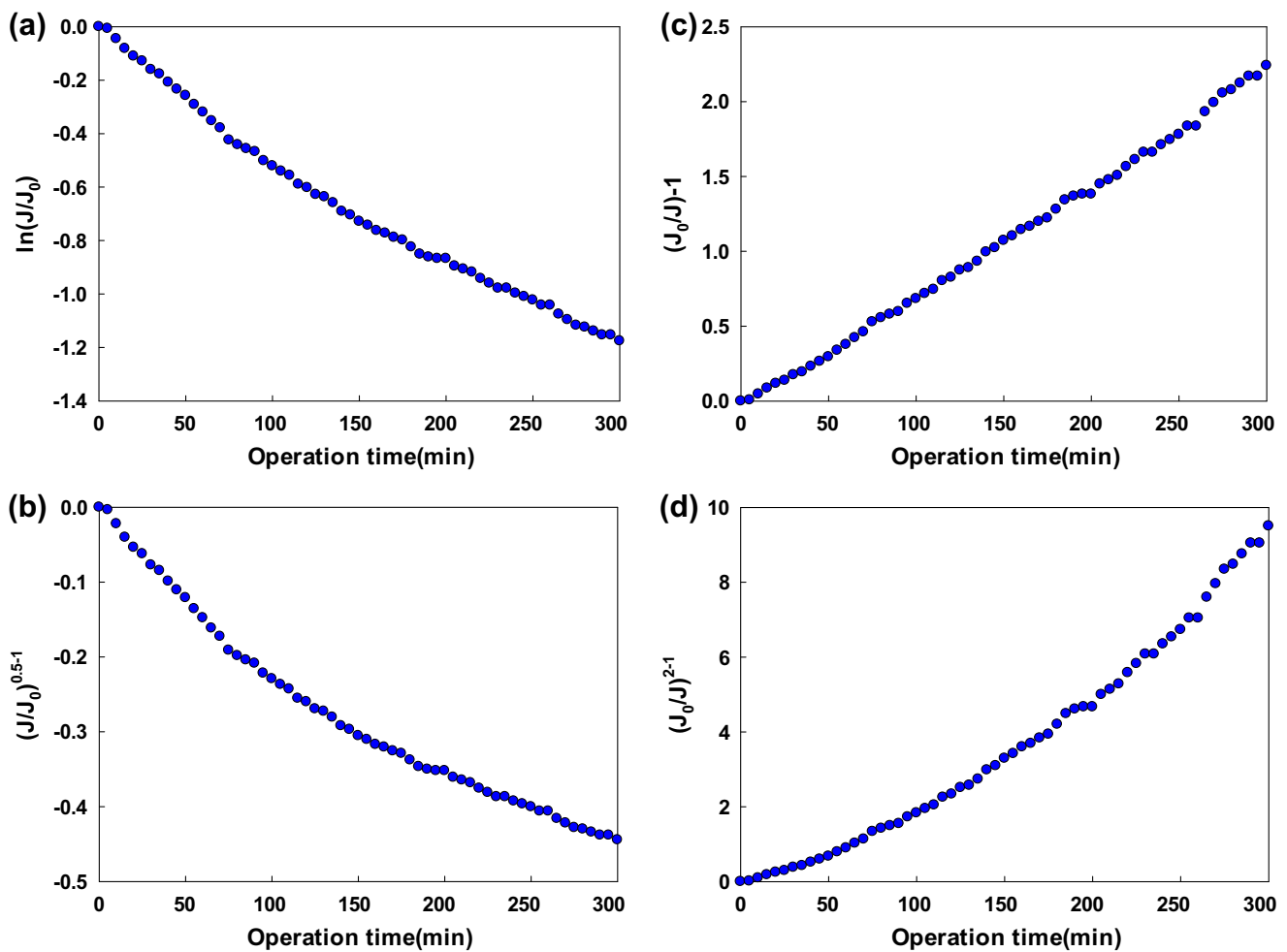


Fig. 2. Investigation of the HA filtration experiments according to the linear expressions modeling mechanism: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake filtration.

