Identification of key factors affecting the organic fouling on low-pressure ultrafiltration membranes

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The fouling behavior of the hollow fiber ultrafiltration (UF) membrane by the mixtures of dissolved organic matters (DOMs) has been systematically investigated. The organic foulants included humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA), which represented humic substances, proteins and polysaccharides, respectively. According to the experimental results, the filtration process of organic mixtures could be divided into a fast fouling stage and a slow fouling stage no matter what mixture was used. Scanning electronic microscopy (SEM) and the attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis of the surface of the fouled membranes revealed a significant difference in the structure of fouling layer, which may be attributed to the different deposition rates of the organics. More importantly, the molecular weight of DOMs, solution zeta potential (ZP) and particle size were examined in order to identify the key factors contributing to the fouling behavior. A strong correlation was found between fouling resistance and the content of small molecules in DOMs and solution zeta potential based on statistical analysis. Both factors played significant roles in membrane fouling. A more serious fouling could be observed with a higher proportion of small molecules or a more negative charge density of solution. Furthermore, the normalization data indicated that the effect of small molecule on membrane fouling was more important compared to the ZP of the solution.

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1. Introduction

Membrane filtration has been extensively used for water treatment in the past decades [1]. However, a major challenge to the applications of membrane technology at different scales is fouling, which causes a great reduction in the productivity, leading to a severe filtration flux decline [2]. Membrane fouling is a complex issue [3]. Generally, dissolved organic matters (DOMs) including humic substances, proteins and polysaccharides are recognized as the major foulants that block the membrane pore and reduce permeate flux. Many studies have been conducted to investigate the organic matters responsible for membrane fouling and subsequently to understand the fouling mechanisms. Using model organic foulants to investigate the fouling behavior is a common method employed in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [4-5]. Humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA) are used as representative compounds of DOMs. A complete understanding of the mechanisms governing HA fouling has been unraveled, including the effects of adsorption (foulant–foulant, foulant–membrane), concentration polarization and aggregate desorption during UF and NF filtration [6,7]. Huisman et al. reported that the initial stage of filtration was mainly controlled by protein–membrane interactions (hydrophobic interactions, electrostatic interactions, aggregation behavior), but in the later stages of filtration, protein–protein interactions (cake layer) dominated the fouling behavior [8]. Because of a broad size distribution, SA has both small molecules with high diffusivities and large molecules with low diffusivities. Therefore, they would be fractionated in the deposited cake with larger molecules closer to the membrane and smaller ones in the bulk [9].

However, compared to an individual foulant, membrane fouling caused by the mixtures of different organic foulants is more complicated. Hence, a new approach to investigate the membrane fouling behavior of combined foulants becomes more important [10,11]. A few studies investigated the combined fouling effect by using both inorganic/organic colloids and NOMs. It was found that flux decline rate in combined fouling experiments was higher than what was expected based on the sum of colloidal and organic fouling alone during silica colloids and HA in NF membrane [11]. This aggravated membrane fouling referred to a significant synergistic effect, which is attributed to a mechanism of hindered back diffusion of colloidal and organic foulants. In addition, Contreras et al. reported...
three mechanisms, increased hydraulic resistance of the mixed cake layer structure, hindered foulant diffusion and changed colloidal surface properties due to organic adsorption, which played a role in combined fouling to various degrees [12]. These studies focused on the interactions between different organic matters, but ignored the interaction between organics. Tomaszewski et al. demonstrated that electrostatic attraction of humic substances–protein drove encapsulation of positively charged protein by HA, which could alter the surface properties of the complexes [13]. A number of literatures have shown that protein and polysaccharide molecules could link together with chemical and physical interactions [14,15]. These interactions result in modification of molecular structure, and affect interfacial characteristics. Therefore, the interactions between NOMs might also lead to the change in membrane fouling behavior.

Recently, a few of studies investigated the effect of combined organic mixtures on the fouling of UF and RO membranes. Jermann et al. [16] revealed the impact of molecular interactions between HA and SA on UF fouling mechanisms. This effort led to the conclusion that a mutual influence could affect each other due to steric effects and chemical interactions. HA can function as a bridge between alginate and membrane, causing a more stable and less reversible fouling layer than the individual alginate cake. However, Katsou et al. [17] studied the effect of HA/SA mixtures during UF hollow fibers in dead-end mode in the presence and absence of calcium ions. The experimental results manifested that no significant synergistic effects occurred. The fouling behavior of the mixtures was quite similar to that of polysaccharides alone. Research efforts on organic fouling have also been made on RO membranes [18,19], which discovered that there was an inverse correlation between the size of the foulants aggregates and the intermolecular adhesion force. Foulant aggregate size generally decreases with the increase in intermolecular adhesion force.

