Experimental Study of Fouling Behavior of Main Substances (BSA, HA, SA) of Dissolved Organic Matter (DOM) in Dead-end Membrane Filtration

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Abstract. In this study, the fouling behavior of PES ultrafiltration (UF) membrane with different DOM fractions including bovine serum albumin (BSA), sodium alginate (SA) and humic acid (HA) was systematically investigated. The result showed that the fouling mechanism of HA was cake formation while that of BSA and SA was caused by both pore blocking and cake formation due to the different particle size. Moreover, membrane fouling became more severe with the increase of feed concentration and TMP and it could be accurately described by the cake-complete model. The pore blocking resistance for SA was larger than that for BSA, whereas the cake resistance followed the sequence SA>BSA>HA. This observation offered insight into the differences in fouling behavior of the various DOM components and was further used as guidance for practical application.

Keywords: DOM; UF membrane; Fouling mechanism.

1. Introduction
Membrane bioreactor (MBR) is a robust membrane ultrafiltration technique to replace the traditional secondary settling pond water treatment technique [1]. Among all of the sewage treatment techniques, MBR possesses relatively high efficiency and good effluent quality [2]. However, the membrane fouling in MBR filtration still restricts its wide application [3].

Membrane fouling indicates the significant decrease of flux caused by the deposition of suspended solids and soluble substances on the membrane surface as well as in the pores of the membrane [4]. Many studies indicate that the dissolved organic matter is one of the main foulants leading to the membrane fouling [5]. In general, dissolved organic matter is the carbon based organic compounds which could transit the filtration membrane with the pore size of 0.45μm [6]. According to different molecular sizes, the small molecular chemical compounds include monosaccharide and amino acid etc. while the big ones indicate polysaccharide, protein, xylene and humus etc. [7]. It is reported that the dissolved organic matters contribute 26%-52% of the whole membrane fouling resistance [8-9].
Furthermore, the distribution of dissolved organic matter composition is influential on the level of membrane fouling. Consequently, it is necessary to study the impact of main compositions including protein, polysaccharide and humic acid on membrane fouling under different conditions.

2. Material and Methods

2.1. Experimental Equipment and Operating Conditions
The microfiltration experiment was performed at different TMP of 0.04 MPa, 0.08 MPa and 0.12 MPa with a laboratory scale dead-end filtration system, consisting of a filtration cell with effective membrane area of 28.27 cm$^2$ at 25 °C and stirring speed 200r/min [10].

2.2. Membranes
Flat sheet polyethersulfone membrane (PES, Mw = 50000 Da) with pore size of 0.1 μm (Ande Membrane Separation Technology and Engineering (Beijing, China)) was used as filtration membrane. Before each experiment, PES membrane was soaked in DI-water for 6-10 h to remove protective agent glycerin.

2.3. Extraction of DOM
The actual DOM solution was extracted from the secondary clarifier of Gaobeidian water reclamation plant (Figure 1). The water was placed for 1.5 h and then the supernatant was carefully decanted away. After testing, the concentration of protein, polysaccharide and humic acid was 12 mg/L, 18 mg/L and 6 mg/L, respectively.

2.4. Analytical Methods
The contents of protein and humic substance in actual DOM solution were measured by the modified Lowry method [11], where BSA and sodium alginate were used as respective standards. The content of polysaccharide was measured by the anthrone method [12], where glucose was used as a standard. The pH was measured using a pH meter (pHS-3C, Leici, China). The constant temperature experiments were operated in water bath (DFD700). The membrane flux was analyzed by Eq. (1).

\[
J = \frac{J_0((-1-K)\exp(-\frac{K_b}{K_cJ_0^2}(1+2K_cJ_0^2t)^{1/2} - 1) + K)}{(1+2K_cJ_0^2t)^{1/2}}
\]

2.5. Model DOM Solutions
Sodium alginate (SA) was supplied by Sinopharm (China). Bovine serum albumin (BSA, Mw = 67000 Da) was supplied by Fuchen (China). Humic acid (HA) was purchased from Beijing Chemical Reagent Co. (China). All chemicals were used without further purification. The preparation of model DOM solution as follows: the polysaccharide solution (11 mg/L, 18 mg/L and 25 mg/L) was prepared by mixing sodium alginate (SA) with sodium bicarbonate buffer solution. The protein solution (2 mg/L, 12 mg/L and 20 mg/L) was prepared by dissolving bovine serum albumin (BSA) in a potassium
dihydrogen phosphate/sodium hydroxide buffer solution at pH = 7.0. The humic substance solution (3 mg/L, 6 mg/L and 12 mg/L) was prepared by mixing humic acid (HA) with sodium bicarbonate buffer solution at pH = 8.0 and then added 100mM NaCl and 10mM CaCl$_2$ to regulate ionic strength. Finally, the prepared solutions were stored in a refrigerator.