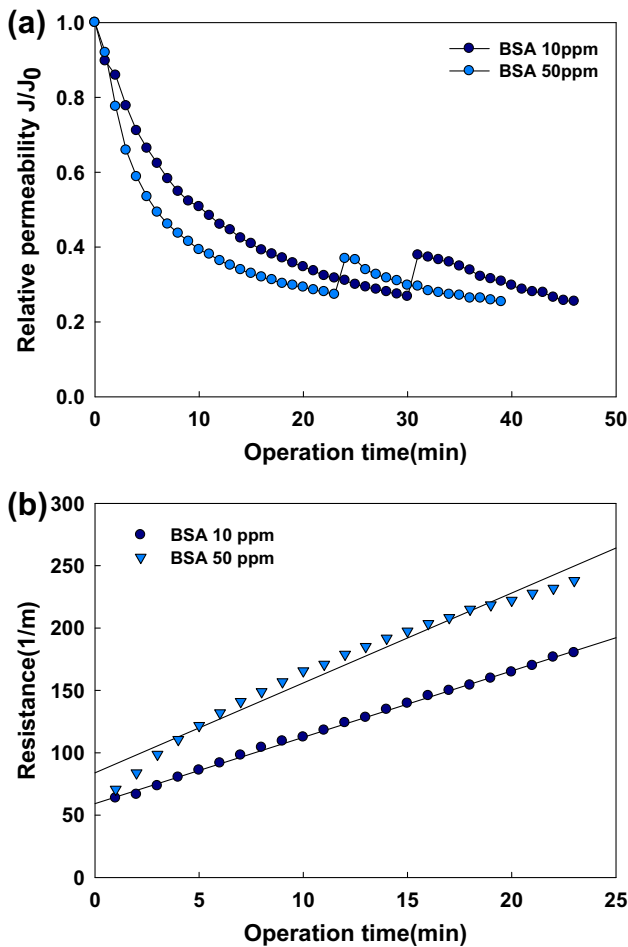


Fig. 3. The relative permeability vs. filtration time with clean water flux after hydraulic backwashing (a) and the resistance vs. filtration time of BSA at 10 and 50 ppm (b).

The cake filtration phenomenon is present when no unblocked space remains on the membrane, and new particles can settle only on already deposited particles. The flux variation as a function of time can be presented as follows:

$$J = \frac{J_0}{\sqrt{1 + C_\tau}} \quad (6)$$

$$C = (2R_r)K_c\mu_0 \quad (7)$$

where  $K_c^{-1}$  is the total permeate volume per unit of membrane area, and  $R_r$  is the ratio of the resistance of the cake to the resistance of the clean membrane.

During membrane filtration, a complex phenomenon of flux decline is expected, rather than the mechanism of a single theoretical fouling model. The

use of an internal or external fouling model depends on the theoretical resistance curve. When the slope of total resistance increases with increasing resistance, it can be described using internal fouling models; when the slope decreases with increasing resistance, it can be described using the external cake filtration model [10,11].

