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Effect of under-dosing coagulant on coagulation–ultrafiltration process for treatment of humic-rich water with divalent calcium ion

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ABSTRACT

The strategy of under-dosing coagulant was firstly applied in a coagulation–ultrafiltration (UF) process for treatment of humic-rich water in this study. When polyaluminum chloride (PACl) dosage was set as 0.025 mM (as alum), the removal efficiency of organic matter and residual turbidity were slightly inferior to 0.1 mM (as alum), but four times dosage lowered than the optimal-dosing. Although permeate flux of ultrafiltration membrane was larger at the optimal-doing than that of under-dosing, the less proportion of irreversible fouling and large proportion of reversible fouling were proved that under-dosing strategy has more meaningful engineering application value for deep investigation. The impacts of Ca^{2+} on coagulation and ultrafiltration performance are also investigated under different coagulant doses. Removal of humic-like substance, floc size and incompactness were appreciably enhanced at under-dose with increasing Ca^{2+} concentration, but did not distinctly change at the optimal-dosing. Besides, lower positive charge of flocs produced at under-dosing hindered the foulants transport to membrane surface. The interactions between humic substance, positively-charged coagulants, and structure of cake layer firstly systemically investigated the impacts on the performance of ultrafiltration in our study. The results shown that the technology of under-dosing with addition of Ca^{2+} has dramatically increased the UV_{254} removal efficiency, formed loose and porous flocs still outside of the critical electrostatic distance of membrane surface, which significantly remit the membrane fouling and improve the reversibility of membrane fouling.

1. Introduction

Low pressure driven membrane filtration, ultrafiltration (UF), has been widely applied in the past decade with improvement in membrane quality and decrease in membrane costs [1]. UF can effectively remove particles, turbidity, microorganisms (bacteria, protozoa, algae), and some viruses [2]. However, a major limitation in widespread application of the lower membrane technology is the membrane fouling [3,4]. As well known, the membrane fouling could be recovered through hydraulic backwashing, and then the reversibility of membrane fouling can be distinguished. The increase of energy consumption and operational complexity urged many researchers to further investigate the control of membrane fouling [5–7]. Natural organic matter (NOM) has been considered as a detrimental foulant during the ultrafiltration of surface water, because the complex mixture of fulvic acids, humic acids (HA), proteins, carbohydrates of various molecular sizes and functional groups can either stick to the membrane surface or improve the development of microbiological fouling [8]. HA was used as a model contaminant to represent the NOM in surface water for its widely application in many studies [9,10].

Using pretreatment to lower foulants concentration has been a useful approach to retard membrane fouling. Coagulation was the most common process to remove particles and nature organic matter in water treatment, especially by "in-line" (without settling) chemical coagulation and coagulation-hydraulic flocculation [11–13]. Al/Fe salts could produce a series of cationic hydrolytic species and force dispersed particles to aggregate large flocs after reacting with water, which charge neutralization and adsorption are the two typical mechanisms for removal humic substances [14]. Yuankui et al. has stated that $FeCl_3$ as pre-coagulant effectively reduced the UF membrane fouling through removal of natural organic matter [15]. Konieczny et al. found that removal efficiency of organic materials was higher with aluminum salt coagulant than with ferric salt [12]. Lee et al. reported that there was an optimal PACl dosage with respect to fouling minimization [16]. Shon et al. has also addressed that there was an optimal dose of $FeCl_3$ to cause any flux decline during the whole operation of UF in

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6 h [17]. Until now, most studies are still concentrating on finding the optimal coagulant dose for reducing membrane fouling. Although the performance of optimal coagulant did satisfy the increasing demand for natural organic matter removal, the high positive charge could severely foul the negative-charged membrane fouling. Electrostatic attachment between negatively-charged membrane surface and oppositely charged metal salts would cause a intensive particle attachment or organic pollutants transporting on the pore walls of the membrane [18]. Therefore, it should pay more attention to the phenomenon that whether the membrane fouling could be reduced by a lower dose of coagulant or not.

