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Purification, characterization and application of dual coagulants containing chitosan and different Al species in coagulation and ultrafiltration process

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ABSTRACT

The objective of this study was to investigate the effect of different Al species and chitosan (CS) dosages on coagulation performance, floc characteristics (floc sizes, strength and regrowth ability and fractal dimension) and membrane resistance in a coagulation–ultrafiltration hybrid process. Results showed that different Al species combined with humic acid in diverse ways. Al_a had better removal efficiency, as determined by UV_{254} and dissolved organic carbon, which could be further improved by the addition of CS. In addition, the optimal dosage of different Al species was determined to be 4.0 mg/L with the CS concentration of 1.0 mg/L, by orthogonal coagulation experiments. Combining Al_a/Al_b/Al_c with CS resulted in larger flocs, higher recovery, and higher fractal dimension values corresponding to denser flocs; in particular, the floc size at the steady state stage was four times larger than that obtained with Al species coagulants alone. The results of ultrafiltration experiments indicated that the external fouling percentage was significantly higher than that of internal fouling, at around 85% and 15%, respectively. In addition, the total membrane resistance was significantly decreased due to CS addition.

Introduction

The availability of clean water has been limited during the past decades, and coagulation is the most common process for removal of particulates and natural organic matter (NOM) in water treatment (Liu et al., 2011). Moreover, the coagulant hydrolysate can eliminate the electric charges of particles, which destabilizes them and causes them to coalesce with each other, so colloids can be changed and form larger molecules for removal by the coagulation process (Jarvis et al., 2005a). However, coagulants, of which polyaluminium chloride (PACl) is used widely throughout the world, are receiving more and more attention. According to the reaction rate with ferron reagent (8-hydroxy-7-iodoquinoline-5-sulfonic acid) and the size of hydrolysate species, the hydrolysate of PACl can be divided into three species: Al_a (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$) as mononuclear Al species, Al_b ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) as medium-sized polymeric species, and Al_c ($[(AlO_4)_2Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$) as colloidal species (C. Zhao et al., 2011; Zhou et al., 2006). Although Al_b and Al_c are more stable than Al_a, some studies have showed that Al_a

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has better removal efficiency for NOM under certain conditions (Yan et al., 2007). However, high concentrations of residual Al may result, depending on coagulant dosing, pH, or the presence of other chemicals, and can pose a serious threat to human health and the environment. Therefore, it is desirable to develop a highly efficient and non-toxic coagulant aid which can reduce the dosage of coagulant needed for water treatment.

Recently, chitosan (CS), prepared by deacetylation of chitin, a major component of the shells of crustaceans, has been used as a renewable bio-flocculant (Benhabiles et al., 2012). CS is a copolymer of glucosamine and N-acetylglucosamine (Laribi-Habchi et al., 2015), and the amino groups are easily protonated in weakly acidic solution. In addition, the amino groups of CS enhance its activity and adsorption for pollutants (Szygula et al., 2009). The main removal mechanism of CS has been investigated, and is thought to mainly be due to positively charged CS uniting with HA by electrostatic attraction, so that the adjacent particles combine with each other by adsorption bridging to form large and dense flocs that settle easily in water. In addition, previous researchers found that CS, as a biological coagulant aid, was different from most metal salt coagulants that might cause residual metals after treatment (Ng et al., 2012; Ruhsing Pan et al., 1999). Accordingly, considering the advantages of CS such as being natural, nontoxic, biodegradable and causing no secondary pollution, CS is worth investigating as a potential coagulant aid in water treatment (Ng et al., 2012; Renault et al., 2009).

