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Experimental study of filterability behavior of model extracellular polymeric substance solutions in dead-end membrane filtration

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ABSTRACT

A series of model extracellular polymeric substance (EPS) solutions was prepared by using sodium alginate, humic acid and some proteins on the basis of the components of actual EPS extracted from sludge for laboratory-scale SBR by the formaldehyde–NaOH method. The dead-end model filter of these solutions was carried out with 0.1 μm PVDF MF membrane under a transmembrane pressure of 0.1 MPa and the filterability behaviors of these solutions were also investigated. The experimental results showed that the filterability behaviors of BSA, β-lactoglobulin and lysozyme model solutions with five times the protein concentration in the actual EPS were similar with that of the actual EPS solution; in addition, the addition of sodium alginate and humic acid enhanced the rejection of proteins, and the values of α_c of model solutions increased with the addition of sodium alginate or humic acid, and especially the values of α_c of the model solution greatly increased with the addition of humic acid, and the presence of protein in the mixed components model solutions caused the decrease of the α_c values of sodium alginate.

1. Introduction

It is known that the major obstacle of MBR is membrane fouling, which leads to a decline in membrane flux and shortens the longevity of membrane module service in MBR. Therefore, it is very important to ascertain the main substance that causes membrane fouling in MBR and to investigate its filterability behavior.

Many researches take the macromolecular components, known as extracellular polymeric substances (EPS), that are composed of polysaccharide, protein, humic substances, uronic acid and deoxyribonucleic acids (DNA) [1–6], as a major fouling component [7–10], and the correlation between EPS and membrane fouling is investigated deeply [11–15]. For instance, the impact of operating conditions on the filterability of sludge has been investigated [11–13]; moreover, the contribution of different components in EPS to membrane fouling is another attractive branch in MBR research field [16–22]. Houghton [16] insists that proteins and polysaccharides play an important role in sludge filterability and the polysaccharides had the greatest influence on the operation of MBR. Lesjean [17] found a correlation between the filtration resistance and polysaccharide concentration. Tarnacki [18] believes that the permeate flux is inversely related to the polysaccharide concentration in activated sludge. Because the extracted EPS has variability in composition, concentration, and complexity in real MBR systems, many researchers use alginate [19,20], dextran [21], bovine serum albumin (BSA) [19], β-lactoglobulin [22], lysozyme [21], myoglobin [21], cytochrome *C* [21] and BSA + alginate [19] to model the actual EPS solution in MBR. However, the present researches cannot provide an alternative between the model solution and actual EPS solution, therefore, how to choose the proper model solution to exactly describe the filterability behaviors of the actual EPS solution is very significant.

The aim of this paper is to compare the different model EPS solutions (sodium alginate, BSA, β-lactoglobulin, lysozyme, humic acid and their combination) with the actual EPS solution in its filterability behaviors (the cumulative filtrate volume (V_{cumu}), observed rejection of the membrane (R_{obs}) and specific cake resistance (α_c)) by using 0.1 μm PVDF membranes under 0.1 MPa TMP in order to get a model EPS solution that can replace the actual EPS solution in filterability behavior.

2. Material and methods

2.1. Experimental equipment and operating conditions

In this paper, the EPS were extracted from two activated sludge samples respectively produced by two sequencing batch reactors (SBRs) (Fig. 1a) in our laboratory. One treated a synthetic wastewater comprising of glucose, starch soluble and trace nutrients. This SBR was called SBR1. The other treated domestic wastewater, and was called SBR2.

The components and concentrations of the synthetic wastewater are glucose 278 mg L^{-1}, starch soluble 278 mg L^{-1}, peptone 28 mg L^{-1},

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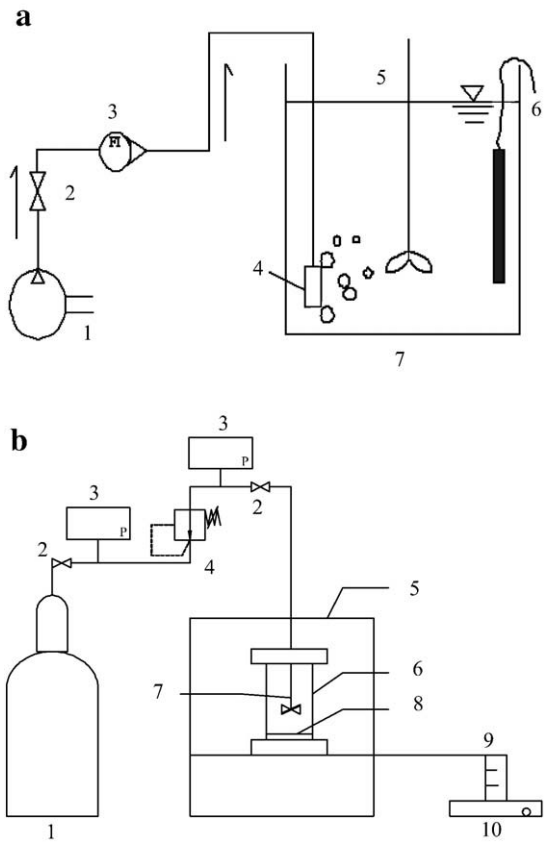

Fig. 1. A diagram of an SBR system (a) and a diagram of a dead-end filtration system (b). (a): 1. air compressor, 2. valve, 3. rotameter, 4. air blower, 5. stirrer, 6. temperature controller, 7. bioreactor; (b): 1. compressed air, 2. valve, 3. manometer, 4. manometer pressure reducer, 5. temperature humidity controller, 6. UF cell, 7. stirring rod, 8. membrane, 9. measuring cylinder, 10. electronic scale.