Although researchers have made their efforts to understand the role of organics on membrane fouling, their results however are often insufficient and/or contradictory. The present study systematically investigated the fouling characteristics of UF membrane by using HA, BSA and SA as model compounds. The objective is to reveal the key factors governing the fouling behavior in combined foulants. Emphasis is placed on finding the relationship between fouling resistance and solution properties. The distribution of solution molecular weight and electrostatic interaction between foulant–foulant and foulant–membrane are used to explain the fouling behavior.

### 2. Materials and methods

#### 2.1. Organic foulants

Polysaccharide, protein and HA were chosen to represent typical NOMs in drinking water. The stock solution was prepared by dissolving 1 g of HA (Sigma-Aldrich, USA) into 500 ml of 0.01 mol/L NaOH solution. BSA and SA (from brown algae) solutions were purchased from Genview (0BS10440, purity > 99%) and Sigma-Aldrich (A2158), respectively. The two solutions were dissolved in 500 mL deionized (DI) water with 1 g of BSA or SA. All solutions were stirred for 24 h, and then filtered through a 0.45 μm glassfiber membrane to remove residual non-dissolved matters. The filtered solutions were stored in a sterilized glass bottle (1000 mL) at 4 °C. Dissolved organic carbon (DOC) was measured by a TOC analyzer (TOC-VcpH, Shimadzu, Japan). The distribution of the apparent molecular weight (AMW) of the organics in solution was analyzed by high pressure size exclusion chromatography (HPSEC) (Fig. S1).

#### 2.2. The hollow-fiber polyvinyl chloride membrane module

The hollow-fiber UF membrane module is made of Polyvinyl Chloride (PVC) (Litree Co., Hainan, China). It has a filtration area of 0.01 m², with the inner and outer diameters of 0.85 mm and 1.45 mm, respectively. The nominal pore size is 0.01 μm and molecular weight cutoff (MWCO) is 50 kDa. Each module contains 10 fibers, with an effective length of 23.0 ± 1 cm. The contact angle of the PVC membrane is measured as 33.67 ± 0.46, indicating a hydrophilic property [20].

#### 2.3. Experimental procedures

A schematic diagram of the UF system is shown in Fig. 1. Feed solution was pumped into a membrane module (dead-end mode, outside-in) at a transmembrane pressure of 30 kPa. The permeate production was measured by a balance connected to a computer. A virgin membrane was used in each experiment in order to compare the results under the same condition. Prior to ultrafiltration test, the virgin membrane was soaked in deionized (DI) water for 24 h. DI water was initially permeated and pure water flux was measured until a constant flux was achieved (30 min was shown to be enough). It is well known that membrane flux imposes significant influence on membrane fouling [21]. So the initial flux (pure water flux) was set at 60 ± 3 L/(m² h). The organic solution (3 L) was then filtered and the flux was measured for 4 h. Every experiment was repeated three times.

The degree of membrane fouling is evaluated by membrane filtration resistance calculated by Darcy’s law:

\[
J = \frac{\Delta P}{\mu(R_m + R_f)}
\]  

(1)
where \( J \) is the permeate flux (L/h m\(^2\)), \( \Delta P \) is the transmembrane pressure (Pa), \( \mu \) is the dynamic viscosity of the solution (Pa s), \( R_m \) is the resistance of the membrane (m\(^{-1}\)) and \( R_f \) is the fouling resistance (m\(^{-1}\)).

### 2.4. Analytical methods

Molecular weight (MW) distributions were determined by HPSEC. Before measuring, all samples were filtered through a 0.22 \( \mu \)m fiber membrane. Detailed description of the method can be found in previous publication [22].

The attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR, 8700, Nicolet, USA) was used with a resolution of 4 cm\(^{-1}\) in the range of 600–4000 cm\(^{-1}\), to provide the information of the functional groups of the foulants on membrane surface. Before the FTIR analysis, the samples were totally air-dried at room temperature. The dried samples were then cut to obtain the flat external surface for FTIR analyzed.