### 2.3. Membrane filtration of NOM solutions

A monolith ceramic membrane with a diameter of 30 mm was used in all experiments. The membrane had a nominal pore size of  $0.2 \mu\text{m}$ , 55 channels, and a membrane surface area of  $0.04 \text{ m}^2$ . The size of the inner channel was 2.5 mm. The monolith ceramic membrane was encased in a stainless steel filter holder. HA, BSA, and SA (Sigma-Aldrich, USA) were used for fouling and cleaning in all experiments. The electroconductivities of all stock solutions were adjusted to  $1,734 \mu\text{S/cm}$  using  $0.5 \text{ mM NaHCO}_3$  and  $10.0 \text{ mM NaCl}$  solutions. The pH of the solutions was adjusted to  $7.2 \pm 0.03$  using  $0.1 \text{ M}$  solutions of HCl or NaOH. The fouling characteristics of each foulant were determined at a concentration of  $10 \text{ mg/L}$ , and the stock solutions were kept at  $4^\circ\text{C}$  in sterilized glass bottles. The characteristics of the synthetic feed water are summarized in Table S1. Fig. S2 shows the laboratory-scale ceramic membrane filtration apparatus. All experiments were carried out in dead-end mode under a constant TMP of  $50 \pm 0.5 \text{ kPa}$ . Prior to ceramic MF, the virgin membrane was rinsed with distilled (DI) water for 24 h, and the pure water flux ( $J_0$ ) was obtained using DI water. The performance of the ceramic MF was monitored until the flux is less than 30% of its initial value. In this experiment, the hydraulic backwashing parameter was operated for 5 s at a TMP of 50 kPa, and then, the pure water flux was measured at a TMP of 50 kPa as the hydraulic washing recovery ( $J_{hw}$ ). After the ceramic MF experiments, the ceramic membrane was rinsed with NaOCl ( $3,000 \text{ mg/L}$ ) for 10 h to remove the irreversible foulants due to further eliminated by chemical cleaning [11]. After that, the pure water flux was obtained as the chemical cleaning recovery ( $J_{cc}$ ). All ceramic MF experiments were repeated two times Table 1.

### 2.4. Analysis

Dissolved organic carbon (DOC) and total organic carbon (TOC) were measured with a TOC analyzer (TOC-VCPh, Shimadzu, Japan). The absorbance at 254 nm was measured with a UV-vis recording spectrometer (DR6000, HACH, USA). Prior to analysis, all

