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Antifouling by pre-deposited Al hydrolytic flocs on ultrafiltration membrane in the presence of humic acid and bovine serum albumin

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ABSTRACT

Pre-deposition technology is a promising method for alleviating membrane fouling, and in situ hydrolytic flocs have strong adsorption ability. In comparison with iron salts, less corrosiveness is induced by aluminum salts. Here, flocs formed by aluminum salts were pre-deposited onto the surface of an ultrafiltration (UF) membrane, aimed at investigating the antifouling performance with humic acid (HA) or bovine serum albumin (BSA). The results showed that Al-based flocs were well distributed onto the membrane surface, and a relatively dense and homogeneous deposition layer was formed. Both HA and BSA could largely be adsorbed/rejected by the pre-deposited layer during filtration. In comparison to results for solution pH of 8.0, the floc layer was much denser with a larger surface specific area and smaller average pore diameter at pH 6.0. Due to the existence of Al_{13} species, a more positively charged floc layer occurred at lower pH values, leading to stronger adsorption abilities toward the negatively charged HA and BSA molecules. The floc layer significantly reduced the possibility of HA and BSA molecules reaching the UF membrane, which helped alleviate membrane fouling under lower pH conditions. Furthermore, the results for effluent with pH between 6.0 and 8.0 showed that the removal efficiency of HA molecules with small molecular weight (< 3 kDa) was also higher, especially at pH 6.0.

1. Introduction

Ultrafiltration (UF) membranes have been applied in water treatment worldwide, due to the better effluent quality obtained even with varying feed-water properties. Membrane fouling is, however, inevitable because the membrane pores will gradually adsorb and be blocked by particles, followed by cake layer formation during filtration [1–4]. Larger molecular weight (MW) organic matter, such as humic substances and proteins, always tend to induce serious UF membrane fouling to some extent, owing to the pore blocking and cake layer formation [5–9].

To alleviate membrane fouling effectively, three membrane processes combined with adsorption technology have been investigated to remove pollutants: (1) pre-adsorption process, in which a sedimentation tank is required after adsorption and the adsorbents are deposited before the membrane system; (2) direct-filtration process, in which raw water is flowed into the membrane tank directly after adsorption; (3) pre-deposition process, in which adsorbent layers are pre-deposited onto the membrane surface before filtration [10,11].

The first two processes have been investigated in detail, and have already been applied in many water plants. However, the last process has only been tested in the laboratory with flat sheet microfiltration/ultrafiltration membranes [12,13]. In comparison with the pre-adsorption process, the pre-deposition process further reduces land use, owing to the lack of a need for sedimentation. Additionally, serious membrane fouling is often caused when using the pre-adsorption process because of the higher chance of membrane pore blocking after the sedimentation process [14]. For the direct-filtration process, larger sludge discharge always occurs due to the lack of a sedimentation tank. Compared with the other two processes, the pre-deposition technology has demonstrated much better removal of organic compounds [11,15].

Up to now, various kinds of adsorption materials have been coated or layered onto the surface of membranes to investigate their adsorption/rejection properties with various target pollutants, and less membrane fouling was indeed observed. However, the use of powdered activated carbon (PAC) alone could cause severe membrane damage by shearing the membrane surface, especially after long running time [16], while the high cost of other adsorbents prohibited their use in actual operations, for example carbon nanotubes (CNTs) [13], heated iron oxide particles (HIOPs) [17], heated aluminum oxide particles (HAOPs) [18], nanoscale zerovalent iron (NZVI) [19], and so on. In addition, some adsorbents were found to exhibit preferential removal ability

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toward specific pollutants, while performing worse on removal of other types. It has been demonstrated that PAC preferentially adsorbs many non-fouling natural organic matter (NOM) molecules during filtration [18].

It is known that aluminum salts and iron salts have been successfully used in drinking water and wastewater treatment, and their favorable performance is due to the strong adsorption capability of their flocs [20–22]. For the combined process of coagulation and UF membrane, Al-based and Fe-based flocs have been shown to play an important role in alleviating membrane fouling [7,14,22]. In comparison to iron salts, however, aluminum salts have lower corrosiveness in water treatment [22,23]. In addition, humic substances and proteins are formed by the decomposition of plants/animals and are commonly present in natural waters [7,24,25]. The concentration of humic substances and proteins are in the range of a few mg/L to a few hundred mg/L C [26,27]. Owing to their large molecular weight distributions and physical properties, severe UF membrane fouling is inevitably induced [19,28,29]. Herein, this study focuses on an UF membrane with pre-deposited Al-based flocs, aiming to understand the characteristics of membrane fouling caused by humic substances and proteins. Furthermore, some influencing factors were also investigated, such as dosage and solution pH, and the membrane fouling alleviation mechanisms were elucidated finally.

