Study on the model binary mixtures for actual EPS extracted from the activated sludge in MBR on membrane fouling

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Abstract. In order to find a model solution to simulate actual extracellular polymeric substances (EPS) solution in terms of filterability behavior, a series of experiments were conducted in a dead-end unstirred cell with 0.1 μm polyvinylidene fluoride membranes using single/ binary mixtures consisting of sodium alginate (SA), bovine serum albumin (BSA) and humic acid (HA). It can obtain that the presence of BSA and SA is a necessary condition for model the filtration behavior of the actual EPS solution. Meanwhile, compared the actual EPS solution with binary mixtures model EPS solution can find that BSA/SA=140/58.3 and SA/HA=107/28.5 can exhibit the similar filtration behavior as actual EPS, while BSA/HA are far from that of actual EPS solution. The suitable type and combination of simulated solution were determined to improve the consistency with EPS solution in actual MBR system.

1. Introduction

The membrane bioreactor (MBR) technology effectively realizes the coupling of membrane technology and biotechnology, which has shown a good application prospect in the field of industrial wastewater treatment and food industry due to the advantages of good effluent quality, small occupation area and simple operation [1,2]. However, the membrane fouling will occur in the long-term operation of MBR, and restrict significantly its wide application in industry [3,4]. Therefore, there will be a formidable challenge to alleviate membrane fouling in MBR process. Consequently, the determination of the main foulants causing membrane fouling and explore fouling regularity are significant for the real MBR system [5].

Moreover, a series of the model EPS solutions (sodium alginate (SA) [6], bovine serum albumin(BSA) [7] and humic acid (HA) [8] and their compounds) were employed to replace the actual EPS solutions to investigate fouling behaviors and identify fouling mechanisms due to the variability in extracting mass, composition and concentration information for real MBR. For example, Jiang et al [6] used Sodium alginate (SA) to replace EPS solutions to investigate membrane fouling. Additionally, the EPS model solution has also been shifted from a single substance to binary mixture. Ye et al [9] used a binary mixture (SA and BSA) to simulate the actual EPS solution. K.S. Katsoufidou et al [10]
concluded the fouling behavior of binary mixtures (SA and HA) is quite like that of polysaccharides alone. However, an appropriate substitute reminds further to explore membrane fouling behaviors and fouling mechanisms for the actual EPS solution in real MBR system.

The objective of this study aims to compare the difference between the model EPS solution and the actual EPS solution and select the appropriate types and combinations of simulated solutions to improve the consistency with the actual EPS solution. In the first part, sodium alginate (SA), bovine serum albumin (BSA) and humic acid (HA) were respectively employed to simulate polysaccharides, protein and humic substances of the actual EPS solution because many extracellular polymers were extracted from activated sludge in MBR is difficult. However, an appropriate substitute reminds further to explore membrane fouling behaviors and fouling mechanisms for the actual EPS solution in real MBR system.

2. Materials and methods

2.1. Materials
The flat sheet PVDF membrane with pore size of 0.1 μm was purchase in Ande Membrane Separation Technology and Engineering (Beijing, China). The protective agent glycerin on the membrane surface was removed by soaking in deionized (DI) water at 4 ℃ for 8-10h before experiment. In order to reduce the systematic error, the membrane with similar pure water flux (<10%) was selected for filtration experiment and fouling experiment.

![Figure 1](image1.png)

Figure 1. (a) Schematic of EPSs structure, (b) Particle diameter distribution of BSA, SA and HA solution.

The actual EPS solution was extracted by formaldehyde-sodium hydroxide method and its composition (protein, polysaccharide, humus) (figure 1 (a) and (b)) was determined. A series of EPS simulated solutions (BSA, SA, two kinds of humic acid) were prepared according to the content of various components in the actual EPS solution, which were used as experimental material solution. Three model solutions were prepared to replace the actual EPS solution as following: Sodium alginate (SA) solutions were obtained by dissolving sodium alginate powder(supplied by Sinopharm (China)) in DI-water and placing at 4 ℃ for 12 hour. Bovine serum albumin (BSA) solutions were prepared by dissolving BSA powder (supplied by Fuchen (China)) in phosphate buffer saline (PBS) solution (8.0 g NaCl, 0.2 g KCl, 0.27 g KH2PO4 and 1.42 g Na2HPO4 in 1 L DI-water, pH=7.4) to obtain 1 g/L homogeneous BSA-PBS solution. Humic acid (HA) (purchased from Beijing Chemical Reagent Co. (China)). was dissolved in pure water at 4 ℃.

2.2. Experimental Equipment
The pure water flux was measured with DI-water under 0.1 MPa, and then feed solution (the EPS solution and the model solution) was used in in a dead-end filtration cell with an effective membrane area of 28.0 cm2 and a working volume of 600 ml (figure 2). The feed solution was stirred with a magnetic rotator. The stirring speed of the magnetic rotator was 180 rpm and temperature of 20 ± 1 ℃
in all experiments. The permeate weight was recorded with an electronic balance every 30 s.