The structure of cake layer on membrane surface is believed to be the significant factor that extent of membrane fouling, and the accumulated layer is independent on the membrane type [19,20]. The characteristics of flocs are not only influences in the solid/liquid separation process, but will in-turn determine the structure of cake layer, and thus the efficiency of filtration [21,22]. Looser aggregates appear to favorite procedure performance though there is an increased tendency of the resulting porous cakes to restructure [23]. As a result, fractal dimension of flocs was seemed as other significant factor of membrane fouling. Park et al. [24] found that cake compactness was independent on fractal dimension of flocs with low fractal dimension in a coagulation–microfiltration process, whereas for high fractal dimension it decreased with increasing fractal dimension.

Divalent cations (e.g. Ca^{2+}) played an important role in interaction between humic acid and lead to formation of HA–Ca aggregates, which displayed significant fouling effect on ultrafiltration membrane [25]. Calcium ion can interact specially with humic carboxyl functional groups, and substantially decreased HA charge and the electrostatic repulsion between HA molecules [26]. Some studies have stated that a significant increased in the rate of flux decline occurred since calcium was added in the water solution, and this trend was accelerated as calcium concentration increased [27]. Yang et al. thought that calcium addition leads to a dramatic decrease of the specific resistance to filtration of calcium–humic aggregates accumulated on the polyvinylidine fluoride (PVDF) membranes [28]. These previous observations are very suggestive, because calcium addition could change the existence form of humic acid and morphological structure of flocs, which would also impact on the subsequent membrane fouling. Nonetheless, there were few literatures concerning the effect of divalent calcium ion on membrane fouling using PACl as a coagulant during the coagulation–ultrafiltration process. The addition of calcium under different PACl doses will have different effects on membrane fouling.

In view of this, the interactions between humic substance, positively-charged coagulants, and structure of cake layer have not been systemically investigated so far and the impacts on the performance of ultrafiltration also remain unclear. Thus, the motivation of this research was to contribute towards a better understanding of the NOM fouling behaviors on pre-coagulation/UF membrane based on the three important factors. The technology of under-dosing was firstly proposed to use during the pre-coagulation process, which effectively removed humic-like substance from raw water and improve the performance of ultrafiltration process. The mechanisms involved of morphological properties of flocs produced with different coagulation conditions of the humic-rich water were discussed by analysis of floc properties including size, fractal dimension, floc size distribution in water treatment. The impact of Ca^{2+} on these characteristics and on performance of the pre-coagulation/UF process was also investigated. In particular, membrane performance was quantified by the removal of organic matter, by hydraulic resistance of filtration, and by the permeability recovery of the fouled membrane after sequential hydraulic cleanings.

2. Materials and methods

2.1. Suspension

Kaolin clay (Tianjin, China) and humic acid (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 mol/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 0.01 mol/L NaOH or HCl and the solution diluted to 1000 mL in a measuring flask [29]. The solution was stored in the dark. In some experiments, $CaCl_2$ was added at different concentration to investigate the effect of Ca^{2+} on the performance of coagulation and ultrafiltration.

The raw water used in this study was prepared by diluting the stock solution of humic acid and kaolin clay in local (Harbin, China) tap water, to give the raw water with a humic acid concentration of 5 mg/L and an initial turbidity of 50 NTU. Synthetic raw water has been chosen here to simplify the study since natural surface water would have implied reproducibility issues. The characteristic of tap water was shown in Table 1.

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 [30]. PACl 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, and the schematic diagram was shown in Fig. 1. 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 [31]. This basic procedure was similar as the work of Chakraborti et al. and has been widely used by our research fellows [32–34]. 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

Table1
Characteristic of tap water (Harbin, China).

Parameters	Tap water
pH	7.5 ± 0.1
Turbidity (NTU)	0.75 ± 0.12
Conductivity (μS/cm)	85 ± 2
DOC (mg/L)	2.14 ± 0.20
UV_{254} (1/cm)	0.046 ± 0.006
Al (mg/L)	0.075 ± 0.030
Temperature (°C)	22 ± 2