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Optimization of coagulation pre-treatment for alleviating ultrafiltration membrane fouling: The role of floc properties on Al species

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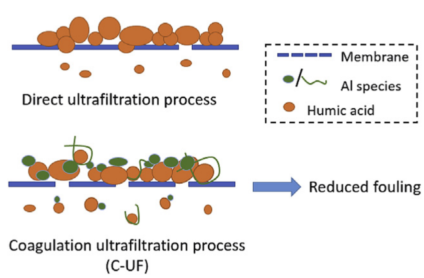
HIGHLIGHTS

- Pretreatment with Al species coagulants before UF caused low fouling.
- The floc properties of coagulated effluents was discussed.
- Large and loose flocs with porous cake layer induced lower external fouling.
- The size distribution of UF was correlated with irreversible fouling.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated membrane fouling in a coagulation/ultrafiltration (C-UF) process by comparing the floc properties and humic acid (HA) removal efficiency of three hydrous Al(III) species (Al_a, Al_b, and Al_c). The results indicated that the coagulation and membrane mechanisms were different for all three Al species because of the differences in floc properties. The HA removal efficiency increased with increasing Al dosage until an equilibrium was reached at the optimal dosage of 6 mg L^{-1}. In addition, membrane fouling gradually decreased as the Al dosages increased. Regardless of coagulant type, the —OH and —COOH functional groups of HA reacted with the Al species. Both external and internal membrane fouling were strongly dependent on the porosity of the cake layer and on the size distribution of the floc particulates, respectively. The pore area of the cake layer formed by the Al_a-coagulated effluent was large because of the strong charge neutralization. Moreover, Al_a generated large and loose flocs with a porous cake layer that mitigated external fouling. However, the internal fouling with the Al_c coagulant was significant because the concentration of residual aggregates in the membrane pores was high.

1. Introduction

Ultrafiltration (UF) process is an attractive technology for water treatment because it can efficiently remove turbidity, bacteria, and viruses from water at low pressure. However, membrane fouling is the main limiting factor for the application of UF processes in water treatment because it requires chemical washing and have high long-term operation costs (Yu et al., 2017). Natural organic matter (NOM), such as humic acid (HA) (500–2000 Da), polysaccharides, and proteins, is a heterogeneous mixture and is recognized as the main water contaminant (Racar et al., 2017), which causes

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membrane fouling by cake layer formation and pore plugging (Jermann et al., 2007; Shao et al., 2016). Although cake layer can cause concentration polarization, cake layer fouling is reversible. Indeed, the cake layer can be removed by increasing the shear force or decreasing the tangential flow. Pore plugging leads to irreversible fouling, and the floc particulates that cause plugging cannot be removed and can need to be washed chemically, thus affecting the long-term operation of the membranes (Y. Besslere and Jefferson, 2005). Therefore, the operating conditions of the UF processes, including backwashing and air scouring, need to be optimized. To reduce maintenance costs and control membrane fouling, pretreatment methods should be considered.

Coagulation is a pre-treatment method applied before the UF process, which can improve NOM removal performance and alleviate membrane fouling (Konieczny et al., 2009; Liu et al., 2017); such an integrated approached is thus referred to as a coagulation-ultrafiltration (C-UF) process. Because the size of HA is similar or smaller than that of the membrane pores, HA hybrid particles can be formed by coagulation without sedimentation before the UF process, and thus mitigate membrane fouling. In this process, the removal efficiency of HA from coagulated water with different coagulant dosages varies because of the different coagulation mechanisms (Sher et al., 2013; Gonzalez-Torres et al., 2014). The flocs formed by coagulation accumulate on the membrane surface to generate cake layer (Dong et al., 2015), which then determines the degree of membrane fouling. Better removal efficiency of the cake layer occurs at the optimal conditions and can directly reduce the HA concentration (Zhu et al., 2016). The porosity of the cake layer and the characteristics of the floc particulates are the main factors that control membrane resistance, i.e., floc particulates of larger size and better settling ability and/or loose cake layers can mitigate membrane fouling (Yao et al., 2015). However, matter that cannot be removed by hydraulic cleaning and backwashing remains in the membrane pores and causes irreversible fouling. Membrane fouling is intimately related to floc properties including floc sizes, shear force, and floc structure (Yu et al., 2016). Hence, the relationship between coagulant type, coagulation conditions, floc properties, and filtration efficiency needs to be further investigated.

