The Study of Fouling Behavior for the Model Binary Mixture

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Abstract. This study systematically investigated the fouling behavior and mechanism of PAN Microfiltration (MF) membrane fouled with the model binary mixture (bovine serum albumin (BSA) and sodium alginate (SA)) of extracellular polymer substance (EPS) solution under different concentration and transmembrane pressure (TMP). The result showed that the fouling mechanism of the model binary mixture was the pore blocking and cake formation. Moreover, the SA plays a dominant role in the model binary mixture (BSA/SA). The higher SA concentration could cause the more serious membrane fouling (both the flux (J) and the available membrane area (A/A₀) decreased), and the total resistance increased and caused the fouling mechanism changing from combined complete blocking and cake filtration into individual cake filtration appeared earlier. In addition, increasing of the TMP can also aggravate membrane fouling and it could be accurately described by the cake-complete model. This studied offered insight into the model binary mixture in the fouling behavior and mechanism, which can be used as guidance for practical application.

1. Introduction

Membrane bioreactor (MBR) has gained wide attention as it possesses relatively high efficiency and good effluent quality [1]. However, the significant decrease in the permeate flux due to the membrane fouling is a serious problem for MBR [2], which seriously restricted its application in industry.

The main foulant in MBR has been investigated extensively and the key factor affecting the membrane fouling in MBR is extracellular polymer substance (EPS), which mainly consists of polysaccharide, protein, humic substances, uronic acid and DNA [3]. Although EPS extracted from
MBR has been well reported, the filterability behavior and fouling mechanism of EPS were not well understood due to the variability for real MBR systems. Thus, a series of the model EPS solutions (bovine serum albumin (BSA), sodium alginate (SA), humic acid (HA) and so on) were employed to replace the actual EPS solutions to explore their filterability and fouling behaviors [4, 5]. Many studies have extensively studied the membrane fouling using one component system [3, 6] while the variation of available membrane area for the binary mixed systems is rarely studied. Consequently, it is necessary to study the impact of the different conditions (concentration and TMP) on the fouling behavior (the flux \( J \)), the complete pore blocking resistance \( R_p \), the cake resistance \( R_c \) and the available membrane area \( (A/A_0) \)) by using the model binary mixture (BSA/SA) in end-dead filtration cell.

2. Materials and Methods

2.1. Materials
The polyacrylonitrile (PAN) microfiltration membrane (0.1 \( \mu \)m) used in the experiments was obtained from Beijing Ande Membrane Separation Technology and Engineering (Beijing) Co., Ltd. Each virgin membrane sample was immersed into DI-water at a temperature of 4 \( ^\circ\)C for 10-12 h before use to remove glycerol from the membrane. The DI-water was produced by the Milli-Q water system (Millipore, France). Sodium alginate (SA) was supplied by Sinopharm (China). Bovine serum albumin (BSA, Mw = 67kDa) was supplied by Fuchen (China). All chemicals were used without further purification.

2.2. Model EPS solutions
The preparation of model EPS solution as follows: 1 g bovine serum albumin (BSA) and 1g sodium alginate (SA) dissolved in DI-water respectively, then transfer to 1 L volumetric flask to prepare 1 g/L BSA and 1 g/L SA solution. A required concentration of binary mixture solution was obtained by mixing the certain volume of BSA solution and SA solution.

2.3. Experimental equipment and operating conditions
The microfiltration experiment was performed at different TMPs and concentrations (table 1) with a laboratory scale dead-end filtration system, consisting of a filtration cell with effective membrane area of 38.00 cm\(^2\) at 25 \( ^\circ\)C.

| Table 1. The operating conditions |
|----------------------------------|
| TMP (MPa) | 0.04 | 0.08 | 0.12 |
| BSA(g/L)/SA(g/L) | 0.28/0.25 | 0.28/0.25 | 0.28/0.5 | 0.14/0.25 | 0.56/0.25 |

2.4. Analytical methods
In this study, to explore the membrane fouling behavior of the binary mixture for the EPS solution, the variation of the flux was predicted (equation (1)), the available membrane area ratio (equation (2)) and corresponding resistances (the complete pore blocking resistance and the cake resistance) (equation (3) and equation (4)) were calculated [7] as follow:

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

\[
\frac{A}{A_0} = (1-K)\exp(-\frac{K_{v}}{K_{v}J_0^2}((1+2K_{v}J_0^2t)^{1/2}-1)) + K
\]  

where \( A \) is the available membrane area (m\(^2\)), \( A_0 \) is the initial membrane area (m\(^2\)), \( J \) is the permeation
flux (m³/(m²·s)), J₀ is the initial permeation flux (m³/(m²·s)), Kᵇ is complete blocking constant (s⁻¹),
Kᶜ is cake filtration constant (s·m⁻²) and K is steady membrane frontal area (m²).

\[
\frac{R_c}{R_{total}} = \frac{(R_c + R_m) - R_m}{R_{total}} \quad (3)
\]

\[
\frac{R_p}{R_{total}} = \frac{R_{total} - R_c - R_m}{R_{total}} \quad (4)
\]

where \(R_c\), \(R_m\), \(R_p\) and \(R_{total}\) was the cake resistance (m⁻¹), the virgin membrane resistance (m⁻¹),
the complete blocking resistance (m⁻¹) and the total resistance (m⁻¹), respectively.

