Journal of the Taiwan Institute of Chemical Engineers 000 (2016) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Floc proprieties and ultrafiltration characteristics by chitosan compound aluminum species coagulant under different pH conditions

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ARTICLE INFO

Article history:
Received 25 February 2016
Revised 20 August 2016
Accepted 25 August 2016
Available online xxx

Keywords:
pH
Al species
Chitosan
Floc characteristics
Membrane resistances

ABSTRACT

In this study, the tendency of coagulation performances, floc characteristics and membrane resistances under different pH conditions in coagulation–ultrafiltration hybrid process was investigated by different Al species and chitosan (CS). Results indicated that CS as coagulation aid was independent of aluminum species. Coagulation efficiencies of three Al species (Al_a, Al_b and Al_c) combined with CS were enhanced comparing with Al species used alone and shown similar variation tendencies during the pH range. The values of floc size and strength/recovery factor were relatively high at pH 6, and the maximum fractal dimension was achieved under alkaline conditions generally due to adsorption sweeping. $Al_a/Al_b/Al_c$ combined with CS contributed to larger flocs, higher recovery factors and smaller fractal dimension values than those without CS. The results of ultrafiltration experiments shown that membrane resistances during alkaline ranges were higher than those of acidic conditions, which indicated membrane fouling was more serious in alkaline range. In addition, the total membrane resistance was decreased significantly by CS addition.

1. Introduction

In water treatment process, many types of coagulants have been widely used, especially aluminum salt coagulants. As aluminum salt dosed into water, there would be a series of hydrolysis reactions and different Al species were generated: Al_a, Al_b, and Al_c [1]. Previous study has shown that Al_a has better removal efficiency of natural organic matter (NOM) under certain conditions [2], since the hydrolysate species were unstable and hard to control as a small fluctuation of conditions, such as pH [3], basicity values (B) [4] and temperature, *etc*. It has been demonstrated that the amount of electric charges for hydrolyzed Al was determined by the solution pH, thus pH is a crucial way to control the hydrolysis species of Al salt. The NOM removal efficiency of coagulants is usually not perfect and some of which are harmful to environment [5]. In order to improve the NOM removal efficiency, it is indispensable to find high efficient and non-toxic coagulant aids. As a kind of bio-coagulant, chitosan (CS) was the second most abundant biopolymer after cellulose in the word which produced by the deacetylation of chitin [6]. In the process of coagulation, CS which is described as a cationic polyelectrolyte is easy to exposure to protons by hydrolysis [7], and then the micro particles combine to settle down mutually. These novel three Al species combined with CS was better than their individual components, which could enhance coagulant stability and widen effective pH range than that of Al salts individually. In this paper, the combination of Al species with CS was short for $Al_a/Al_b/Al_c$–CS.

Recently, the removal of turbidity and NOM from water is a problem for producing potable water, of which coagulation are considered to be the most common process. In coagulation process, adjustment of pH is a significant way to enhance turbidity and NOM removal efficiency. In addition, membrane fouling is an important issue and face with enormous challenges in the ultrafiltration (UF) process. In general, to improve the efficiency removal of NOM and alleviate membrane fouling, combination of coagulation and UF (C–UF) is necessary. As previous research [8], in C–UF process the performance was closely related to coagulant type, coagulation condition and floc characteristics which were strongly affected by pH. Thus, the coagulation performance, floc characteristics and membrane fouling under different pH conditions by three Al species as coagulant and CS as coagulant aid in C–UF process should be further researched.

In this study, the coagulation performance of $Al_a/Al_b/Al_c$–CS and $Al_a/Al_b/Al_c$ were compared to demonstrate its flocculating efficiency. The effect of solution pH on floc proprieties (strength factor, recovery factor and fractal dimension) were comparatively studied.

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http://dx.doi.org/10.1016/j.jtice.2016.08.041
1876-1070/

Membrane resistances under different pH conditions were used to measure the degree of membrane fouling. In general, coagulation models of three Al species combined with CS under different pH conditions were described to further research the mechanisms in humic acid (HA)-Kaolin treatment, and a detailed investigation on coagulation efficiency, floc characteristic and membrane fouling mechanism was discussed.

2. Materials and methods

2.1. Coagulants

Three different Al species were used as coagulant and CS was selected as coagulant aid. The procedures of coagulants preparation were listed as follows:

Al_a solution was prepared by directly dissolving $AlCl_3{\cdot}6H_2O$ in deionized water. The synthesis method of Al_b, NaOH was added into $AlCl_3{\cdot}6H_2O$ solution with the B ($[OH^-]/[Al^{3+}]$ mole ratio) of 2.4, and then purify with ethanol–acetone solution (1:4) [9]. The method of Al_c is similar to that of Al_b but the reaction temperature is much higher, and the process of purification uses methanol/acetone solution (1:9).

CS solution was prepared by dissolving 0.05 g CS in 1% (w/w) HCl to make the concentration of 1 mg/l. The physicochemical properties of CS are listed as follows: deacetylation degree = 90 ± 5%, molecular weight = 590–630 kDa and viscosity (100 rpm at 25 °C) = 57.1 ± 2.3 mPa s.