The surface and cross-section of the virgin and fouled membrane were analyzed by scanning electron microscopy (SEM, LEO-1530, Germany). For surface imaging, a small piece of a sample was air-dried and sputter coated with gold (Au) before being examined at 30 kV accelerating voltage for SEM analysis. For cross-section imaging, the fouled membrane was immersed into liquid nitrogen and broken. Then, the fractured sample was air-dried and sputter coated with gold (Au) for SEM analysis.

Solution zeta potential (ZP) was determined by a Master Nano 1000 (Malvern Instruments, UK). Surface ZP (streaming potential) and diameter of organic solution were characterized by electrophoretic mobility and dynamic light scattering (DLS) using a DelsaNano C zeta potential analyzer (Beckman-Coulter, USA). Surface ZP is the potential at the electrokinetic slipping plane between the surface and solution when relative motion occurs between them. It has often been used in membranes to infer the charge of surface and pores or channels [23]. The surface ZP is an important property that affects the membrane fouling.

### 2.5. Data processing

Nguyen et al. have postulated that the membrane resistance was increased linearly with the volume of the produced permeate [24]. Accordingly, a constant rate \( K \) could be calculated, demonstrating the fouling rate. The method of data processing is detailed elsewhere [24]. In order to analyze the key factors contributing to fouling, the Pearson correlation coefficient (bivariate correlation) was performed to assess the correlation between fouling resistance and feed water properties by using statistical product and service solutions (SPSS) software. Moreover, two-tailed test (a test of significance) was concerned with the hypothesis that an observed value of a sampling statistic differed significantly from a given value, where probability \( P < 0.01 \) indicated that correlation was significant at the 0.01 level.

To eliminate the incomparability, the data was normalized, which were calculated as follows:

\[
X_T = \frac{\sum_{i=1}^{n} X_i}{n}
\]

\[
P_i = \frac{X_i}{X_T}
\]

where \( X_i \) are the measurements, \( X_T \) is the sum of these values, and \( P_i \) is the special proportion of the corresponding values.

### 3. Results and discussion

#### 3.1. Variation of membrane fouling resistance

Fig. 2 shows the increase of the filtration resistances \( (R_f) \) during membrane filtration of organic foulant mixtures. The change of \( R_f \) can be divided into two stages in the whole filtration process: a fast increasing stage and a slow one. \( R_f \) increased sharply over a short filtration time (1 h) and reached about 58\% (2.5 \times 10^5 m\(^{-1}\)), 56\% (5.7 \times 10^5 m\(^{-1}\)) and 71\% (6.8 \times 10^5 m\(^{-1}\)), respectively in HA/BSA, BSA/SA and HA/SA mixtures (2:1). Then \( R_f \) gradually increased 42\%, 44\% and 29\% with the following filtration (Fig. 2a). Similar phenomena were observed in other mixtures under different conditions.
concentration ratios. Table S1 displays the slope of $R_f$ increased with time in these two stages. The slope was larger in the fast fouling stage than the slow one.

This illustrates that the different interactions between organics and membrane were predominant in two stages. In order to explain the fouling mechanisms, blocking models were adopted according to Kang et al. [25]. In the fast fouling stage, foulant–membrane interaction may have a significant effect on the fouling behavior. In the initial filtration regime, standard blocking model ($R^2 > 0.85$ in all cases, refer Table S2) had the best fit. It indicated that organics could cause pore blocking as they absorbed or deposited on membrane surface, leading to the reduction of effective permeate area and a rapid $R_f$ increase. Subsequently, the fouling layer formed owing to the interaction between foulants led to a steady change of $R_f$. This was consistent with cake formation model ($R^2 > 0.89$ in all cases, refer Table S2). Apparently, the results showed that foulant–foulant interaction became predominant in the slow stage. Previous researches [10,26] have the same opinion on this phenomenon.

$R_f$ of HA/BSA mixtures increased more slowly compared to the other two mixtures. It increased to $4.3 \times 10^8$ m$^{-1}$, $6.7 \times 10^8$ m$^{-1}$ and $5.0 \times 10^7$ m$^{-1}$ respectively with concentration ratios of 2:1, 1:1 and 1:2 at the end of filtration. And the HA/SA mixtures were found to have the maximum resistance of $9.9 \times 10^5$ m$^{-1}$, $1.2 \times 10^6$ m$^{-1}$ and $1.3 \times 10^6$ m$^{-1}$ under the same ratios. The overall order of fouling resistance regardless of concentration ratios was HA/SA > BSA/SA > HA/BSA.

