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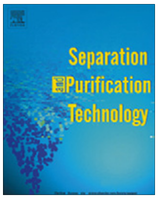

Effect of pH on humic acid removal performance in coagulation–ultrafiltration process and the subsequent effects on chlorine decay

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ABSTRACT

The effect of pH on coagulation performance and floc characteristics with respect to the treatment of humic acid (HA) solution using polyferric chloride (PFC) as coagulant was investigated in this study. Ultrafiltration was used after coagulation to further remove organics under three pH conditions. The subsequent effects on chlorine decay were studied using a first decay model and AQUASIM modeling software. The results indicated that PFC had different coagulation mechanisms in different pH regions. Charge neutralization was the dominant mechanism in acidic region, while sweep was the predominant mechanism at pH >6.0. HA was effectively removed in acidic region and turbidity removal efficiency was higher in neutral and alkaline regions. The median equivalent volumetric diameter (d_{50}) of flocs formed in coagulation process in acidic region was larger than that of flocs formed at pH 9.0. The flocs formed at pH 5.0 were more compact because larger floc fractal dimension (D_f) was observed. Floc breakage behavior showed that flocs formed at different pH values gave different floc strength and recovery ability, and the strength and recovery factors of the flocs varied in the following order: pH 5.0 >4.0 >9.0. The treated water at pH 5.0 possibly contained the minimal amount of disinfection by-products (DBPs) precursors due to the minimal reacting compounds present in the treated water. DBPs precursors were probably prone to be removed by coagulation process during which flocs with larger strength factor, recovery factor and D_f were formed.

1. Introduction

Natural organic matter (NOM) in raw water could react with chlorine to form disinfection by-products (DBPs) [1,2] in drinking water after chlorination and the DBPs may cause cancer and other hazards to humans such as abnormal embryos and mutations [3]. Thus, the research focus on drinking water treatment has shifted from the removal of particles to the removal of NOM [4]. Coagulation has been widely used in drinking water treatment to remove high concentration of NOM [5]. In addition, the application of ultrafiltration in drinking water treatment has also been studied by many researchers [6,7]. However, there has been little attention to the effect of pH on the NOM removal in coagulation–ultrafiltration process.

As the removal of NOM by coagulation has been widely studied, the focus of the studies has been shifted toward the floc properties [8,9]. The operational parameters of flocs, such as floc strength and recovery ability, have a significant impact on the treatment processes. For example, small increases in shear during coagulation processes give rise to floc breakage, reduce floc size, and subsequently cause decrease of the removal efficiency [10]. Moreover the fractal structure and particle size of flocs are generally recognized as two crucial physical characteristics [11] which have significant impact on the efficiency of unit processes. The physical characteristics of NOM flocs have been studied by many researchers [12,13]. However, there are few reports focusing on the relationship between the floc characteristics and the formation of potential DBPs.

Treatment units, such as coagulation and ultrafiltration, display different NOM removal efficiency, which alters the water quality and then affects the chlorine decay kinetics after dosing chlorine for disinfection. Although the effects of advanced treatment on the kinetics of chlorine decay have been studied [14], the relationship between coagulation pH conditions and the kinetics of chlorine decay has not been well investigated.

In this study, a good model humic substance, humic acid (HA), which has been extensively used [15,16], was selected for investigation. Polyferric chloride (PFC) which has shown to be superior to monomeric iron salt in removal of turbidity and NOM [17] was used to treat the humic acid solution under various pH conditions. According to the coagulation efficiency, comparative investigation was carried out in ultrafiltration unit, with respect to floc breakage and growth properties in the coagulation process. The evolution of

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floc size as a function of coagulation time was monitored and the fractal dimension (D_f) of the resultant aggregate was analyzed. The relationship between pH conditions and chlorine decay process was also discussed. The fast and slow reacting compounds were calculated by a chlorine model and the formation potential of DBPs was estimated in order to evaluate the treated water quality. Furthermore the effect of floc characteristics on the removal of DBPs precursors was discussed preliminarily.

2. Materials and methods

2.1. Preparation of PFC

PFC was prepared using $FeCl_3{\cdot}6H_2O$ (AR) and Na_2CO_3 (A.R.). Firstly, $FeCl_3$ solution with a Fe concentration of 7% (w/w) was prepared by dissolving $FeCl_3{\cdot}6H_2O$ (AR) in distilled water. Then, Na_2CO_3 powder was gradually added to $FeCl_3$ solutions under stirring at room temperature to obtain the PFC solution with desired $[OH^-]/[Fe]$ ratio (B). The mixture was stirred until foam disappeared and the solution became transparent. Subsequently, Na_2HPO_4 (AR) was added to the PFC solution as a stabilizer ($[Na_2HPO_4]/[Fe] = 0.08$). The target PFC had the following characteristics: W (Fe_2O_3) = 10%, $B = 0.5$, pH 0.56 and pHzpc ≈ 7.0.