2. Materials and methods

2.1. Chemical reagents

All chemicals used were analytical reagent grade unless otherwise specified, and the stock solutions were prepared using deionized (DI) water (Millipore, Milli-Q). Humic acid sodium salt (HA, Aldrich, USA) is typically used to represent HS [6,19], and was stored in the dark at 4 °C (10 g/L). Bovine serum albumin (BSA, Sinopharm Chemical Reagent, Co., Ltd, China; 67 kDa) is usually used as a representative of protein [30]. It was dissolved in a phosphate-buffered salt solution (PBS, composed of 0.03 M $Na_2HPO_4 \cdot 12H_2O$ and 0.03 M KH_2PO_4) and was used within 8 h [31]. The concentration of BSA stock solution was also 10 g/L, and 0.02 M $AlCl_3 \cdot 6H_2O$ solution was freshly prepared each time.

2.2. UF membrane process

A polyvinylidene fluoride (PVDF) flat sheet UF membrane was used with a molecular weight cut-off (MWCO) of 100 kDa. The membranes were obtained from Tianjin Motimo Membrane Tech. Co., Ltd, China. All membranes were firstly immersed in DI water for 24 h, and the water was changed three times. To keep membrane flux constant, fresh membranes were firstly filtrated with DI water (300 mL). The Millipore UF stirred cell (Amicon 8400, USA) was driven by N_2, which was maintained at 0.1 MPa during filtration.

For the tests, the aluminum solution was diluted by DI water to the specific concentration with $NaHCO_3$ (0.1 M, 3 mL) as buffer. The final solution pH was determined by prior addition of a corresponding amount of HCl or NaOH (0.1 M). In order to form flocs gradually, the rapid mixing of 300 rpm lasted for 1 min, while the slow mixing of 100 rpm lasted for 14 min. Afterward, the stirrer was taken out carefully, and the UF cell was maintained under static conditions to let the Al-based flocs settle naturally (20 min), forming a homogeneous layer on the membrane surface. Finally, the corresponding HA or BSA stock solution was added into the aforementioned water, and allowed to dissolve completely by keeping the cell static for 30 min.

2.3. Floc size measurement

A beaker (1.0 L) with a flocculator device was used in the jar tests without HA or BSA. 300 rpm (rapid mixing) was maintained for 1 min, followed by decreasing the speed to 100 rpm for another 14 min to allow flocs to grow. The properties of flocs were measured by a laser particle size analyzer (Mastersizer 2000, Malvern, UK) during the coagulation process, including particle size and fractal dimension (D_f). The particle size of flocs was automatically recorded by computer every 0.5 min. Fractal dimension was measured by using small angle-light scattering [32,33], which has been successfully used in previous studies [34,35]. Moreover, the specific surface area of the Al-based flocs was analyzed by the Brunauer-Emmett-Teller method (BET, ASAP2020HD88).

2.4. Other measurement methods

An Orion pH meter (USA) was used to measure the solution pH; The variation of membrane flux as a function of time was recorded by computer; The zeta potential was analyzed by a Malvern Zetasizer 2000 (UK); The concentration of HA or BSA and the MW distributions were measured by gel permeation chromatography (GPC, Agilent Technologies, USA); The morphology of the membrane surface was measured by scanning electron microscopy (SEM, JEOL Ltd., Tokyo, Japan). The average pore size of the pre-layered membrane was analyzed by ImageJ software, which measured the apparent pore size on the surface (without considering the 3-dimensional structure of the membrane and Al-based floc layer) [13].

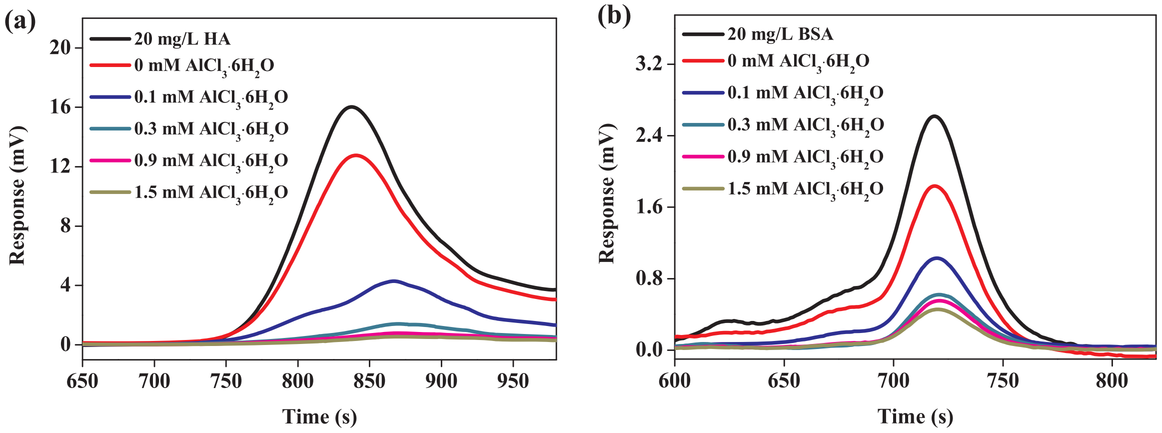

Fig. 1. Concentration of (a) HA or (b) BSA for membrane with pre-deposited flocs formed by different doses of $AlCl_3 \cdot 6H_2O$ at pH 7.0. The original concentration of HA or BSA was 20 mg/L.