Membrane fouling of actual extracellular polymeric substances

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Abstract. Extracellular polymeric substances (EPSs) in activated sludge suspensions are the key substances leading to the membrane fouling. In order to understand the effect of EPSs on the membrane fouling, the actual EPSs solution extracted from activated sludge suspensions was used as the feed solution to conduct dead-end microfiltration experiment under different pressures by using different membranes. The flux ($J$), fouling resistances ($R_m$, $R_p$, $R_c$ and $R_{total}$) and the available membrane area ($A/A_0$) were used to describe the membrane fouling. The results showed that with the increase of pressure, $J$ and $R_{total}$ increased. $R_p$ firstly increased and then kept constant, $R_c$ always increased and became the dominant resistance. $A/A_0$ decreased from 1 to a constant. $R_c$ plays a key role on $R_{total}$ for different membranes under the same pressure. The sequence of the steady available membrane area ($A_{steady}/A_0$) for different pressures was: 63.0% (0.05MPa) > 56.5% (0.08MPa) > 53.6% (0.10MPa), and that for different
membranes was: 80.1% (0.2μm PES) > 79.9% (0.1μm PES) > 78.4% (0.1μm PAN) > 53.6% (0.1μm PVDF).

1. Introduction
Membrane bioreactor (MBR) technology is a combination of activated sludge process and membrane filtration technology [1,2], which is widely used in sewage treatment process because of its high separation efficiency and low price [3,4]. However, the membrane fouling is still unavoidable in MBR, and it will decrease production efficiency, increase operation cost and limit the application of MBR in various sewage treatment [5,6]. The membrane fouling is caused by the interaction between activated sludge and the membrane [7]. And the extracellular polymeric substances (EPSs) play a key role in the membrane fouling process [8]. Therefore, it is necessary to explore the influence of EPSs on the membrane fouling. For example, Zhang et al. [9] found that the EPSs were very difficult to degrade and polysaccharide was a key component in the membrane fouling. Wang et al. [10] found that lower pH and in the presence of calcium may induce the formation of an elastic and viscous EPSs layer fouling the membrane. Ou et al. [11] studied the characteristics and fouling mechanisms of extracellular polymeric substances, and found that the main resistance was loose cake layer. Liu et al. [12] studied the effect of different operating conditions on the filtration behavior of actual EPSs. Ding et al. [13] studied the fouling properties of soluble EPSs, loosely bound EPSs and tightly bound EPSs in the mesophilic anaerobic membrane bioreactor. However, the role of actual EPSs in the membrane fouling is still not well understood and has not been uniformly reported. It is therefore necessary to continue to explore the impact of actual EPSs on the membrane fouling.

In this study, the actual EPSs solution was extracted from activated sludge suspensions as the feed solution. The flux ($J$), fouling resistances ($R_m$, $R_p$, $R_c$ and $R_{total}$) and the available membrane area ($A/A_0$) were explored under different pressures (0.05MPa, 0.08MPa, 0.1MPa) by using different microfiltration membranes (0.1μm polyvinylidene fluoride (PVDF)/polyacrylonitrile (PAN)/polyether sulfone (PES) and 0.2μm PES) and the combined cake-complete model.

2. Materials and Methods

2.1. Material
The experimental membranes (0.1μm PVDF, 0.1μm PAN, 0.1μm PES and 0.2μm PES membranes) were purchased from ANDE Membrane Separation Technology Engineering Company, Beijing Co., Ltd. Before each experiment, the membrane should be soaked in DI-water at 4℃ for at least 12 h to remove the glycerol from the membrane surface.

2.2. Experiment
The actual EPSs solution was extracted by the formaldehyde-NaOH extraction method [14]. And the compositions of EPSs extracted from activated sludge suspensions were shown in Table 1.

| Substance       | Polysaccharide | Protein | Humus substance | DNA | EPS       |
|-----------------|----------------|---------|-----------------|-----|-----------|
| Concentration (mg/L) | 93.6±8.7       | 103.4±1 | 9.2±3.8         | 0   | 206.3±13.5|

The experiments were carried out in constant pressure dead-end filtration cell [12] and the actual EPSs solution as the feed solution. The operating conditions of different pressures included 0.05MPa, 0.08MPa and 0.1MPa. All the experiments were operated at 25℃.

