



Effects of humic acid on recoverability and fractal structure of alum-kaolin flocs

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Abstract

Particle surface characteristics, floc recoverability and fractal structure of alum-kaolin flocs were investigated using *in situ* particle image velocimetry (PIV) and microbalance with or without humic acid. Experimental results indicated that the zeta potential of kaolin particle surface after adsorption of humic acid was related with humic acid concentration and its acid-base buffering capacity. Adsorption of humic acid resulted in more negative electrophoresis on the particle surface. Coagulant dosages for particles to form flocs would increase with increasing humic concentration. PIV was used to evaluate floc structural fragmentation, floc surface erosion as well as recoverability after high shear. It was found that the floc size during the steady phase of growth was small, while the regrowing capability decreased in the presence of humic acid. The recoverability was closely related with floc breakage modes including floc structural fragmentation and floc surface erosion. The fractal dimensions of alum-kaolin flocs by mass-size method based on microbalance would decrease with increasing humic concentration. This study proved that humic acid had adverse influences on the performance of coagulation process.

Key words: humic acid; particle image velocimetry; floc breakage; recoverability; fractal dimension

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Introduction

Coagulation is a critical process used for the removal of turbidity particles and natural organic matter (NOM) at drinking water treatment works (WTWs) (Gao and Yue, 2005; Gregory, 2009). While the major coagulation mechanisms and operational parameter optimization including coagulation dosage, physicochemical and hydrodynamic conditions have been well studied (Gregory, 2006), little thought is given to the physical properties of flocs formed in WTWs, such as floc size, compaction, strength, and recoverability that denotes the potential for flocs to regrow after being broken (Jarvis et al., 2005a, 2005b). Coagulation and sedimentation processes at WTWs are generally designed to minimize floc breakage; however, often in practice this is not the case because most coagulation processes are carried out in agitated suspensions, nearly always under turbulent conditions (McCurdy et al., 2004). It is inevitable that some breakage of flocs will occur in these cases. The capacity to regrow may improve particle removal efficiency at WTWs if broken flocs are subsequently allowed to re-form after being broken. Floc

strength and regrowing capacity after being broken in different flocculated systems have been extensively analyzed in several studies (Francois, 1987; Gregory, 2004; Yukseken and Gregory, 2004; Li et al., 2007). The relative floc strength tests have arisen from the relationship between the applied hydrodynamic shear rate and the resulting floc size (Jarvis et al., 2005a). In these studies, the method of floc size determination is crucial which rely mainly upon taking flocs from the containing vessel and observation using microscopy and image analysis (Wu et al., 2003) or determination by light scattering (Francois, 1987; Spicer et al., 1998; Biggs and Lant, 2000) or from analysis of video frames or photographs using image analysis (Leentvaar and Rebhun, 1983; Bache et al., 1999; Bache and Rasool, 2001; Bouyer et al., 2001). However, it is difficult to imagine that removing flocs in this manner can not damage and break the flocs due to their highly fragile nature. Thus, the nondestructive or nonintrusive technique needs to be developed.

Particles in natural and engineered systems are coated readily with ubiquitous natural organic matter (NOM) (Wilkinson et al., 1997). This occurrence modifies the physicochemical characteristics of the particle surface with the result that interactions between surfaces can be, to

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a large extent, dominated by the presence of an organic adsorbed layer (Kretzschmar et al., 1997; Wilkinson and Reinhardt, 2005), and then have significant influences on the properties of flocs formed, such as floc sizes, floc structure, and settling velocity. Previous research has indicated the importance of the presence of dissolved NOM on the stability of suspended particles. However, few studies have addressed the effect of NOM on mineral particle coagulation and flocs properties (Gibbs, 1983; Kretzschmar et al., 1997; Tirado-Miranda et al., 2003).

The objectives of this article were to investigate the physicochemical characteristics of the kaolin particle surface after adsorption of humic acid, and compare the floc size, capacities to regrow and fractal structures of kaolin flocs in the presence of humic acid using *in situ* particle image velocimetry (PIV) and microbalance.

