Chemical Engineering Journal 223 (2013) 412–417

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Effect of humic acid on coagulation performance during aggregation at low temperature

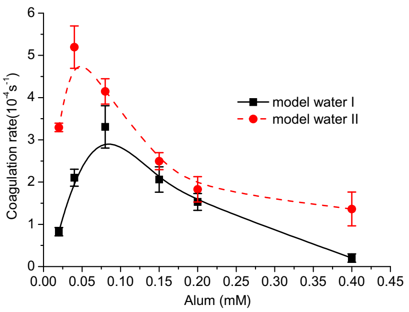
Wen-zheng Yu [a,b,c], John Gregory [b], Gui-bai Li [c], Jiu-hui Qu [a,*]

[a] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China
[b] Department of Civil, Environmental and Geomatic Engineering, University College London (UCL), Gower Street, London WC1E 6BT, UK
[c] State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), School of Municipal & Environmental Engineering, Harbin Institute of Technology, PO 202 Haihe Road, Nangang District, Harbin 150090, PR China

HIGHLIGHTS

- The presence of humic acid promoted the aggregation kinetics at low temperature.
- The optimum dosage of coagulant decreased in the presence of humic acid.
- D_2 was always lower in the presence of humic acid.
- The residual turbidity and small flocs was significantly lower in the presence of humic acid.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 November 2012
Received in revised form 1 March 2013
Accepted 5 March 2013
Available online 13 March 2013

Keywords:
Coagulation
PDA
Kaolin
Humic acid
Fractal dimension
Low temperature

ABSTRACT

In order to discuss the effect of humic acid on improving coagulation performance at low temperature, an optical method was employed to investigate the aggregation kinetics of kaolin with and without humic acid at low temperature using a photometric dispersion analyzer (PDA). Moreover, the fractal dimension (D_2) of the aggregates was obtained by photographic technique coupled with image analysis. The presence of humic acid in the water significantly increased the rate of aggregation at low temperature and caused a decrease in the number of small flocs. It was found that the optimal dosage of coagulant decreased in the presence of humic acid. In the model water with only kaolin, the fractal dimension of flocs with different dosage of alum was nearly the same when coagulation time was longer than 20 min. However, in the presence of humic acid, the fractal dimension of the flocs initially decreased, and then increased with dosage of coagulant, which suggested that median dosage of alum caused looser flocs. Comparing the flocs with and without humic acid, D_2 was always lower in the presence of humic acid, which showed that the coagulation mechanisms for these two model waters were dramatically different. The residual turbidity in the model water with humic acid was significantly lower than that without humic acid, and the optimal dosage of alum was two times lower than that without humic acid. $Al(OH)_3$–humic acid precipitates worked as polymers, which interact with charged particles by bridging flocculation, charge neutralization or other interactions.

1. Introduction

Normally, in order to remove particles and other contaminants from water, coagulation is the most common process. The characteristic of flocs formed in the coagulation are influenced by coagulant type and dosage, mixing intensity and water quality. The size

---

* Corresponding author. Tel.: +86 10 62849160.
E-mail addresses: wzyu@rcees.ac.cn (W.-z. Yu), j.gregory@ucl.ac.uk (J. Gregory), hitliguibai@163.com (G.-b. Li), jhqu@rcees.ac.cn (J.-h. Qu).

1385-8947/$ - see front matter Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.03.008

and structure of flocs influence the efficiency of solid/liquid separation processes, and the characteristics of flocs, change during the coagulation–flocculation process. Fractal dimensions of flocs determined by Kim et al. [1], Lin et al. [2,3] and Oles [4] were contradictory. These results may suggest that changes of fractal dimension of flocs are dependent on mixing pH, coagulant species and raw water quality.

The collision frequency and growth of aggregates depend on the chemical surface of micro-flocs with different dosages and species of coagulant, local shear forces and the suspending electrolyte; while low temperature retards the coagulation effect, which is a real problem in cold regions. It is difficult to treat the surface water with low turbidity at low temperature, such as in the winter of north China. But the literature is limited and contradictory with regard to coagulation at low temperature [5–7]. Compared to single coagulant, the combined coagulants showed superior coagulation performance at low temperature [8]. With the addition of polyelectrolytes as coagulant aids, the coagulation performance is significantly improved at low temperature [9]. Ultrasound can improve coagulation efficiency for low turbidity water at low temperature [10]. Although there were many methods can improve coagulation efficiency, the coagulation mechanism at low temperature has not been explored. Hanson and Cleasby [11] found that the effect of both energy input parameters and flow field characteristics on coagulation performance were insignificant at low temperature. Xiao et al. [12] examined the chemical aspects of coagulation, coagulation rate (CR), and turbidity removal efficiency at low temperature, and identified some mechanisms of slow coagulation at low temperature. The results show that low temperature slowed down the coagulation process as reflected in the decrease in aggregation rate and rate constants [13]. A very important factor is the effect of temperature on Al hydrolysis.