3.2. Characterization of fouled membrane

3.2.1. Morphology analysis

The samples of virgin and fouled membranes were observed with SEM to demonstrate the change in morphology. As displayed in Fig. 3a and e, the surface of virgin membrane was rather smooth, and the strips and pores in the surface were quite clear. By contrast, obviously the surfaces of the fouled membranes were covered by a fouling layer after filtration (Fig. 3b–d). However, the density of the layer formed by organic mixtures was different. The fouling layer formed by HA/BSA mixture (2:1) was uniform, but the morphology of the membrane surfaces fouled by BSA/SA and HA/SA mixtures (2:1) had a notable change, having thicker fouling layers. Similar results were also observed in the other two ratios (1:1 and 1:2); the images are not shown here. Apparently, surface pores were blocked by some small particulates (Fig. 3f–h), and the internal channels became narrow and obscured near the membrane surface, causing serious fouling [27].

3.2.2. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis

The foulants on the fouled membrane fiber samples were further characterized by the ATR-FTIR analysis. The results are presented in Fig. 4 (the membrane spectrum has been digitally subtracted). The membrane surfaces have shown some typical functional groups which revealed the characteristic of foulants after filtration. The results performed a significant adsorption at 1037 cm$^{-1}$ and a weak absorption at 1393 cm$^{-1}$ in Fig. 4a, although concentration ratio was 2:1 in HA/BSA mixture. According to previous research [28–30], the absorption peaks close to 1034 and 1100 cm$^{-1}$ manifested the C–O bond of ethers (protein), alcohols and polysaccharides, while the peak at 1393 cm$^{-1}$ (–OH deformation vibration, C–O stretch vibration of phenolic hydroxyl group) would suggest the presence of HA. Therefore, the peak at 1037 cm$^{-1}$ was inferred as protein, which was more notable than that of HA. With an increasing concentration of BSA, the spectra of HA disappeared (Fig. 4b and c). Consequently, it can be inferred that HA was close to the membrane surface, while a large amount of proteins were in the outer layer of the fouling layer.

Similar results are exhibited in membrane surface fouled by BSA/SA (Fig. 4g–i). After being fouled by BSA/SA mixtures, the peaks at 1655 cm$^{-1}$ and 1543 cm$^{-1}$ (amide I and amide II bands of protein respectively), 1400 cm$^{-1}$ (carboxylate) and a strong absorption band between 1100 and 1000 cm$^{-1}$ (C–O bond of ethers (protein) and polysaccharide) displayed the appearance of protein and polysaccharide. And the appearance of peak near 1076 cm$^{-1}$ attributed to C–O bond of polysaccharide was notably increased with the SA concentration. However, the peaks of BSA (1655 cm$^{-1}$ and 1543 cm$^{-1}$) were more dominant than those of SA regardless of concentration, suggesting that protein had an important contribution to the outer layer of fouling. From the spectra of the foulants from HA/SA mixture, it was found that both HA and SA had contribution to the outer fouling layer. The reason for their differences may come from the different deposition efficiencies. Sioutopoulos et al. [31] calculated the deposition factor values of organics in RO membrane, which were estimated to be 0.6, 0.9 and 0.9 for HAs, SA and their mixtures respectively. They found that the difference of deposition factor may affect the characteristics of the fouling layer.

3.2.3. Proposed structure of organic fouling layer

According to the results of SEM and ATR-FTIR, a preliminary structure of fouling layer under various mixed orgnics could be portrayed. The fouling layer had a structure resulting from the formation of the protein mainly in the outer layer and HA at the inner layer and closer to the membrane surface (Fig. 5a). Both HA and SA were located on the outer fouling layer, and, as shown in Fig. 5b, a compacted layer was formed because of the competitive absorption between HA and polysaccharide. This result is in agreement with previous research, which had found the density of the layer and a coherent cake structure was promoted to form a more compacted layer in HA/SA mixtures [18,32]. Proteins and polysaccharides were just co-soluble, and no complexes tended to form [33]. In addition, surface morphology of the fouled membrane underwent a great change. Hence, the resultant fouling layer was attributed to competitive absorption with protein mainly in the outer and polysaccharide mainly in the inner layer (Fig. 5c). Meanwhile, the structure of the layer was thicker compared to that formed by HA/SA mixtures.

