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Influence of flocs breakage process on membrane fouling in coagulation/ultrafiltration process—Effect of additional coagulant of poly-aluminum chloride and polyacrylamide

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ABSTRACT

The additional coagulant dosing strategy was applied in a coagulation–ultrafiltration (UF) process for treatment of drinking water. When poly-aluminum chloride (PACl) dose was set as the optimal coagulant dosage (alum 0.15 mM), the additional PACl and polyacrylamide (PAM) were added after breakage to further examine their benefits and impact on membrane fouling. The average size of flocs re-formed with additional non-ionic PAM was larger than that of additional PACl. The fractal dimension of flocs (d_{pf}) was proved to play an important role on membrane fouling. Broken flocs re-formed with additional non-ionic PAM has more convoluted boundaries and lower effective density than the one with additional PACl, which is available to form loose and porosity cake layer on surface of membrane. Microscopic observations of membrane surface demonstrated that there was obvious correlation between the structure of cake layer and the fractal dimension of flocs. Besides, reversible fouling (RF) and irreversible fouling (IF) were also investigated in our study. The additional PACl dosing could lower membrane fouling, but irreversible fouling did not reduce because much more positive charged of flocs may adsorb on the surface of membrane under electrostatic attraction. As for non-ionic PAM, both of RF and IF were simultaneously decreased. As a result, the structural characteristics and surface electrical of flocs are two main mechanisms caused irreversible fouling.

1. Introduction

Ultrafiltration (UF) membrane is considered as a very promising process for treatment of groundwaters and surface waters since its compactness, easy automation, and high removal rate of turbidity, organic matters (such as humic substances), biopolymers, Giardia and virus [1–4]. However, membrane fouling has been the main limiting factor for widely application of membrane in water and wastewater treatment [5]. Particles' fouling is considered to be formed as cake layer on membrane surface by accumulation of particles. Organic fouling is caused by natural organic matter (NOM) from the source waters, since it contains a complex mixture of humic acids, proteins, and function groups, which can either stick to the surface of membrane or leading to the development of microbiological fouling [6–8]. Hence, how to mitigate the membrane fouling is research focus in recent years.

Using pretreatment to lower the foulants concentration has been a useful approach to retard membrane fouling. Coagulation has been shown to be an effective way to control membrane fouling and improve general water quality, especially by “in-line” (without settling) chemical coagulation and coagulation-hydraulic flocculation [9–11]. Shirasaki et al. [12] has stated that virus can be removed by the in-line coagulation and MF process. Guigui et al. [13] reported that applying a coagulation step before membrane filtration can dramatically improve the permeate quality in terms of organic matter content in surface water treatment. Previous lectures thought that Ferri-coagulant has an evident effect on the performance of UF system to remove NOM and retard the membrane fouling [14]. Owing to produce color for Fe^{3+}, which causes another problem in water, alum was chosen as the coagulant in the present research. Nevertheless, the results of previous investigations on effect of coagulation pre-treatment on membrane permeability are different, which is likely attribute to various water qualities and experimental conditions [15,16].

The structure of cake layer on membrane surface is believed to be the significant factor that extent of membrane fouling, and the

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accumulated layer is independent on the membrane type [17,18]. Where coagulation/flocculation pre-treatment is used, the characteristics of the flocs will in-turn determine the structure of cake layer, and thus the efficiency of filtration [19,20]. Coagulation conditions, such as coagulant type and dose, [21,22] water quality, mixing mode [23,24], etc., have a great impact on characteristics of flocs. Looser aggregates appear to favor procedure performance though there is an increased tendency of the resulting porous cakes to restructure [25]. Hwang and Lin [26] stated that effective conventional coagulation conditions generally produced larger particles, and then reduced membrane fouling by reducing adsorption in membrane pores, increasing cake porosity and transport of contaminant away from the membrane surface. Fractal dimension of flocs was seemed as another significant factor of membrane fouling. Park et al. [27] found that cake compactness was independent on the fractal dimension of flocs with low fractal dimensions in a coagulation–microfiltration process, whereas for high fractal dimensions it decreased with increasing fractal dimension. Based on other research [28], large size and irregular shape of flocs could effectively form the loose and porous cake layer, which mitigate membrane fouling.

Breakage and regrowth are considered as the important processes to reshape the structure of flocs during coagulation/flocculation treatment. Some researchers found flocs formed under charged neutralization have fully reversibility after breakage [29–31]. Yu et al. [5] has studied that the characteristics of flocs surface changed after breakage and re-growth and this effectively modified the membrane fouling. It is obvious that flocs formed by hydrolyzed metal ion precipitates and polymer coagulants will be significantly different, and this could in-turn lead to differences in the nature of cake layer on the surface of a downstream membrane, where coagulants are used as a pre-treatment [32].