3. Results and Discussion

3.1. Effects of Operating Conditions

The fouling behavior of the PES UF membrane with different concentrations and TMPs of BSA, HA and SA could be accurately predicted by the cake-complete model (Figure 2). The flux declined rapidly with the increase of the mode DOM concentration and TMP since a thicker and denser cake was formed on the membrane surface at higher concentration and TMP [13]. In addition, the flux of HA solution decreased slowly compared to BSA and SA solution at the same concentration owing to the different particle size of BSA and SA. As the molecules of HA was bigger than the pore size of the membrane, the fouling mechanism was mainly cake formation. However, the small molecules of BSA or SA are easier to fill into membrane pores and cause pore blocking, which could reduce the effective filtration area and accumulate the membrane resistance significantly [14].

![Figure 2](image)

**Figure 2.** The variation of flux as a function of time under different concentrations and different TMPs of BSA(a1) and (a2), HA (b1) and (b2), and SA (c1) and (c2) using PES 50 kDa membrane at 0.08 MPa.

3.2. Resistance Analysis

The cake resistance and its proportion in total resistance increased with the increase of the BSA concentration (Figure 3 and Figure 4). And the cake resistance raised whereas its proportion decreased with the increase of TMP. Moreover, the pore blocking resistance raised with TMP whereas decreased with the increase of concentration. This similar variation trend was also observed for SA and BSA solution, which was consistent with reported literature [15].

The cake resistance and pore blocking resistance for SA solution were the largest, whereas the cake resistance for HA solution was the smallest and the pore blocking did not appeared. It could be rationalized that SA with smaller particle size would result in more severe pore blocking than BSA (Figure 5). Moreover, the biggest specific cake resistance ($6.52\times10^{10}$ m$^{-1}$/kg) calculated by cake-complete model for SA was observed in comparison with BSA and HA solution (Table 1). In addition, the increasing rate of resistance was calculated (Table 2). The increasing rate of cake resistance for HA solution ($1.59\times10^{12}$ m$^{-1}$/h) was larger than SA ($9.18\times10^{11}$ m$^{-1}$/h) and BSA solution
(6.33×10^{11} \text{ m}^{-1}/\text{h}). And the increasing rate of pore blocking resistance for SA solution (1.51×10^{12} \text{ m}^{-1}/\text{h}) was larger than that for BSA solution (2.93×10^{11} \text{ m}^{-1}/\text{h}).

![Figure 3](image)

**Figure 3.** The membrane resistance (Rm), cake resistance (Re) and pore blocking resistance (Rp) as a function of filtration time using PES 50 kDa membrane at different BSA (a1, a2), SA (b1, b2) and HA (c1, c2) concentrations.

![Figure 4](image)

**Figure 4.** The membrane resistance (Rm), cake resistance (Re) and pore blocking resistance (Rp) as a function of filtration time using PES 50 kDa membrane under different TMPs for BSA (a1, a2), SA (b1, b2) and HA (c1, c2).
Figure 5. The comparison of different feed solutions on cake and pore blocking resistance.

Table 1. The specific cake resistance of different feed.

|             | BSA     | SA      | HA       |
|-------------|---------|---------|----------|
| Specific cake resistance(α)(m/kg) | 6.16×10^{10} | 6.52×10^{10} | 3.28×10^{11} |

Table 2. The increasing rate of cake and pore blocking resistance for feed solutions

|             | BSA solution | SA solution | HA solution |
|-------------|--------------|-------------|-------------|
| Increasing rate of cake resistance (m⁻¹/h) | 6.33×10^{11} | 9.18×10^{11} | 1.59×10^{12} |
| Increasing rate of pore blocking resistance (m⁻¹/h) | 2.93×10^{11} | 1.51×10^{12} | 0.00 |

4. Conclusions
This study aims to systematically investigate the fouling mechanism and the corresponding resistances of mainly components (BSA, SA and HA) of DOM during ultrafiltration process. The results show that SA causes severer membrane fouling compared with BSA and HA. The fouling mechanism of HA is predominated by cake formation while that of BSA and SA is caused by cake formation and pore blocking. Moreover, with increasing the feed concentration and TMP, the membrane fouling becomes more severe and it can be accurately described by the cake-complete model. The pore blocking resistance for SA is larger than that for BSA, whereas the cake resistance follows the sequence of SA>BSA>HA. This observation offers insight into the differences in fouling behavior of the various DOM components and it could be employed in practical application.

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6. References
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