1 Materials and methods

1.1 Kaolin particle and humic acid

Humic acid (Pahokee Peat, IHSS, USA) was selected as model NOM. Kaolin obtained from Tianjin Fuchen Company (China). Portions of the kaolin (10 g) were mixed with 250 mL ultrapure water (resistance $> 1.82 \times 10^7 \Omega/\text{cm}$, total organic carbon $< 2 \mu\text{g/L}$, Milli-Q, Millipore, USA) and suspension pH was adjusted to 9.5 by 6% NaOH addition, resulting in complete particle dispersion. The clay was soaked in the thermostatic bath at 80°C over night. The size fraction $< 2 \mu\text{m}$ was then separated by centrifugation and redispersion steps. This procedure aimed to remove the impurities and NOM from kaolin particle surface. The $< 2 \mu\text{m}$ fraction was collected and washed five times with 1 mol/L NaCl solutions to saturate the clay with Na^+ . In each washing steps, the clay was allowed to equilibrate for at least 3 hr with 1 mol/L NaCl. The Na-kaolin was washed three times to remove excess salt using ultrapure water.

1.2 Adsorption experiment

Batch experiments were conducted to measure the adsorption of humic acid on kaolin particles as a function of ionic strength and pH. Solutions containing kaolin particles and humic acid (concentration ranging between 0–10 mg/L) were equilibrated for 24 hr by agitation in a shaking incubator at 150 r/min at $(25.0 \pm 0.1)^\circ\text{C}$. The NaCl concentration varied between 10^{-3} and 0.05 mol/L, and pH was held constant at 7.05 using a 10^{-4} mol/L NaHCO_3 buffer. In a further series of experiments, the pH ranged from 5 to 9 while the NaCl concentration kept at 0.01 mol/L.

For the adsorption of humic acid on kaolin particles, 0.1 g kaolin particles were added to the 100 mL solution containing humic acid. After agitation and centrifugation, a 20 mL aliquot of the supernatant was collected for the measurement of total organic carbon (TOC) using TOC analyzer (Model Vcsh, Shimadzu, Japan).

1.3 Zeta potential

The zeta potentials of kaolin particles in solutions with NaCl concentration up to 0.05 mol/L were measured using a laser zeta potential analyzer (Model Delsa 440SX, Beckman Coulter Inc., USA). The calibration of the apparatus was tested using a colloidal reference material supplied by Beckman Coulter (USA). For a jar-test run, a suspension sample of 10 mL was extracted from each beaker for zeta potential measurement after the coagulant addition and rapid mixing at 100 r/min for 1 min.

1.4 Coagulation and floc recoverability experiments

A suspension of 10 mg/L kaolin was made for coagulation experiments at constant pH 7.05 using 10^{-4} mol/L NaHCO_3 buffer. The concentration of humic acid introduced into suspension ranged from 0–10 mg/L.

Flocs were formed by performing a series of jar tests. A ZR-6 variable speed jar tester (Zhongrun Water Ltd., China) was used with flat paddle impellers (76 mm \times 25 mm) and rectangular jars (80 mm \times 80 mm \times 200 mm) containing 1 L samples of each suspension. Coagulation procedure involving alum was carried out as follows: a rapid mix at 200 r/min for 1 min, a slow stir phase at 20 r/min for 30 min, followed by a breakage phase at 100 r/min. Two separate breakage periods were investigated: (1) a long breakage period of 15 min and (2) a short breakage period of 30 sec. After the breakage phase, a slow stir at 20 r/min was reintroduced for a further 30 min.

An *in situ* PIV system was employed to track the change in particle size distribution (PSD) during floc formation, breakage and regrowth. As a non-intrusive optical setup, the PIV was able to record the image of particles in a jar-test beaker within a millisecond (Fig. 1). The PIV system consists of a laser source (600 nm in wavelength, Coherent, USA), a high-speed CCD video camera (Imaging 1200 hs with a resolution of 1280×1024 pixels, PCO, Germany), a process control (Camware, PCO, Germany) and image processing software package (Scion Image, Scion, USA). More than 20 consecutive images were analyzed to produce a size distribution of the particles, and the result was presented as a volume-based discrete PSD.