3.3. Characterization of feed solution

3.3.1. Molecular weight distribution

HPSEC chromatographs had been processed by peak fitting software. The peak fitting results of AMW profiles are shown in Fig. 5. The results exhibited the distribution of molecular weight of organics. Using the chromatogram of sample HA/BSA mixture with 2:1 as an example, five peaks were identified and the AMWs of the resolved peaks were calculated to be 1127 Da (peak 1), 3282 Da (peak 2), 18.6 kDa (peak 3), 25.2 kDa (peak 4) and 33.2 kDa (peak 5). From Fig. 5, it can be observed that the AMWs of each solution were different. However, two ranges of molecular weight were summarized, less than 5000 Da and above 11 kDa. And the ratios of these two ranges of molecular weight are listed in Table 2. In various mixtures of two organics at the same concentration ratios, fouling resistance increased as the proportion of small molecules increased. Therefore, small molecules may have more crucial effects on fouling behavior.

3.3.2. Zeta potential

As shown in Fig. 6a, ZPs of all solutions used in the experiments were negative. It is worth to note that ZPs of these solutions
showed significant difference. BSA/SA mixtures had negative surface ZP of $-10.06 \pm 2.57$ mV, $-14.85 \pm 3.88$ mV and $-19.05 \pm 4.05$ mV, while HA/SA and HA/BSA mixtures had a much more negative surface ZP, measuring $-37.32 \pm 3.15$ mV, $-36.08 \pm 4.2$ mV and $-35.94 \pm 4.17$ mV and $-26.96 \pm 3.49$ mV, $-17.43 \pm 3.84$ mV and $12.91 \pm 2.4$ mV, respectively, under the ratios of 2:1, 1:1 and 1:2.

The ZP of the virgin membrane at neutral pH was $-5.36 \pm 0.73$ mV. Membrane surface ZP after being fouled by each foulant was performed using the same membrane coupons. Fig. 6b illustrates the effect of the organic foulants on membrane surface ZP. All organic foulants caused notable changes in membrane surface ZP, manifesting significant adsorption on membrane surface [34,35]. Adsorption of the highly negatively charged...
foulants led to an increase in the magnitude of the negative membrane surface ZP, while less negatively charged solutions just caused a slight increase. Moreover, the changes in ZPs of fouled membrane caused by organic mixture were similar to those of solutions, which demonstrated the effect of adsorption of foulants on membrane fouling [32]. Therefore, a hypothesis is put forward that electrostatic repulsion might play an important role in the interaction between NOMs and membrane.
3.4. Particle size

Recent studies conclude that particle size also affected the membrane fouling process, especially the structure of cake layer [11,18]. Hence, all feed solutions were characterized for their size under the solution conditions. The mean hydrodynamic diameter was derived from an average number-based-distribution based on three measurements. It is important to note that organic colloids formed in mixtures only when HA existed (Fig. 7). However, BSA and SA could not form detected colloids in their mixtures, because their sizes were beyond the detection limit for DLS measurement or they were just co-soluble. Under the same conditions, no obvious differences were observed between HA/BSA mixtures and HA/SA mixtures, except in the ratio of 1:1. The comparison between different test results suggests that, at least in this case, particle size had little effect on the membrane fouling process.

3.5. Fouling mechanism

Previous studies have demonstrated that organic fouling behavior in filtration was dependent on chemical characteristics of feed water, membrane properties, foulant–foulant and foulant–membrane interactions [8,17,32,35]. As discussed in Section 3.1, in HA/BSA mixtures ultrafiltration experiments, fouling resistance increased slowly compared to other organic mixtures, while HA/SA mixtures exhibited the highest fouling resistance, regardless of the concentration ratios (Fig. 2). Therefore, the fouling phenomena were quite different from that of the individual foulant, indicating that a combined effect occurred.