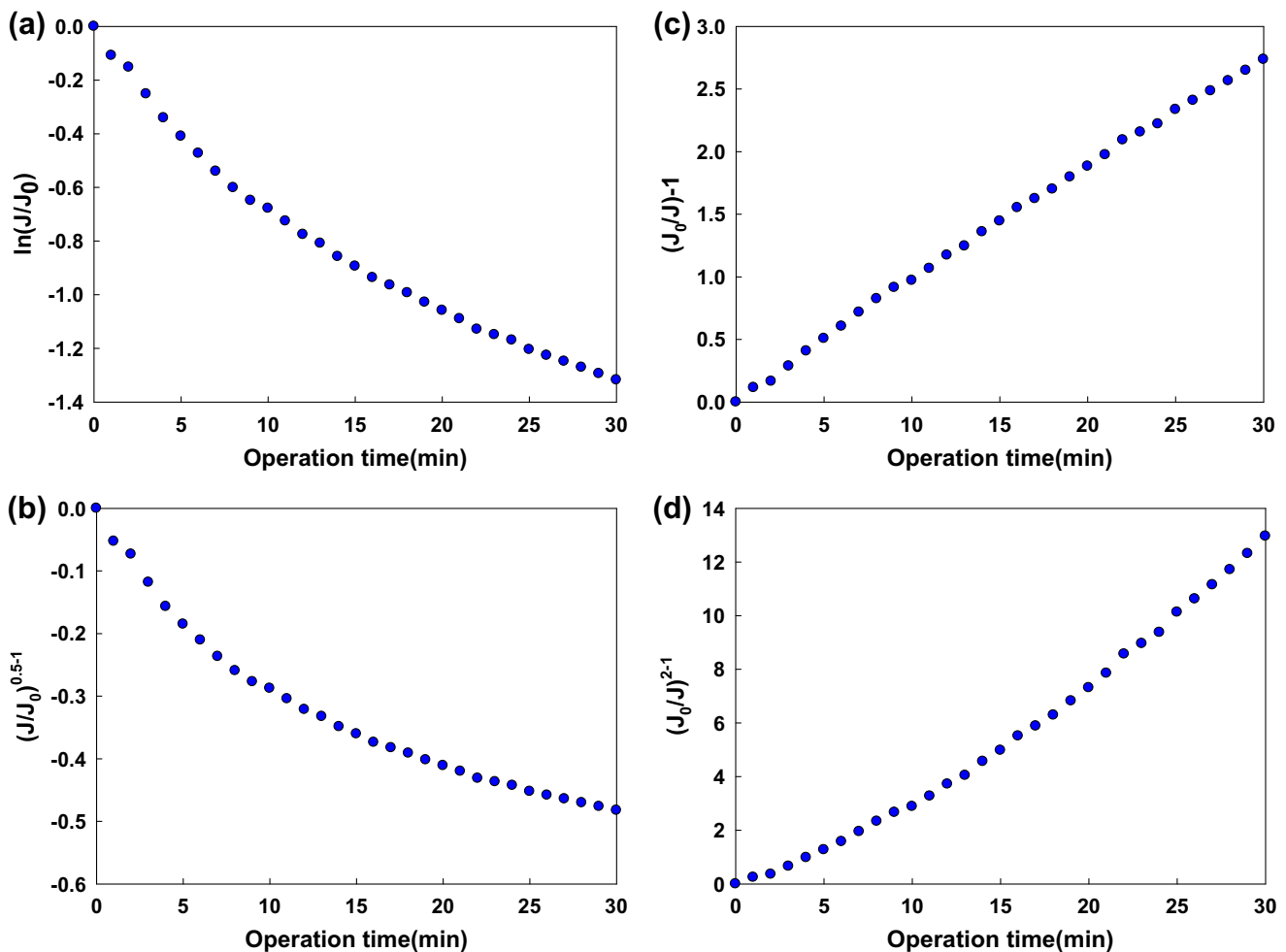


Fig. 4. Investigation of the BSA filtration experiments according to the linear expressions modeling mechanism: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake filtration.

samples were filtered using a 0.45- $\mu\text{m}$  cellulose fabric membrane.

### 3. Results and discussion

#### 3.1. Membrane fouling

In this study, the relative fouling effects of three organic compounds (HA, BSA, SA) were investigated, and their mixed effects on a MF ceramic membrane were determined. Several parameters were investigated, including relative permeability, total filtration resistance, fouling reversibility, and fouling model mechanism. Evaluations of the fouling potential of these three organic compounds were obtained. NOM solutions were filtered to a value 70% less than the initial flux. Two concentrations of HA and BSA were tested (10 and 50 ppm) based on a previous study, so a general fouling potential was expected [12,13].

##### 3.1.1. Effect of foulant concentration

The relative fouling phenomena of three different organic compounds, as well as the effects of their mixture, were investigated on a MF ceramic membrane. Concentrations of HA and BSA (50 ppm) higher than those typical of natural water were used to accelerate the fouling phenomena.

Fig. 1 shows the relative permeability and total resistance of HA after filtration. At the higher concentration, a sharper flux decline was observed, and hydraulic reversible fouling was reduced due to increased pore blocking and cake formation [1]. After hydraulic backwashing with permeate, the flux recovery of HA with 10 and 50 mg/L was 15.1 and 40.0%, but it was reduced sharply. As shown in Fig. 1(b), the total resistance increased with increasing slope after 20 min, which indicates that HA followed the internal fouling model during ceramic MF.