![Figure 2. Schematic diagram of filtration experimental setup for dead-end mode](image)

3. Results & Discussion

3.1. Roles of different substances in the binary mixtures

In order to compare the filterability between different actual and model EPS solutions, the arbitrary pair of the binary mixtures consisting of SA, BSA and HA were selected as shown in Table 1.

| NO | SA     | BSA   | BSA   | HA     | SA     | HA     |
|----|--------|-------|-------|--------|--------|--------|
| 1  | 10.07(0.1) | 140.4(1.0) | 140.4(1.0) | 5.7(0.5) | 10.07(0.1) | 5.7(0.5) |
| 2  | 50.35(0.5) | 140.4(1.0) | 140.4(1.0) | 28.5(2.5) | 10.07(0.1) | 28.5(2.5) |
| 3  | 100.7(1.0) | 140.4(1.0) | 140.4(1.0) | 57.0(5.0) | 10.07(0.1) | 57.0(5.0) |
| 4  | 10.07(0.1) | 351.0(2.5) | 351.0(2.5) | 5.70(0.5) | 50.35(0.5) | 5.7(0.5) |
| 5  | 50.35(0.5) | 351.0(2.5) | 351.0(2.5) | 28.5(2.5) | 50.35(0.5) | 28.5(2.5) |
| 6  | 100.7(1.0) | 351.0(2.5) | 351.0(2.5) | 57.0(5.0) | 50.35(0.5) | 57.0(5.0) |
| 7  | 10.07(0.1) | 702.0(5.0) | 702.0(5.0) | 5.7(0.5) | 100.7(1.0) | 5.7(0.5) |
| 8  | 50.35(0.5) | 702.0(5.0) | 702.0(5.0) | 28.5(2.5) | 100.7(1.0) | 28.5(2.5) |
| 9  | 100.7(1.0) | 702.0(5.0) | 702.0(5.0) | 57.0(5.0) | 100.7(1.0) | 57.0(5.0) |

3.2. Flux decline for the actual EPS solution with the model EPS solution

The permeate fluxes decline of the actual EPS solution, BSA, SA, HA (figure 3) and the binary mixtures of BSA/SA, BSA/HA and SA/HA with time (figure 4 (a), (b) and (c)). The fluxes of the mixtures vary with time can be divided into two stages: (1) initial flux decline rapidly due to pore blocking in pores and rapid build-up of the cake at the membrane surface [11], and (2) flux decline slowly due to the cake formation on the membrane surface [12]. For example, in the range of 0 s to 300 s as presented in figure 4, the fluxes of BSA/SA and SA/HA show faster decline trend (the average decline rate of 9 experiments is 28.2% or 31.3%, respectively) than that of BSA/HA (16.3%).

3.3. Compared the actual EPS solution with single model EPS solution (BSA, SA and HA)

According to the permeate fluxes decline of the actual EPS solution, BSA, SA and HA (Figure 3) can observe that BSA solution and SA solution are closer to the results of actual EPS solution, while HA solution deviates from that of actual EPS solution. It can be explained that the addition of BSA or SA to any single solute solution will result in the decrease of membrane flux and the increase of membrane resistance. The increase of concentration of BSA or SA will aggravate the phenomenon of
concentration polarization and the blockage pore, and accelerate the membrane fouling [13]. Therefore, the presence of BSA and SA is a necessary condition for model the filtration behavior of the actual EPS solution.

Figure 3. The variation of the permeate flux as function of filtration time for the actual EPS solution with single model EPS solution (BSA, SA and HA).

3.4. Compared the actual EPS solution with binary mixtures model EPS solution

If comparing the composition of BSA/HA with that of the others (BSA/SA and SA/HA), it can observe that the fluxes curves for the whole series of BSA/HA are far from that of actual EPS solution (figure 4). This means that BSA/HA combination cannot exhibit the similar filtration behavior as actual EPS solution due to absence of SA in BSA/HA. In another word, SA has a more significant impact on the permeate fluxes. In addition, when the SA content was changed from 2.23 % (SA: BSA=10.7:351), 10.14 % (SA: BSA=50.35:351) to 21.54% (SA: BSA=107:351), the fluxes decreased from 34.6 %, 44.9 % to 51.1 %. Therefore, the presence of SA is a necessary condition for model the filtration behavior of the actual EPS solution [14]. Contrary to the above, some fluxes curves, for example, one (BSA/SA=351/50.35) in subsequent stage (figure 4 (a)) and another (SA/HA=50.35/57) in initial stage (figure 4 (b)) is close to that of the actual EPS solution. This provides the possibility to model the filtration behavior of the actual EPS solution by changing the substances and its content in the mixtures.
Figure 4. The variation of the permeate flux as function of filtration time for (a) the actual EPS solution with binary mixtures of BSA/SA, (b) the actual EPS solution with binary mixtures of SA/HA, (c) the actual EPS solution with binary mixtures of BSA/HA.

4. Conclusions
The objective of study aims to compare the difference between the model EPS solution and the actual EPS solution and select the appropriate types and combinations of simulated solutions to improve the consistency with the actual EPS solution. The presence of BSA and SA is a necessary condition for model the filtration behavior of the actual EPS solution. Meanwhile, comparing the actual EPS solution with binary mixtures model EPS solution can find that BSA/SA=140/58.3 and SA/HA=107/28.5 can exhibit the similar filtration behavior as actual EPS, while BSA/HA are far from that of actual EPS.

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