NH_4Cl 297 mg L^{-1}, $NaHCO_3$ 111 mg L^{-1}, $CaC1_2$ 6 mg L^{-1}, $MgSO_4 \cdot 7H_2O$ 66 mg L^{-1}, $MnSO_4 \cdot 7H_2O$ 6 mg L^{-1}, $FeSO_4$ 0.3 mg L^{-1}, and KH_2PO_4 52.8 mg L^{-1}. The COD, NH_3–N, and pH are 350–500 mg L^{-1}, 65–80 mg L^{-1} and 7.0 respectively. The COD, NH_3–N and pH of the domestic wastewater are 206–285 mg L^{-1}, 49–63 mg L^{-1} and 7.5 respectively.

The working volume of SBR1 was 17 L and SBR2 had a working volume of 10 L. They were run at mixed liquor suspended solids (MLSS) of 3000 mg L^{-1}, an organic loading of 0.25 kg COD/(kg MLSS d), a hydraulic retention time (HRT) of 13 h, a sludge retention time (SRT) of 30 days and a dissolved oxygen concentration (DO) in a bioreactor of 5.3 mg L^{-1}. The temperature was maintained at 25 °C with temperature controllers. The pH was 7.0~8.0. Both of them were operated at 6 h of nitrification and 2 h of denitrification per day. The COD and NH_3–N removal efficiencies of SBR1 were over 90% and 99% respectively. The COD and NH_3–N removal efficiencies of SBR2 were over 91% and 98% respectively.

The dead-end filtration experiments were performed using the setup represented in Fig. 1b.

2.2. Membranes

Based on the membranes commonly used in MBR [13,23–26] and in the research of membrane fouling mechanism of EPS [18–21,27], a 0.1 μm PVDF membrane was selected in this paper, which was purchased from Ande Membrane Separation Technology and Engineering (Beijing, China).

2.3. Extraction of EPS

The EPS quantification strongly depends upon the extraction methods [28], so the extraction method should be chosen carefully. Comparing with formaldehyde–ultrasonication, EDTA, cation exchange resin and formaldehyde, Hong [29] reported that the formaldehyde–NaOH process extracted the highest amounts of EPS from all the sludges, and the formaldehyde could fix the cell and prevent cell lysis efficiently. Thus, the formaldehyde–NaOH extraction method was chosen in this paper. The sampled activated sludge was settled for 1.5 h and then the supernatant was decanted. The thickened sludge was centrifuged at 2000*g* for 15 min at 4 °C. The sludge pellets were resuspended to their original volume using a buffer consisting of 2 mmol · L^{-1} Na_3PO_4, 4 mmol · L^{-1} NaH_2PO_4, 9 mmol · L^{-1} NaCl and 1 mmol · L^{-1} KCl at pH = 7. EPS extraction was performed as follows: formaldehyde was added to the above suspension for 1 h at 4 °C, and then added 1 N NaOH for 3 h at 4 °C. The extracted EPS were harvested by centrifugation of a sample of the formaldehyde/NaOH/sludge suspension at 20,000*g* for 20 min, followed by 0.2 μm membrane filtration at 25 °C. Extractant residues in the solution were removed by the dialysis membrane filtration (3500 Da; Pierce, USA) in the subsequent treatment [1,29]. The comparisons of EPS compositions extracted from the activated sludge from SBRs by the formaldehyde–NaOH are shown in Table 1.

As shown in Table 1, for the two extracted EPS solutions, the quantity of DNA was small, which indicated that the cells were not lysed during the extraction process. Their TOC values were almost equal to the sum of the concentrations of protein, polysaccharide and humic substance and this confirmed that these substances are the major composition of EPS, and on the other hand, it indicated that the amount of EPS could be obtained by measuring the TOC value of the EPS solution. The quantities of the humic substance in EPS from sludge 1 were small because the synthetic wastewater did not include the humic substance. The quantity of protein in the EPS from sludge 2 was more than that of polysaccharides, which is in accord with the results by Fang and Veiga [30,31]. In this experiment, the extracted EPS solution from the activated sludge 1 was chosen as the actual EPS solution.

2.4. Model EPS solutions

In this paper, sodium alginate (Sinopharm Chemical Reagent Co., Ltd., China), BSA (Beijing Shuangxuan Microbe Culture Products Factory, China), β-lactoglobulin (Sigma, from bovine milk, approx. 90%), lysozyme (Sigma, Solarbio) and humic acid (Beijing Chemical Reagent Co., China) were chosen to model actual EPS solutions on the basis of the experimental data of extracted EPS. The components of model EPS were the same as or five times the concentration of protein, polysaccharide and humic acid in the EPS respectively, and the results were shown in Table 2.

Table 1
Compositions of EPS extracted from activated sludge (mg L^{-1}).

Activated sludge	Polysaccharide	Protein	Humic substance	DNA	EPS	TOC
Sludge 1 (SBR1)	93.6 ± 8.7	103.4 ± 1	9.2 ± 3.8	0	206.3 ± 13.5	209.5 ± 10.2
Sludge 2 (SBR2)	60.7 ± 4.2	157.3 ± 2.4	22.4 ± 1.4	0	240.3 ± 5.1	263.5 ± 5.3

Note: mean value ($n = 2$) ± S.D.