Humic acid is one component of natural organic matter (NOM) in water, also usually NOM determines the dosage of coagulant. Thus it is chosen here by to explore the coagulation mechanism with alum. The mechanism of low coagulation efficiency at low temperature, using a mathematical model will be discussed in another paper. Here the coagulation mechanism in the presence and absence of humic acid at low temperature is explored.

2. Materials and methods

2.1. Materials

Aluminum sulfate hydrate ($Al_2(SO_4)_3{\cdot}18H_2O$; analytical reagent) was used as the coagulant. Stock alum solution was prepared at a concentration of 0.1 M and kept at 4 °C in a refrigerator.

Kaolin clay (Shanghai, China) was used as the model suspension. The stock suspension was prepared in a way similar to that of Yukselen and Gregory [14] and diluted to give a final solids content of 50.0 g/L. The mass mean particle size of kaolin suspension was about 1.3 μm (Mastersize 2000E, Malvern Inc., UK).

Five grams of humic acid (Shanghai, China) was dissolved in 0.1 M NaOH, and mixed with a magnetic stirrer for 24 h. The pH of the filtered solution was adjusted to 7.5 by adding 0.1 M NaOH. The suspension was filtered using a filter paper and by a 0.45 μm membrane filter. The solution was diluted to 1000 mL in a measuring flask and was stored in the dark. Total Organic Carbon (TOC) was measured by high temperature oxidation at 680 °C (SHIMADZU, TOC-V_{CPN}), and the TOC of the stock humic acid solution was found to be about 1.94 g/L.

Two model waters were prepared for flocculation tests. For model water I, the stock suspension was diluted in Harbin tap water, China, to give a clay concentration (16.3 mg/L) with turbidity of 8.0 NTU. For model water II, 5 mg/L of humic acid solution (1.94 mg/L TOC) was added into model water I. Model water II was put aside for 12 h to achieve adsorption equilibrium (less than 5% HA here). Harbin tap water has medium total hardness (Ca. 160 mg/L as $CaCO_3$) and alkalinity (Ca.60 mg/L as $CaCO_3$) and a pH of around 7.7 in winter. The temperature of the water was kept 4 ± 1 °C.

2.2. Apparatus and procedures

2.2.1. Jar test

Experiments on the kinetics of coagulation were performed using the "turbidity fluctuation" technique, as used in the Photometric Dispersion Analyzer (PDA-2000, Rank Brothers, UK). The experimental procedure was similar to that of Yukselen and Gregory [14]. In this method, the average transmitted light intensity (dc value) and the root mean square (rms) value of the fluctuating component are measured. The ratio (rms/dc) is often termed the Flocculation Index (FI) and it provides a sensitive measure of particle aggregation [15]. After the FI value reached an initial steady value, coagulant was added into the model water and the FI value was recorded via a PC computer every 1 s. The stirring speed of the flocculator was set as 400 rpm for 1 min and then 40 rpm for 30 min.

2.2.2. Image acquisition and analysis

As the diameter of the primary particles used in this study was larger than the laser wavelength, the fractal dimension of the flocs was not suitable to be measured by the small-angle light scattering [16,17]. Thus the real-time image analysis technique was used to measure the particle morphology in the stirred jar directly.

The main components of the image-processing system [18], included a computer-controlled digital CCD camera, lighting provided by a strobe light, image acquisition, and image analysis software, as our previous research [19]. The images were obtained from an interrogation window of about 10 mm × 7.5 mm with a resolution of 205 pixels/mm for the present set of experiments. Although the small branches of the flocs were difficult to capture, compared with the method of Chakraborti et al. [18], the field of view was 10 times larger, and it could easily capture more and larger flocs. All data were recorded on the hard drive of a PC and a public domain software package, Scion-image (Scion Corporation), was used to analyze the captured images. The two-dimensional fractal dimension is defined by a power law relation between projected area (A_s) and the characteristic length of the aggregates, l [18,20,21]:

$$A_s \sim l^{D_2} \tag{1}$$

where D_2 is the two-dimensional fractal dimension.

Here real l and real area were substituted with the long dimension (in pixels) and the total pixels in the aggregate image, respectively. Flocs with l value larger than 15 pixels (75 μm) were used for the calculation of fractal dimension, and flocs larger than 2 pixels (10 μm) were used to calculate the average floc size, since smaller flocs are difficult to resolve. The size of a floc is calculated as the diameter of a circle with the same projected area.

2.2.3. Zeta potential and turbidity

The zeta potential of flocs was measured using a zeta sizer (Nano series, Malvern Inc., UK). The residual turbidity was determined by a WTW TURB555IR turbidimeter (Germany).

3. Results and discussion

3.1. Zeta potential of model waters

As shown in Fig. 1, the zeta potential of the flocs increased with dosage of alum. Zeta potential in model water II was lower than that