2.2. Test waters

The commercial humic acid (HA) with a carbon content of 52.6% (w/w) was purchased from the Jufeng Chemical Technology Co., Ltd., Shanghai, China. Stock HA was prepared as follows: 1.00 g humic acid was dissolved in 1 L of 1.0×10^{-4} mol/L NaOH solution, and then the solution was stirred for 30 min and stored in brown reagent bottle for later use. Kaolin clay was purchased from the same company while humic acid was used as a model suspension. 5.00 g kaolin was dispersed in 800 ml deionized water with continuous stirring for 30 min, then clay suspension was diluted to 1 L with deionized water and allowed to settle for 30 min in a measuring cylinder. The top 500 ml was decanted for later use.

Synthetic test water was prepared by diluting the stock HA solution to 10 mg/L as HA. Meanwhile, a certain amount of kaolin suspension was added to adjust the turbidity to 15.0 NTU. The pH of HA solution was about 8.5. The alkalinity of the synthetic water was 100 mg/L as $CaCO_3$. The synthetic water characteristics and the methods of measurement were shown in Table 1.

2.3. Jar test procedures

Coagulation experiments were performed in a jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co., Ltd., China) at room temperature (20 ± 1 °C). During the rapid stir (200 rpm), a measured amount of coagulant was pipetted into the water sample (1.0 L) to obtain a certain PFC concentration 12 mg/L (as Fe_2O_3) based on the previous experimental results. The water samples were mixed rapidly at 200 rpm for 1 min after dosing, and mixed slowly at 40 rpm for 15 min, and then were allowed to settle for 20 min. After sedimentation, supernatant samples were taken from 3 cm below the solution surface for subsequent analysis of residual turbidity, UV absorbance and DOC. Flocs below the supernatant were pipetted to measure the zeta potential.

2.4. Floc size and strength measurement

A laser diffraction instrument Mastersizer 2000 (Malvern, UK) was used to monitor the evolution of floc size as the coagulation proceeded. Jar tests were conducted as before on a jar tester. The suspension was monitored by drawing water through the sample cell of the Mastersizer and back to the jar by a peristaltic pump (LEAD-1, Longer Precision Pump, China) with a 5 mm internal diameter tube at a flow rate of 1.5 L/h. The pump was located downstream of the Mastersizer to prevent flocs from being disturbed prior to measurement. Samples were withdrawn from the same position in the jar, which was located between the impeller and the top of suspension.

Floc breakage and regrowth tests were carried out to study the strength of flocs formed in different coagulation tests. Flocs were exposed to a shear force at 200 rpm for 5 min after the slow stir phase was completed. After the breakage phase, the slow stir at 40 rpm was reintroduced for a further 15 min. Floc size was monitored as before. Floc strength and recovery factors, which had previously been used to compare the relative breakage and regrowth of flocs in different flocculated systems [18,19], were calculated as follows:

$$\text{Strength factor} = \frac{d_2}{d_1} \times 100 \tag{1}$$

$$\text{Recovery factor} = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \tag{2}$$

where d_1 is the average floc size of the steady phase before breakage, d_2 is the floc size after the floc breakage period, and d_3 is the floc size after regrowth to the new steady phase. A larger value of strength factor indicates that flocs are stronger than those with a lower factor. Likewise, the floc with a larger recovery factor shows better regrowth after breakage phase.

2.5. Floc fractal dimension

Fractal theories for particle aggregates provide a new quantitative method to describe the structure of particles aggregates in various water systems [20]. Light scattering method was used for the determination of aggregate mass fractal dimension. The theory of the mass fractal dimension using small-angle laser light scattering technique (SALLS) has been reported in detail in a few literatures [21,22]. The light scattering technique involves measurement of light intensity I as a function of the scatter vector Q. The vector is defined as the difference between the incident and scattered wave vectors of the radiation beam in the medium [21], which is given as follows:

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \tag{3}$$

Table 1
Synthetic water characteristics and methods of measurement.

Characteristic	Value	Methods of measurement
Dissolved organic carbon (DOC) (mg/L)	3.008–3.298	Prefiltered sample measured on a TOC analyzer (Shimadzu, Japan)
Ultraviolet light absorption at 254 nm (UV_{254}) (cm^{-1})	0.088–0.096	Prefiltered sample measured on a UV-754 UV/vis spectrophotometer (Shanghai Jinhua Group Co. Ltd., China)
Turbidity (NTU)	14.5–15.5	Turbidimeter 2100P (Hach, America)
Zeta potential (mV)	−35.53 to −36.27	JS94H micro-electrophoresis meter(Shanghai Zhongchen Digital Technology Equipment Co. Ltd., China)