In order to identify the key factors contributing to fouling behavior, the results of the distribution of molecular weight and solution ZP were analyzed by the SPSS software (Table S3). It was found that the proportion of small molecules and solution zeta potential had an essential effect on fouling resistance. Table S4 lists the correlation coefficient between fouling (K) and small molecules; solution ZPs were 0.806 and –0.653, respectively, manifesting a

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**Table 2**
The distribution ratio of molecular weight.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Concentration ratio</th>
<th>&lt;5 kDa</th>
<th>&gt;11 kDa</th>
<th>Relative proportion (small/big)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA:BSA</td>
<td>2:1</td>
<td>0.29</td>
<td>0.71</td>
<td>0.41</td>
</tr>
<tr>
<td>BSA:SA</td>
<td>2:1</td>
<td>0.36</td>
<td>0.64</td>
<td>0.56</td>
</tr>
<tr>
<td>HA:BSA</td>
<td>1:1</td>
<td>0.41</td>
<td>0.59</td>
<td>0.69</td>
</tr>
<tr>
<td>BSA:SA</td>
<td>1:1</td>
<td>0.19</td>
<td>0.81</td>
<td>0.23</td>
</tr>
<tr>
<td>HA:BSA</td>
<td>1:1</td>
<td>0.48</td>
<td>0.52</td>
<td>0.92</td>
</tr>
<tr>
<td>BSA:SA</td>
<td>1:1</td>
<td>0.48</td>
<td>0.52</td>
<td>0.92</td>
</tr>
<tr>
<td>HA:BSA</td>
<td>1:2</td>
<td>0.30</td>
<td>0.7</td>
<td>0.43</td>
</tr>
<tr>
<td>BSA:SA</td>
<td>1:2</td>
<td>0.35</td>
<td>0.65</td>
<td>0.54</td>
</tr>
<tr>
<td>HA:SA</td>
<td>1:2</td>
<td>0.48</td>
<td>0.52</td>
<td>0.92</td>
</tr>
</tbody>
</table>

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**Fig. 6.** Zeta potentials of all feed water (a) and membrane surface after being fouled (b).

**Fig. 7.** The mean hydrodynamic diameter of foulants in various mixed solutions.
strong correlation between them. Small molecules and solution ZP directly affect membrane fouling behaviors. For negative potential of solution, the fouling resistance increases more rapidly with the increase of the absolute value of solution ZP. This can be explained by the electrostatic interaction, which brought more difficulties for permeation to occur through the membrane due to a strong repulsive interaction between solution and membrane surface (both of them were negative). Furthermore, the correlation coefficient of fouling and small molecules is a strong 0.806, which revealed a significant positive correlation (P < 0.01). It indicates that the value of K increased with the amount of small molecules. Small molecules are easier to pass into membrane pore and cause pore blockage. And also the number of small molecules is larger than big ones under the same conditions, which meant that they could reduce the effective filtration area significantly.

Through normalization, the incomparability of data was eliminated. The influence of solution ZP and small molecules on fouling resistance is directly shown in Fig. 8. Particularly, fouling resistance is found to be more importantly influenced by small molecules (slope = 0.6587), compared to solution ZP (slope = 0.4697). Thus, it suggests that small molecules and solution ZP had come together to decide the membrane fouling behavior, but the former factor is more important. However, it should be pointed out that the organic mixtures displayed different charge properties and particle effects. These observations might be primarily attributed to the change in conformation of organic matters caused by their interactions, which was the intrinsic factor affecting the membrane fouling behavior. Further research would be needed.

4. Conclusions

In this study, the fouling behavior with mixed organics during UF membrane process was investigated in a dead-end mode. According to the results, some conclusions can be drawn as follows:

(1) Two fouling stages were observed by filtering organics mixtures: a fast fouling stage and a slow one. The overall order of the resistance regardless of the concentration ratio was HA/BSA > BSA/SA > HA/SA.

(2) According to the SEM and FTIR examinations, the fouling layer formed by HA/BSA had a structure in which the protein was mainly in the outer layer and HA in the inner layer. Both HA and SA had contributed to the outer compacted fouling layer. The resultant thick fouling layer of BSA and SA was attributed to competitive absorption.

(3) All feed waters were analyzed by HPSEC, ZP and particle size. The results demonstrate that particle size had no apparent effect on membrane fouling behavior, while small molecules and solution ZP played important roles according to the statistical analysis. Fouling resistance increased with the amount of small molecules and negative charge density of solution. Furthermore, the former factor is more significant than the latter. It brings more difficulties for permeation to occur through the membrane due to a strong repulsive force in constant pressure. Small molecules are easier to flow into membrane pores to cause pore blockage, leading to a rapid reduction of the effective filtration area.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2013.07.040.

References