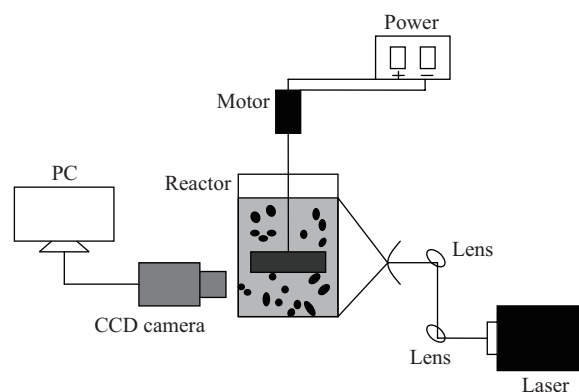


Fig. 1 Schematic diagram of particle image velocimetry setup.

1.5 Determination of fractal dimension

Since Mandelbrot introduced the concept of fractal theory in the 1970s, the application of fractal geometry is now a well-established means of describing the complicated structure of aggregates (Wang and Tang, 2001; Jin and Wang, 2004; Chang et al., 2005; Li et al., 2006; Mu et al., 2008; Wang et al., 2009). Floc aggregates formed at WTWs are fractal that can be characterised by a fractal dimension. The mass of floc aggregates scales with their size according to Eq. (1):

$$m \propto l^D \quad (1)$$

where, m (μg) is the floc dry mass; D (dimensionless) is the mass fractal dimension; l (μm) is the characteristic length, $l = (4A/\pi)^{1/2}$, where A (μm^2) is the projected area. For an Euclidean structure, $D = 3$; while for fractal aggregates, $D < 3$: the fractal dimension can be found from the slope of a log-log plot of the dry mass based on the microbalance (Model AEM 5200, Labror, Shimadzu, Japan) and floc size.

2 Results and discussion

2.1 Changes in surface characteristic of kaolin

The results of the adsorption experiments conducted with kaolin particle as a function of ionic strength (Fig. 2a) and as a function of pH (Fig. 2b). Adsorption of humic acid on kaolin followed similar trends and fit well with Langmuir isotherms.

$$\Gamma = \frac{\Gamma_{\max} b C}{1 + b C} \quad (2)$$

where, Γ (mg C/g) is the adsorbed amount, C (mg C/L) is the measured concentration of humic acid in solution at equilibrium, Γ_{\max} (mg C/g) is the adsorbed amount forming the complete monolayer on the surface, b (L/mg C) is an equilibrium constant related to the energy or net enthalpy of adsorption.

The adsorbed amount of humic acid on kaolin surface increased with increasing ionic until a plateau was reached. It also increased with increasing humic acid until a plateau was reached in correspondence with a low residual humic acid solution concentration of about 1 mg C/L for 0.01 and 0.05 mol/L NaCl. Under all chemical conditions, there was adsorption of humic acid on kaolin particle at > 1 mg C/L humic acid, which is the concentration level used in the coagulation and floc recoverability experiments. Few studies have reported the adsorption of humic acid on kaolin as a function of pH (Akbour et al., 2002; Balcke et al., 2002; Ghabbour et al., 2004). It was observed that the uptake of humic acid increased with decreasing pH.

The results of zeta potential reported in Fig. 3 clearly show a shift from positively charged surface to negatively charged surface at $\text{pH} < 7$ independently of ionic strength, and toward more negatively charged surface at $\text{pH} > 7$ in the presence of 1 mg C/L humic acid, consequently resulting in a higher energy barrier. Zeta potentials of kaolin keep stable at > 1 mg C/L humic acid concentration (data not show). It is believed that the changes in zeta potential of humic-coated kaolin particle resulted from the acid-base buffering capacity of functional groups on humic acid and the extent of adsorption saturation. These demonstrated that surface charge types were controlled by the adsorbed layer of humic acid on kaolin particle.