The efficiency of coagulation is also affected by the size and structure of flocs in solid/liquid separation processes (Yu et al., 2009). In general, bigger flocs usually have better settling ability. Floc breakage and recovery have been deeply researched in recent years (Jarvis et al., 2005a), and this knowledge should be taken into consideration in overall process optimization. Recently, the use of ultrafiltration (UF) was extensively reviewed (Benhabiles et al., 2013; Li et al., 2014), and the application of membranes for water treatment in the UF process was investigated. In this process, the micro-particles (bacteria, protozoa, algae) and macromolecules (inorganic particles, organic colloids and NOM) can be effectively removed. In addition, the accumulation of the retained matter on the membrane surface leads to membrane fouling, which can increase the operating costs, and periodic cleaning is necessary (Liu et al., 2011). Therefore, to enhance NOM removal efficiency and alleviate membrane fouling, coagulation is necessary before the process of UF, referred to as the coagulation–ultrafiltration hybrid process (C-UF). In this system, flocs with unstable aggregates that are generated by the addition of coagulants are liable to be entrapped by the membrane, and then form a cake layer and change the membrane performance. As discussed earlier (Choo et al., 2007), the degree of UF fouling highly depends on the types of coagulants used and the structure of flocs produced, so that the influence of coagulant dosage deserves further research. Accordingly, the effects of three different Al species as coagulants and CS as coagulant aid during C-UF treatment merited study.

The major objective of this paper is to explore the influence of dosage on coagulation efficiency, floc characteristics and the membrane fouling mechanism through a series of comparison tests, for which three different Al species were selected as coagulants and CS was used as coagulant aid in kaolin–HA treatment. By changing coagulant dosage, the coagulation performance was comparatively investigated in terms of the removal efficiency of turbidity, UV_{254} and dissolved organic carbon (DOC). Furthermore, floc characteristics including floc size, strength, recovery factor and fractal dimension were also studied. Finally, a detailed investigation on the membrane fouling mechanism was carried by comparing the resistance of membrane under different conditions. The results of these studies can provide theoretical guidance for practical applications.

1. Experimental section

1.1. *Materials*

The HA stock solution was prepared by dissolving 1.0 g HA (Aladdin, Shanghai, China) and 0.4 g NaOH (Sinopharm Chemical Reagent Co., Shanghai, China) in deionized water, and diluting with deionized water to 1 L. The kaolin solution was prepared from 5.0 g kaolin (Sinopharm Chemical Reagent Co., Shanghai, China) added to 800 mL deionized water with stirring for 30 min. The suspension was transferred to a graduated cylinder and diluted to make up a volume of 1 L, and then settled for 30 min. The top 500 mL was used as the stock kaolin solution.

A HA–kaolin synthetic water mixture was prepared by mixing HA and kaolin solutions to give a concentration of 10 mg HA/L. Physicochemical characteristics of the water sample are as following: Turbidity = 15.0 ± 0.5 NTU, UV_{254} = 0.305 ± 0.100/cm, DOC = 5.300 ± 0.500 mg/L, pH = 8.30 ± 0.10, and Zeta potential = −19.2 ± 2.0 mV.

1.2. *Coagulation experiments*

In this study, three different Al species were used as coagulants and CS was selected as coagulant aid. Al_a was prepared by adding 0.4470 g $AlCl_3{\cdot}6H_2O$ to deionized water, and diluting to 50 mL directly. To obtain PACl with a high Al_b component, NaOH was added to $AlCl_3{\cdot}6H_2O$ obtain a basicity (OH/Al ratio) of 2.4, with the temperature kept around 80 ± 5°C, and then purified by precipitation with an ethanol/acetone (1:4) solution (H.-Z. Zhao et al., 2011), which were filtered in funnel. In addition, in the filter paper the samples could be obtained by air-dried at room temperature. The synthesis method of Al_c was similar to that of Al_b, except that the temperature was raised to 90 ± 5°C, and the process of purification used a methanol/acetone (1:9) solution. According to the National Standard of China, the total aluminum (Al_T) concentration of PACl was measured by the $ZnCl_2$ titrimetric method (Feng et al., 2015; Xu and Gao, 2012). Al species distributions of PACl were determined by the Al–ferron complexation timed spectrophotometry method (Xu and Gao, 2012). The content of Al_b and Al_c was 98.15% and 83.97%, respectively.

CS (Klontech, China) with the degree of deacetylation of 90% ± 5% was prepared using the method of NaOH titration, and the viscosity was 55.4 ± 1.5 mPa·sec measured by a Brookfield viscometer in an aqueous 1% (W/W) CS and 1% acid (W/W) solution at 25°C. The molecular weight of CS was about 620 kDa as measured by gel chromatography. A CS solution was prepared by dissolving 0.05 g CS in 1% HCl with