2.3. Analysis method
To analyze the fouling behaviors ($J$, $R_m$, $R_p$, $R_{total}$ and $A/A_0$), the published equation (1), (2), (3) and (4) were used as follows [15]:
\[ \frac{R_0}{R} = (1 + 2KcJ_0^2t)^{-1/2} \]  
\[ \frac{A}{A_0} = (1 - K)\exp\left(\frac{-Kb}{KcJ_0^2}\left((1 + 2KcJ_0^2t)^{1/2} - 1\right)\right) + K \]  
\[ J = \frac{J_0(1-K)\exp\left(\frac{-Kb}{KcJ_0^2}\left((1 + 2KcJ_0^2t)^{1/2} - 1\right)\right) + K}{(1 + 2KcJ_0^2t)^{1/2}} \]  
\[ R_{\text{total}} = R_p + R = R_p + R_m + R_c \]  

where $R_0$ is the initial resistance to filtration (m$^{-1}$), $R$ is the sum of the membrane resistance and cake resistance (m$^{-1}$), $R_m$ is the membrane resistance (m$^{-1}$), $R_c$ is the cake resistance (m$^{-1}$), $R_p$ is the complete blocking resistance (m$^{-1}$), $R_{\text{total}}$ is the total resistance (m$^{-1}$), $J_0$ is the initial flux (m/s), $A$ is available membrane frontal area (m$^2$), $A_0$ is initial membrane frontal area (m$^2$), $K_b$, $K_c$ and $K$ are constants.

3. Results & Discussion
3.1. Different pressure
The fouling behaviors \((J, R_c, R_m, R_p, R_{total} and A/A_0)\) under different pressures (0.05, 0.08 and 0.1MPa) using 0.1μm PVDF membrane were shown in Fig. 1. The model predictions were in good agreement with the experimental data, and \(J\) increased with the increasing of the pressure (Fig. 1(a)). Then, \(R_{total}\) increased with the increasing of the pressure (Fig. 1(b)), and \(R_c\) was the dominant resistance. It could be explained that higher \(J\) makes more particles accumulate on the membrane surface, and the cake forms at a faster rate [16]. Meanwhile, due to the cake is compressible, it became denser under higher pressure [17]. \(A/A_0\) did not decrease continuously, but tended to be stable value after a certain period of time (Fig. 1(c)), and the sequence of the steady available membrane area \((A_{steady}/A_0)\) for different pressures was: 63.0% (0.05MPa) > 56.5% (0.08MPa) > 53.6% (0.10MPa). The increased of pressure reduced \(A_{steady}/A_0\), this is because the increased pressure provides a higher driving force for the particles to pass through the cake layer and reach the membrane surface, thus blocking more pores [14].

3.2. Different membrane
The fouling behaviors \((J, R_c, R_m, R_p, R_{total} and A/A_0)\) under 0.1MPa using different membranes (0.1 μm PES, 0.1 μm PVDF, 0.1 μm PAN and 0.2 μm PES) were shown in Fig. 2. \(J\) of 0.1μm PVDF membrane was higher than that of the others, and 0.1μm PES membrane had the smallest \(J\) (Fig. 2(a)). Compared with the resistance of different membranes, 0.1μm PVDF membrane had the least \(R_m\) while its \(R_p\) is the greatest (Fig. 2(b)). \(R_c\) of 0.1μm PES and 0.2μm PES membrane was significantly higher than other membranes. This is because the PES membrane has relatively high roughness and hydrophobicity [18]. It could be seen that both \(R_c\) and \(R_p\) exist at the same time, and \(R_c\) was always obviously greater than \(R_p\). Consequently, cake filtration was the main fouling mechanism in different membranes. The sequence of the steady available membrane area \((A_{steady}/A_0)\) for these membranes in Fig. 2(c) was: 80.1% (PES 0.2μm) > 79.9% (PES 0.1μm) > 78.4% (PAN 0.1μm) > 53.6% (PVDF 0.1μm). However, \(A_{steady}/A_0\) of 0.1μm PVDF membrane was the least, but \(J\) is the highest. Therefore, \(R_c\) plays a key role on \(R_{total}\) for different membranes by using actual EPS solution under the same pressure as reported by other researcher [11].
4. Conclusions
In this study, the flux \((J)\), fouling resistance \((R_m, R_p, R_c, \text{ and } R_{total})\) and available membrane area \((A/A_0)\) were discussed in the dead-end microfiltration of actual EPSs solution. The results showed that the model predictions had good consistency with the experimental data. With the increase of pressure, \(J\) and \(R_{total}\) increased while \(A/A_0\) decreased. However, \(A/A_0\) decreased from 1 to a constant with the filtration time. For different membranes under the same pressure, \(R_c\) was a key role and the main fouling mechanism was the cake filtration.

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