2.2. Water samples

The water sample was prepared by HA and kaolin, which was based on previous methods [10]. HA (Aladdin Industrial Corporation, Shanghai, China) which the mean molecular weight of 2500–2950 Da were dissolved in deionized water and then constant volume to 1 l. The kaolin solution (Sinopharm Chemical Reagent Co., Shanghai, China) was dissolved in a graduated cylinder make a volume of 1 l, and the surface 500 ml was used as the stock kaolin solution.

The water sample was prepared by using tap water to make its concentration of 10 mg HA/l, and the physicochemical parameters were listed as follows: Turbidity = 15.0 ± 0.5 NTU, UV_{254} absorbance = 0.305 ± 0.010 cm^{-1}, Dissolved Organic Carbon = 5.350 ± 0.200 mg/l, Zeta potential = −20.0 ± 0.7 mV, pH = 8.10 ± 0.05.

2.3. Jar tests

Coagulation experiments were operated by using a programmatic jar-test apparatus (Zhongrun Water Industry Technology Development Co., Ltd., China) to confirm the effect of pH on coagulation performance, and predetermined pH values (from 4 to 9) of samples were adjusted by 1.0 mol/l HCl and NaOH solutions. In the first place, amount of Al species coagulants were added into water samples during the rapid stirring (200 rpm), then CS was dosed with a 30 s interval. After that each sample continued rapid stirring for 1 min, followed by slow mixing (40 rpm) for 15 min and quiescent settling for 30 min.

Turbidity of the collected water was measured by turbi-dimeter 2100P (Hach, US), and zeta potential was monitored by Zetasizer Nano ZS (Malvern, UK). The remaining samples were filtered by 0.45 μm fiber for UV_{254} measurement (Precision Scientific Instrument Co., Ltd., China) and DOC analysis (TOC-VCPH, Shimadzu, Japan).

2.4. Floc properties

Dynamic floc sizes were monitored by Mastersizer 2000, Malvern, UK. These experiments were conducted on the jar tester and the procedure was similar to coagulation experiment which without sedimentation. The median volumetric diameter (d_{50}) which reflects floc size was measured every 30 s, and then the data were recorded automatically by computer.

The floc properties were described by strength factor (S_f), recovery factor (R_f) and fractal dimension (D_f). D_f which describe flocs structure was related to the scattered light intensity (I) and scattering vector (Q). They were calculated as follows [11–13]:

$$S_f = d_2/d_1 \times 100 \tag{1}$$

$$R_f = (d_3 - d_2)/(d_1 - d_2) \times 100 \tag{2}$$

$$I \propto Q^{-D_f} \tag{3}$$

In these equations, d_1 is the average floc size in firstly steady period, d_2 is the floc size for the last point at breakage phase and d_3 is the floc size after regrowth to a steady region.

2.5. Membrane fouling experiments

Ultrafiltration experiments were conducted using a 300 ml dead-end stirred batch after coagulation (without sedimentation). UF membranes (PLHK07610, Millipore, USA) were used with molecular weight cutoff of 100 kDa and filter diameter of 76 mm. The mass of infiltration was monitored by an electronic balance (MSU5201S-000-D0, SartoriusAG, Germany), which was connected to computer. Membrane resistances could intuitively reflect the membrane fouling. In general, the total hydraulic resistance (R_t) consisted of external fouling (R_{ef}) and internal fouling (R_{if}). Among them, R_{ef} contains loosely-attached resistance (R_{ef-l}) and strongly-attached resistance (R_{ef-s}), and R_{if} includes reversible resistance (R_{if-r}) and physically irreversible fouling resistance (R_{irr}) [14].

The experiments were carried as follows: (1) 100 ml deionized water was carried out to obtain flux J_0; (2) 1 l water sample which after the process of pre-coagulated was ultra-filtrate to get J_1; (3) deionized water was added with the stirring rate of 200 rpm to obtain flux J_2; (4) the membrane was taken out and wiped to remove the strongly-attached cake layer, and then deionized water was carried out at low stirring speed to get J_3; (5) the reverse side of the membrane was upwards with filtration of 100 ml deionized water, and followed by filtering deionized water to obtain J_4 [15]. According to the experiments above, the R_m, R_{ef-l}, R_{ef-s}, R_{if-r} and R_{irr} can be calculated as follows:

$$R_m = TMP/(\mu J_0) \tag{4}$$

$$R_{ef-l} = TMP/(\mu J_1) - TMP/(\mu J_2) \tag{5}$$

$$R_{ef-S} = TMP/(\mu J_2) - TMP/(\mu J_3) \tag{6}$$

$$R_{if-r} = TMP/(\mu J_3) - TMP/(\mu J_4) \tag{7}$$

$$R_{irr} = TMP/(\mu J_4) - TMP/(\mu J_0) \tag{8}$$

where R_m, TMP and μ are clean membrane resistance (m^{-1}), transmembrane pressure (Pa) and dynamic viscosity of the feed water (Pa s), respectively.

Please cite this article as: W. Wang et al., Floc proprieties and ultrafiltration characteristics by chitosan compound aluminum species coagulant under different pH conditions, Journal of the Taiwan Institute of Chemical Engineers (2016), http://dx.doi.org/10.1016/j.jtice.2016.08.041