An Investigation of the Membrane Fouling Behaviors in Constant Flux Mode

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Abstract. Studying the effect of different operation conditions (bovine serum albumin (BSA) concentration, flux and stirring speed) on the membrane fouling behaviors (the variation of transmembrane pressure (TMP), cake resistance (Rc), pore blocking resistance (Ri) and available membrane area ratio (A/A₀)) is of paramount importance in the membrane bioreactor (MBR) process. The constant flux filtration experiment was conducted to investigate the fouling behaviors of BSA solution, which provides a guidance for controlling the membrane fouling. The intermediate blocking-cake combined model was established and it was described mathematically with good results. The results showed that the influence sequence of operating conditions on the TMP was obtained as flux > concentration > stirring speed. Meanwhile, Rc decreased with the increase of stirring speed, and the A/A₀ decreased with the increase of BSA concentration and the flux.

1. Introduction
Scarc e water resource and water pollution have become increasingly serious, which has turned into one of the most urgent environmental problems [1]. It is challenging but important to supply the increased demands of fresh drinking water. MBR is considered to be an energy-efficient technology for water...
treatment, and its advantages are small footprint, less sludge output and high effluent quality [2]. However, the challenge of long-term stability operation and the obstacle of large-scale application is the membrane fouling. Membrane fouling is mainly caused by the blocking of membrane pores and the deposition of solutes on membrane surface, which will lead to membrane flux decline [3]. The establishment of a corresponding combined model for the complex membrane fouling process and mathematical description can provide a guidance for the MBR and membrane cleaning process [4]. The model of the description of membrane fouling process has been studied. Initially, there were only complete blocking and standard blocking, and then intermediate blocking and cake filtration occurred. The practice shows that no single form of the filtration law can describe the entire filtration process [5-7]. Therefore, some researchers began to use combined models to describe the actual membrane filtration process. For instance, Michio et al. [8] proposed the model of diffusion deposition in pores and surface blocking. Ho and Zydney et al. [9] proposed the combined model of blocking and cake filtration.

The development of the constant pressure model provides new ideas for predictions of flux, but constant flux mode is more commonly used in MBR process. Therefore, Hlavacek et al. [10] proposed the law of blocking in the constant flux process. However, the constant flux combined model is mainly based on the combined form of the blocking model and the adsorption model. Bolton et al. [11] proposed several combined fouling models based on the single fouling mechanism including constant flux mode. However, it is of paramount importance to study the combined blocking-cake fouling mechanism in constant flux filtration process and apply the proposed model to explain the fouling behavior of MBR. In the constant flux process, the increase of $\Delta P$ is based on the reduction of the available membrane area ($A_0$) and the increase of the filtration resistance. Hou et al. [12] proposed a combined model, which believes that $A_0$ will continue to decrease and the resistance of the cake will continue to increase in the fouling process. The resulting cake will weaken the blocking process and gradually transform into cake filtration, contributing to a stable available area and the increase of filter resistance with time.

In this work, based on the theory proposed by combined filtration mechanisms (complete blocking and cake) and the improvement of the constant flux model, this research establishes a combined pore blocking-cake model under constant flux, verifies the fouling mechanism in MBR and explores operating conditions. The effect of different operation conditions (BSA concentration, flux and stirring speed) on the membrane fouling behaviors (the variation of $\Delta P$, $R_c$ and $R_i$) and available membrane area ratio ($A/A_0$) were carefully studied.

2. Materials and Methods

2.1. Materials
Bovine serum albumin (BSA, Mw = 67kDa), sodium chloride (NaCl), potassium chloride (KCl), potassium phosphate monobasic (KH2PO4) and sodium dihydrogen phosphate (Na2HPO4) were given by Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). All chemicals were used without further purification.

Flat sheet membrane polyacrylonitrile (PAN) with pore size of 0.1 μm (Ande Membrane Separation Technology and Engineering (Beijing, China)) was used as filtration membrane. Before each experiment, PAN membrane was soaked in DI-water for 12 h to remove protective agent glycerin.

2.2. Feed solutions
1g BSA, 8g NaCl, 0.2g KCl, 0.27g KH2PO4 and 1.42g Na2HPO4 were dissolved in DI-water to prepare 1g/L PBS-BSA solution. The certain BSA concentrations of diluted PBS solution was employed to prepare desired solution.

2.3. Experimental equipment and operating conditions
The microfiltration experiment was performed at different operation conditions (concentration, flux and stirring speed) with a laboratory scale dead-end filtration system composed of a filtration cell with effective membrane area of 38 cm² at 25 °C (figure 1).
2.4. Analytical methods
During the constant flux operation, the equation of describing the pressure change is,

\[ \frac{\text{TMP}}{\text{TMP}_0} = \frac{RA_0}{R_0A} \]  

(1)

where TMP is the transmembrane pressure (kPa), TMP0 is the initial transmembrane pressure (kPa), R is the total resistance (m-1), R0 is the initial resistance (m-1), A is the available effective membrane area (m2), and A0 is the initial membrane area (m2).