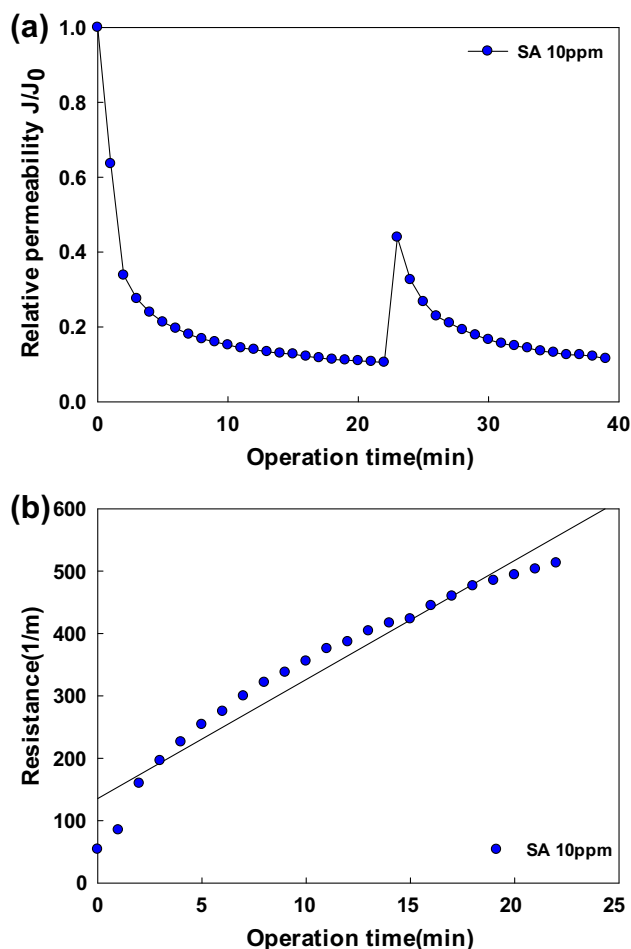


Fig. 5. The relative permeability vs. filtration time with clean water flux after hydraulic backwashing (a) and the resistance vs. filtration time of SA at 10 ppm (b).

Fig. 2 shows the analysis of the HA filtration experiments with the linear expressions modeling mechanism. The complete and standard blocking modeling mechanisms of fouling were observed during the first stage of filtration (~70 min). After this time, intermediate blocking was predominant because solute had accumulated near the membrane surface. The results indicate that complete and standard blocking are better models of HA filtration than intermediate blocking.

A more distinguished effect of the foulant was observed for the BSA filtration than for the HA filtration (Figs. 3 and 4). After hydraulic backwashing with permeate, the flux was not recovered, and a larger fraction of irreversible fouling was observed for BSA than for HA, because BSA is composed of high-molecular weight components with polar groups and can rapidly decrease the flux near the membrane surface. At the higher concentration, the slope of the total

resistance decreased with increasing resistance for 20 min and then it was increased. The higher concentration used in this study might have led to a rapid change to intermediate blocking and cake filtration, because a concentration polarization layer formed on the membrane surface [1]. It can be concluded that the dominant fouling mechanism of BSA was inner pore adsorption with particle superposition. The relatively large fraction of irreversible fouling is consistent with the previously described dominant fouling mechanism of BSA. These phenomena are shown in Figs. 3 and 4. The recovery efficiency of hydraulic backwashing was 9.1–11.1%, and BSA filtration data fit well into the intermediate blocking modeling mechanism.

In the SA filtration experiments (Fig. 5), a sharp flux decline occurred immediately. The flux was reduced more than 80% by SA filtration within 20 min, and the flux recovery was no higher than 40%. Similar phenomena have been observed for alginate filtration using polymeric organic membranes [13,14] due to the rapid formation of a gel layer that completely blocks the membrane surface. After hydraulic backwashing, the flux recovered by 35.4%. The reason for this result may be the high solubility of polysaccharides and the redissolution of the gel layer. SA adhered to the external cake filtration model and had a higher resistance than BSA. As shown in Fig. 6, a more accentuated behavior according to the cake filtration model was observed in the SA experiment than in the HA and BSA filtration experiments. Complete and standard blocking occurred immediately (within 3 min) due to complete blockage of the surface pores by particles, which then are deposited on present particles. Cake filtration occurred rapidly after this blockage. This refers to the point in the filtration time at which the initial sharp flux decline ended, leading to the significantly slower decrease in permeability. A 50% flux decline was observed in the BSA and SA filtration experiments, but only a 27.4% decline was observed for HA. This difference is attributed mainly to the hydrophilic characteristics of the ceramic membrane, which has a higher affinity for polar proteins than for hydrophobic humic substances.