3. Results & Discussion

3.1. Effects of operating conditions

The operating conditions can provide the basis for the process optimization in practical industry [8]. To
alleviate the membrane fouling, the influence of concentration and TMP were investigated in this study.
Obviously, the model predictions provided good agreement with experimental data under different
concentration and TMP (figure 1), and the fouling mechanism was combined complete blocking and
cake filtration.

It is clear to see that the higher concentration of sodium alginate (SA) could result more serious
membrane fouling at a fixed BSA concentration of 0.28 g/L (figure 1(a)). This is in accordance with the
report [9]. However, no obvious change in the membrane fouling was observed with the increasing of
the BSA concentration from 0.14 g/L to 0.56 g/L at the fixed SA concentration of 0.25 g/L (figure 1(b)).
This is because BSA can easily pass through the membrane pores without forming a cake layer on the
membrane surface [4]. This also implied that the SA is the dominant foulant in MBR [10].

With the increase of the TMP from 0.04 MPa to 0.12 MPa, the flux increased from 2.21 m³/(m²·s)
 to 4.37 m³/(m²·s) at the fixed BSA concentration of 0.28 g/L and SA concentration of 0.25 g/L (figure
1(c)). This may due to the higher filtration driving force caused by the higher TMP [11].

3.2. Resistance analysis

The essential reason of the variation of the flux is the variation of the resistance [12]. Thus, it is also
important to explore the effect of operating conditions on the complete blocking resistance (\(R_p\)) and the
cake resistance (\(R_c\)) (figure 2).

\(R_p\) decreased with the increasing of SA concentration while no obvious change with BSA
concentration (figure 2(a1) and (a2)). This is because the higher SA concentration proposed a higher
mass transfer coefficient [9] and a thicker cake would appear earlier on the membrane surface, which
also indicated that SA plays the dominant role over BSA in model binary mixture. In addition, the higher
TMP provided more power to force the particles to go through the cake layer and blocked more pores,
thus \(R_p\) also increased with the increasing of TMP (figure 2(a3)) [7].

\(R_c\) increased with the increasing of SA concentration and TMP (figure 2(a1) and (a3)). However,
there was no observation for this phenomenon with the increasing of BSA concentration. It could be
explained that higher SA concentration and TMP could cause quicker accumulation of particles on the
membrane surface [13] and a denser and closer cake was formed [14]. Moreover, because BSA has little
effect on the membrane fouling than SA [4], there was no obvious change in \(R_c\) (figure 2(a2)).
Figure 1. The variation of the flux as a function of time under different concentration ratios of BSA and SA ((a) and (b)) and different TMPs (c) using 0.1\textmu m PAN membrane

3.3. Available membrane area ratio analysis

The variation of the available membrane area ratio (A/A0) reflects the variation of the resistance on the membrane surface [7], it is essential to explore the effect of operating conditions on A/A0.

A/A0 is increased with increase of the SA concentration, this is because the rapid formation of the cake in the higher SA concentration, which result in Rp decreased (figure 2(b1)). Meanwhile, Asteady/A0 became higher due to the higher SA concentration weakened complete blocking and the thicker cake appears earlier on the membrane surface [7] (figure 2(b1)). This indicates that the fouling mechanism of higher SA concentration changing from combined complete blocking and cake filtration into individual cake filtration appeared earlier. The increasing BSA concentration has no significant change the A/A0 and Asteady/A0 since BSA concentration has little influence on the membrane fouling [4] (figure 2(b2)).

The higher TMP could provide more power to force the particles to go through the cake layer and block more pores [9], thus, the increased Rp cause the decreasing of A/A0. Meanwhile, Asteady/A0 became lower at higher TMP due to the higher TMP enhanced the complete blocking [7] (figure 2(b3)).
4. Conclusions
This study indicated the fouling mechanism of the model binary mixture (BSA/SA) is the pore blocking and cake formation. The higher SA concentration could cause the decreasing of $J$ and $A/A_0$ while this led to the increasing of $R_c$. Meanwhile, higher SA concentration can alter the fouling mechanism from combination mechanism (combined complete blocking and cake filtration) into single mechanism (individual cake filtration) earlier. Moreover, the variation of the concentration of BSA is little contributed to $J$, $A/A_0$, $R_p$ and $R_c$. The above results show that SA played a dominant role in the cake formation while BSA only played a minor role in the binary mixture. In addition, the higher TMP could cause the increasing of $J$, $R_p$ and $R_c$ while it will make $A_{steady}/A_0$ became lower.

Acknowledgements
This paper is one of the phased achievements of the research of evolution regularity of effective area of...
membrane pore in MBR for actual membrane process (pollution + cleaning) and model establishment (No. 22078003), a general project of the National Social Science Fund.

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