As the membrane separation process goes along, pore blocking will lead to a reduction in A (equation (2)), and the membrane resistance increased with the cake formation (equation (3)), and equations are as follows [10]:

\[ \frac{A}{A_0} = e^{-K_iV} \]  

(2)

\[ \frac{R}{R_0} = 1 + K_cJ_0V \]  

(3)

where V is the accumulated volume of permeate (m3), Ki is the intermediate blocking constant (m-1), Kc is the cake filtration constant (s·m-2), and J0 is the membrane flux (m3·m-2·s-1).

A will not decrease to zero all the time, it does not occur simultaneously with the change of the membrane resistance [11]. The critical value k is added to the A to make A’=kA0 after fouling, and the accumulated volume of the permeate in the constant flux process V=J0At. Substitute the equation (2) (3) and the above into the equation (1).

\[ \text{TMP} = \frac{\left(1 + K_cA_0J_0t\right)\text{TMP}_0}{(1 - k)e^{-K_cJ_0At} + k} \]  

(4)

This study uses this equation (4) to describe the constant current fouling process and verify its reliability.

3. Results & Discussion

3.1. Effect of operating conditions
The fouling behaviors of the BSA solution were analyzed in the MBR process under the different operating conditions (BSA concentration, flux and stirring speed). The predictions of the proposed model had a good agreement with experimental data under these different operating conditions (figure 2). Obviously, the variation of TMP for BSA solution increased non-linearly with filtration time because the adsorption between BSA and the membrane is significant in the initial filtration stage. Figure 2(a) showed that the TMP of BSA solution with different concentrations of 20, 30 and 40 mg/L increased to 19, 26 and 28 kPa respectively when the filtration process finished, while most of the increase in TMP occurred in the initial stage. Figure 2(b) exhibited that the influence of the flux on the membrane fouling. Compared to the impact of concentration on the membrane fouling, it is evident that the flux is more likely to cause membrane fouling than that of concentration. Figure 2(c) indicated that the increase of the stirring speed has an effect on the membrane fouling but it has only a minor impact on the actual process by changing the stirring speed.

3.2. Resistance and Available membrane area ratio analysis
Figure 3. The membrane resistance ($R_m$), cake resistance ($R_c$) and pore blocking resistance ($R_i$) under different operation conditions of different concentrations (a1) and fluxes (a2) and stirring speeds (a3) using 0.1μm PAN membrane. The variation of the available effective membrane area ratio ($A/A_0$) as a function of time under different operation condition of different concentrations (b1) and fluxes (b2) and stirring speeds (b3) using 0.1μm PAN membrane.

The cake resistance ($R_c$) and intermediate pore blocking resistance ($R_i$) were calculated and their distributions were shown in figure 3. It is obviously that $R_i$ increased with the increase of BSA concentration, while there was no obvious change for $R_c$ between different BSA concentrations at the same filtration time (figure 3(a1)). Meanwhile, this phenomenon was also observed during the BSA fouling process with different fluxes at a fixed BSA concentration of 20 mg/L and a fixed stirring speed of 200 rpm (figure 3(a2)). However, $R_c$ decreased with the growth of stirring speed at the same filtration.
time while $R_i$ had a little change at different stirring speeds (figure 3(a3)). Both high BSA concentration and high flux can enhance the mass transfer process which forces much more particles to deposit on the membrane surface [12]. Thus, $R_i$ increased with the increase of BSA concentration or filtration flux. Meanwhile, cake was formed on the membrane surface and high shear stress caused by high stirring speed could remove the loose cake easily. Therefore, $R_c$ decreased with the increase of stirring speed.

The available membrane area ratio ($A/A_0$) was analysed under different operation conditions (figure 3). It is obviously $A/A_0$ is decreased with increase of the BSA concentration because higher concentration BSA solutions can rise the mass transfer coefficient, causing more serious pore blocking and lower $A/A_0$ (figure 3(b1)). Meanwhile, $A/A_0$ is decreased with increase of the flux because a higher filtration flux will have a higher TMP in the initial stage, thereby enhancing the mass transfer process and making blocking faster (figure 3(b2)) [12]. However, the increase of the stirring speed had little effect on the stable A because cake could protect the membrane surface from the impact of the shear stress and then it has little effect on the pore of the membrane surface.

4. Conclusions

In this study, it is meaningful to investigate the membrane fouling behaviors (the variation of $R_c$, $R_i$ and $A/A_0$) effected by different operation conditions (BSA concentration, flux and stirring speed). The model in this paper was established in good agreement with the experimental data, which indicates that BSA in MBR can be quantitatively described by the intermediate pore blocking-cake filtration. The results showed that the flux has a more significant effect on the transmembrane pressure (TMP), then is the concentration. The effect of stirring speed on the TMP is minimal. Meanwhile, $R_c$ decreased with the increase of stirring speed, and the $A/A_0$ decreased with the increase of BSA concentration and the flux.

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