### 3.1.2. Effect of foulant mixture

The interactions among the three compounds in ceramic MF were investigated. The effects of mixtures of compounds are of considerable interest because foulants in actual water systems are complex mixtures. The fouling characteristics of the mixed solution were determined in a filtration experiment in which 10 ppm each of HA, BSA, and SA were used. Fig. 7 shows the relative permeability and hydraulic resistance of the

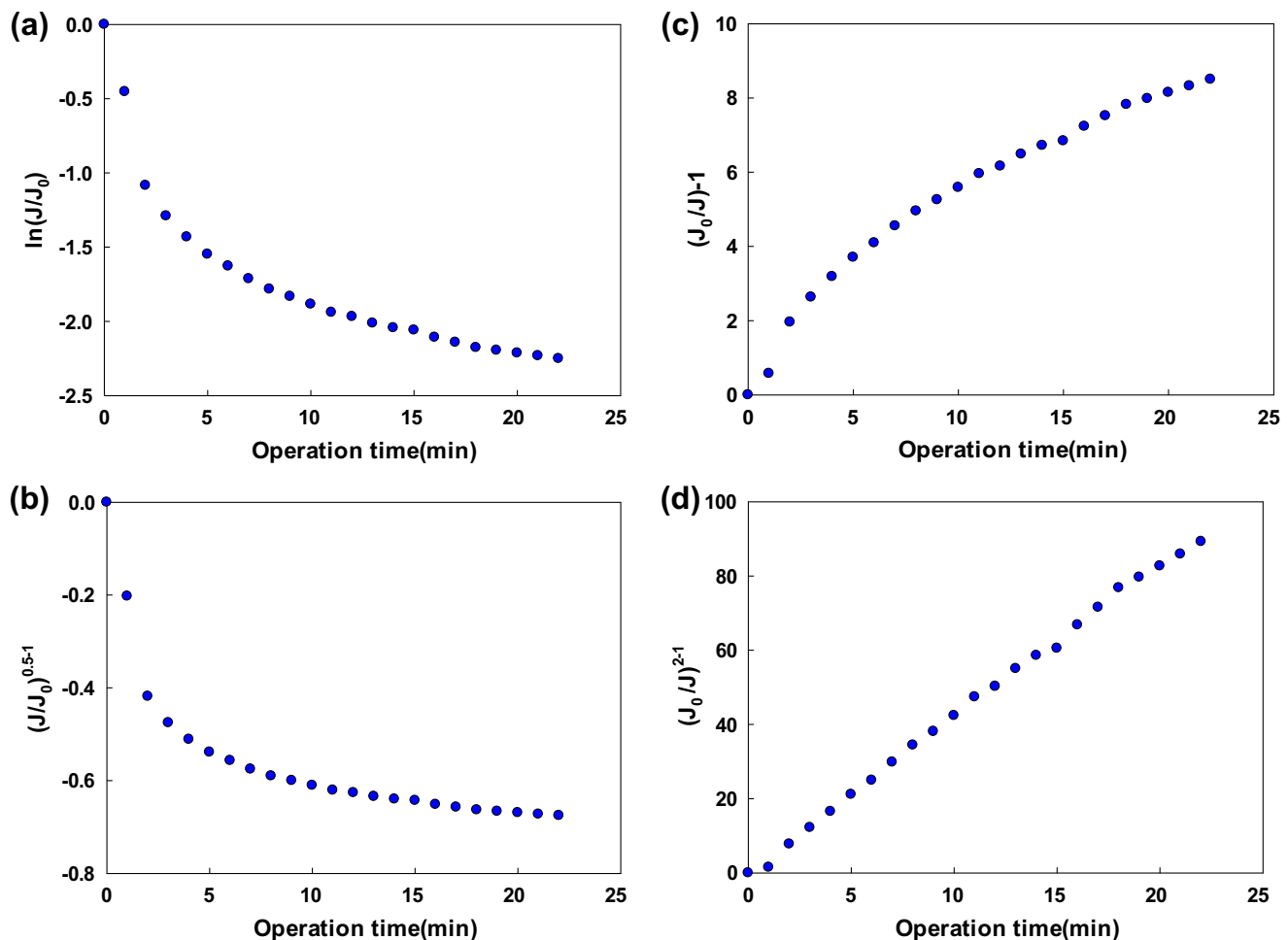


Fig. 6. Investigation of the SA filtration experiments according to the linear expressions modeling mechanism: (a) complete blocking, (b) standard blocking, (c) intermediate blocking, and (d) cake filtration.

mixture of compounds. A synergistic effect was evident during the filtration of the mixture of compounds. A comparison of the flux changes of BSA, SA, HA, and the mixture of compounds revealed increased flux with BSA and SA alone but decreased flux with HA alone. A complicated total resistances occurred with external cake filtration and the internal fouling model, and it was best explained by the observed behavior (Fig. 7(b)). As shown in Fig. 7(c–f), more complicated changes in the complete and standard blocking models were observed for the three compounds than for HA, BSA, and SA alone. Moreover, the intermediate blocking and cake filtration models showed two inflection points. These results indicate that the flux of the three compounds changed significantly and that the presence of each compound, even at a low concentration, modified the fouling characteristics of the others, increasing or reducing the particle–particle deposition, and causing cake filtration.

### 3.2. The recovery of membrane flux

Table S2 shows the flux recovery rates during different operation cycles. After filtration, the flux recovery rates of HA, BSA, and SA were 30.8, 26.8, and 10.5%, respectively. Hydraulic washing and chemical cleaning were performed to investigate the flux recovery rates of the three organic compounds. After hydraulic washing, the flux recovery rates of HA, BSA, and SA were 45.9, 37.8, and 43.9%, respectively. In the case of SA, the higher recovery rate following hydraulic washing showed that the major source of fouling was the cake layer and that reversible fouling had occurred. Although HA and BSA caused pore blocking, adsorption, and mostly irreversible fouling, these could be removed by chemical cleaning. After chemical cleaning, the recovery rates of HA, BSA, and SA increased to 100%, and the membrane appeared close to its virgin state. Most of the membrane foulants were removed