Additional adding coagulants after floc breakage can often enhance the performance of separation processes by changing the properties of flocs. Nevertheless, most of studies investigated on the relationship between additional coagulant dosage and floc properties, while the effect of additional coagulants on the subsequent membrane performances still unclear, which is necessary and of importance meaning. Organic polymeric coagulants, like polyacrylamide (PAM), have been applied in water purification for several decades. An ionic PAM with PACl coagulation effectively increased the microfiltration permeate flux for a waste water [33]. However, charged interactions between polymer and surface of membrane may be important where the polymer is charged. Recently, due to strong electrostatic attraction between positive charged polymer and negative charged membrane surface, the ionic coagulant gave the worst enhanced membrane performance and increased the formation of a fouling layer [34,35]. Based on this, performance of the non-ionic PAM was chosen as the additional coagulant in this study.

In view of this, it is expected that additional coagulant dosing after floc breakage during the coagulation pre-treatment process will alter the characteristics of flocs and their resulting cake layers on membrane surface, and then influence the membrane performance. This study concerned the role of PACl and non-ionic PAM, as the second coagulants, after floc breakage during the pre-treatment of humic–kaolin drinking water prior to UF. The main investigation focused on flocs size, structure and surface characteristic in pre-coagulation combined with the UF membrane process. Flocs formation with two different additional coagulants was compared to this with conventional coagulation process. The mechanisms involved of its effect on membrane fouling were also discussed by analysis of floc properties including size, fractal dimension, floc size distribution in water treatment. Besides, the reversible fouling and irreversible fouling of membrane are still investigated.

2. Materials and methods

2.1. Suspension

Kaolin clay (Tianjin, China) and humic aicd (shanghai, China) were used as testing water sample. Kaolin clay was prepared by dissolving 50.0 g of kaolin clay in 1 L deionized water with continuous magnetic stirring for 24 h. After sedimentation for 1 h, 800 mL supernatant was the stock suspension of kaolin clay.

10 g of humic acid (Shanghai, Jufeng, China) was dispersed in 0.1 mM/L NaOH, and mixed for 24 h by a magnetic stirrer. The suspension was filtered by a 0.45 μm fiber filter membrane. The pH of the filtered solution was adjusted to 7.5 using 0.1 mM/L NaOH or HCl and the solution diluted to 1000 mL in a measuring flask [5]. The solution was stored in the dark.

Harbin tap water, China, has alkalinity of 15 mg/L as $CaCO_3$ and a pH of around 7.2. A small dosage of humic acid was added in the testing water to diminish the disturbance of divalent metal ions, like Ca^{2+} and Mg^{2+} in tap water [36]. For flocculation tests, the stock solution was diluted in the tap water, containing 100 mg/L of clay and 2 mg/L of humic acid. The initial turbidity was about 90 NTU. During the experimental program the temperature of the solution was $25 \pm 2\ ^\circ C$.

2.2. Coagulants

Polyaluminum chloride (PACl) (28% quality calculated as Al_2O_3), the basicity of which was 72.3%, was prepared as a concentration of 1% by dissolving 5 g reagent in 500 mL deionized water. Non-ionic polyacrylamide (PAM, Sinopharm Chemical Reagent Co., Ltd., China), with an approximate molecular weight of 1×10^7 g/mol, was diluted to give a stock solution of 0.1% or 1 g/L [37]. These two coagulants solution renewed 24 h, for the flocculation tests, directly pipetted in the testing water without further dilution.

2.3. Apparatus

A modified version of the jar-test process was used in this research. A non-intrusive optical sampling technique was applied to capture digital images of particles from the moment of coagulant addition, which were then analyzed to form particle size distributions, geometrical properties, and calculations of the fractal dimension [38]. This basic procedure was similar as the work of Chakraborti et al., and has been widely used by our research fellows [24,36,39]. Because of no sample handling during measurements, there is no concern for destroying the floc characteristics.

In this research, the in-site recognition system include a computer-controlled digital CCD camera (SVS-VISTEK GmbH, Germany) with a resolution of 992 (horizontal) × 510 (vertical) pixels to capture particle images, giving an interrogation window of 5665 μm × 2920 μm. Thus 1 pixel means about 5.7 μm for particle imaging. A process control and image processing software package (FMans 10, China) are used to determine floc geometrical parameters. In order to illuminate the particles, the camera was placed on the opposite side of the tank from the lamp, and then backlit shadows of particles were produced.

In our research, the flocculation reactor used was a rectangular stirred tank (homemade) with a bottom length $D = 150$ mm and a liquid height $H = 250$ mm, and filled with 4 L of testing water sample as working fluid. A R1342-type impeller (IKA, Germany) with a diameter $d = 50$ mm was used and the impeller was placed at $C = H/3$ from the tank bottom. This mixing system was used in some of our previous studies, e.g., in Nan et al. [40,41].