In coagulation processes, aluminum salts are used to remove organic matters (Lin et al., 2008, 2014; Sun et al., 2016). Many studies indicated that Al (III) could be hydrolyzed to form polymers by adjusting the [OH]/[Al^{3+}] molar ratio (B value) during the synthesis of polyaluminium chloride (PACls) (Zhao et al., 2011, 2012). The Al coagulant species are generally divided into three types: Al_a (mononuclear Al species), Al_b (polymer species with medium size), and Al_c (higher polymers with colloidal species) according to a series of hydrolysis reactions (He Zhao et al., 2008). The three Al species can be hydrolyzed by varying the B value, and the number of binding sites on the obtained coagulant varies, leading to different coagulation performances. Moreover, the Al species can generally combine with NOM to form complexes that can provide bridges between the membrane surface and the NOM (Jermann et al., 2007; Lok et al., 2017). Concentration polarization and pore plugging can then occur, resulting in membrane fouling. For all three Al species-coagulated water, the NOM removal efficiency and floc properties closely affect membrane fouling in the C-UF process. Feng et al. demonstrated that the type of Al species affects the coagulation removal efficiency and floc properties, leading to different membrane flux declines (Feng et al., 2015). Thus, the decrease in membrane flux relates to both reversible and irreversible fouling. Moreover, external and internal membrane fouling is closely related to the porosity of the cake layer and the size distribution, respectively. Few studies investigating these parameters for the Al coagulant species in C–UF processes have been reported. Therefore, the difference in the coagulation and membrane fouling mechanisms for the three Al species should be evaluated.

In the present work, the objectives were to (1) study the influence of the Al species on coagulation efficiency, floc properties (floc size, shear force, and floc structure), and membrane fouling; (2) compare the relationship between floc properties and membrane fouling by coagulation effluents with three Al species; and (3) investigate reversible and irreversible fouling with respect to the distribution of pore area and floc size, respectively.

2. Materials and methods

2.1. Synthesis of raw water and coagulants

The HA solution (Aladdin Industrial Corporation, Shanghai, China) and kaolin solution (Sinopharm Chemical Reagent Co. Shanghai, China) were prepared according to our previous report (Wang et al., 2017a). To simulate the NOM of surface water, the raw water sample was supplemented with HA and kaolin solution in tap water to achieve a concentration of 10 mg HA L^{-1}. The physicochemical characteristics and measurement methods of the water samples are shown in Table 1.

Three Al species were used as coagulants in this study. Al_a stock solution was prepared by dissolving $AlCl_3 \cdot 6H_2O$ in deionized water to a concentration of 1 mg L^{-1}. Then, Al_b and Al_c solutions with a B value of 2.4 were prepared following a chemical precipitation method and were purified with an ethanol/acetone and methanol/acetone mixture, respectively. The content of each coagulant was measured by Ferron complexation timed spectrophotometry. The distribution of the Al species is shown in Table 2.

2.2. Coagulation kinetics

The coagulation kinetics was studied by the online monitoring of floc sizes (Mastersizer, 2000, Malvern Inc. UK). After freeze-drying, the floc samples were analyzed by Fourier Transform infrared spectroscopy (FTIR) (Fourier-380FTIR, USA). The process of coagulation kinetics included four steps: flocs lag region (200 rpm) for 2 min, growth region (40 rpm) for 15 min, breakage region for 5 min, and regrowth region (40 rpm) for another 15 min, sequentially. The average velocity gradient values (G) of the breakage region were selected to be 27.4 s^{-1} (75 rpm), 40.7 s^{-1} (100 rpm), 104.1 s^{-1} (200 rpm), and 179.7 s^{-1} (300 rpm). The G values reflect the ability to resist shear force, indicating the floc strength in the breakage phase. The relationship between G and floc size (d_{50}) has been previously reported (Jarvis et al., 2005b) (Wang et al., 2016):

$$\lg d_{50} = \lg C - \gamma \lg G \quad (1)$$

where γ is the floc strength exponent and C is the floc size constant.

The fractal dimension (D_f), which reflects the floc structure (with compact aggregates having larger values), was determined based on the scattered light intensity (I) and the scattering vector (Q), according to Eq. (2):

$$I \propto Q^{-D_f} \quad (2)$$

The stirring rate was set to 200 rpm in the breakage region to investigate the ability of floc regrowth. The recovery factor (R) was related to the regrowth ability, and larger R values indicated better floc regrowth abilities. The recovery factor can be calculated by Eq. (3):

$$R = \frac{d_3 - d_2}{d_1 - d_2} * 100 \quad (3)$$

where d_1 is the average floc size during the steady growth period,