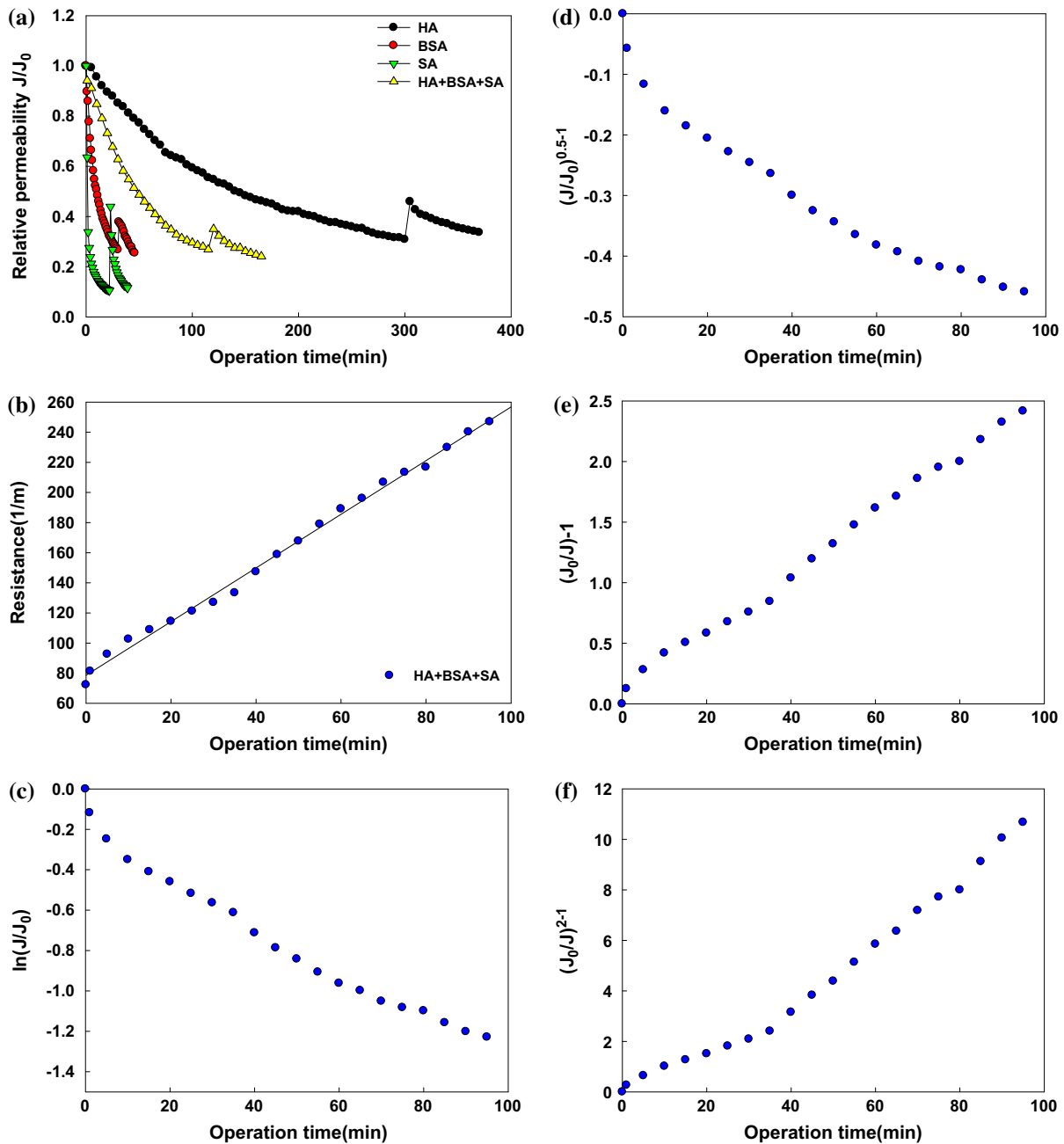


Fig. 7. The relative permeability vs. filtration time (a) and the resistance vs. filtration time (b) and the linear expressions modeling mechanism ((c) complete blocking, (d) standard blocking, (e) intermediate blocking, and (f) cake filtration) with 10 mg/L mixture of HA, BSA, and SA.

after the membrane was soaked in a solution of NaOCl, which improved the membrane surface. As a result, hydraulic washing and chemical cleaning were effective for removing fouling.

#### 4. Conclusions

This study of three organic compounds indicated the significant fouling potential of such compounds on

ceramic MF. The experiments on the fouling characteristics of NOM on ceramic MF revealed the following:

After ceramic MF, HA followed the internal fouling model, while BSA and SA followed the external cake filtration model. Complete blocking occurred in the initial filtration with HA, while the main fouling mechanisms of BSA and SA were intermediate and



cake filtration. The HA molecules became trapped due to their polymeric protein structures and then became part of the cake arrangement. When HA was mixed with the other organic compounds (BSA, SA), a significant change occurred. The flux decline was proportional to the foulant concentration in the HA and BSA filtration experiments. The order of fouling potential of the compounds was SA > BSA > HA. In summary, the adsorption of NOM to a ceramic membrane was accentuated in the cases of BSA and SA due to the hydrophilic functional groups of these molecules. The combined organic compounds had a strong synergistic effect due to foulant–foulant interactions.

### Supplemental material

The supplemental material for this paper is available at <http://dx.doi.org/10.1080/19443994.2015.1057035>.

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