The observed trends of humic acid adsorption on kaolin are considered to be mostly the result of coulombic, chemical, and hydrophobic interactions (Chan et al., 1998; Lin et al., 2005) between kaolin particle and humic molecules, kaolin surface speciation, and the speciation of humic acid in the solution (Wilkinson and Reinhardt, 2005). All of these are functions of the solution chemistry. The adsorption of negatively charged humic on a negatively charged kaolin particle surface suggests that the driving force for adsorption is other than electrostatic. This type of adsorption has been often attributed to specific (non-Coulombic) chemical interactions (e.g., ligand exchange and hydrogen bonding), or hydrophobic interaction between functional groups on humic acid and surface sites

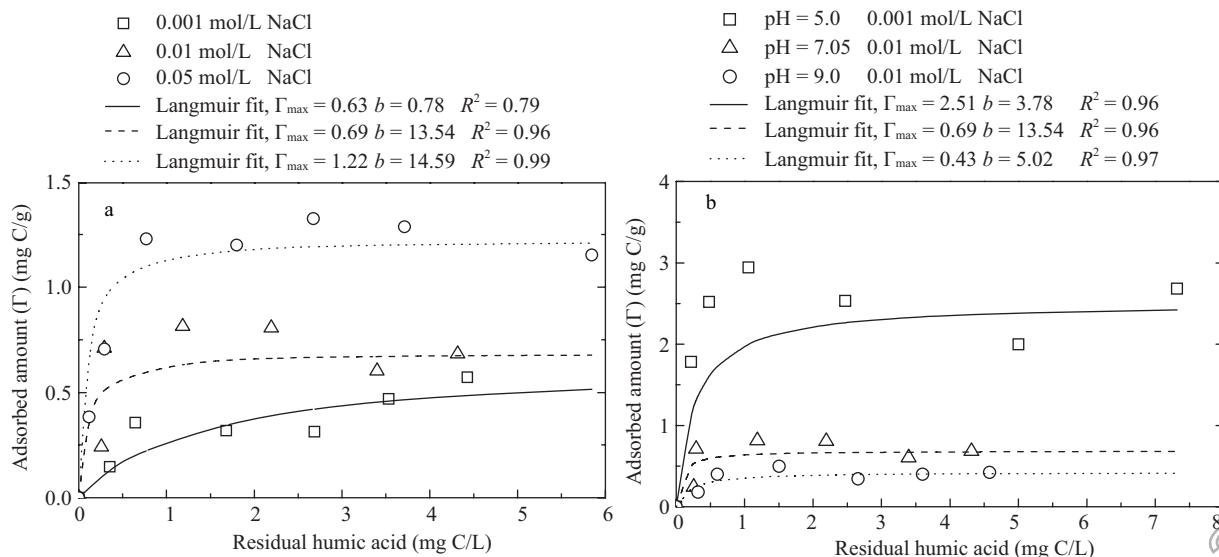


Fig. 2 Effects of ionic strength (a) and pH (b) on the adsorption of humic acid on kaolin particle.

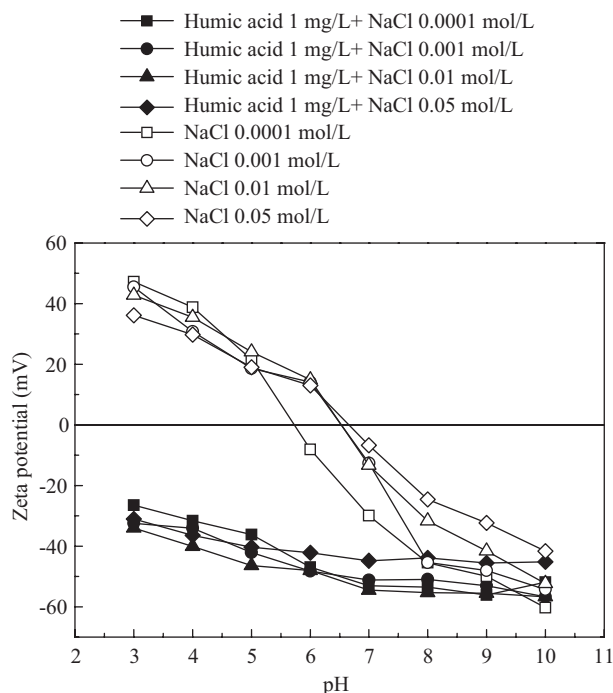


Fig. 3 Effects of ionic strength and humic acid (1 mg/L) on zeta potentials of kaolin particle.

on kaolin particles (Israelachvili, 1982). As the ionic strength increases, or pH decreases, the charge screening of the functional groups on the kaolin particle surface and humic acid increases, resulting in the reduction of electrostatic repulsion, thereby enhancing adsorption. As the electrostatic repulsion between kaolin and humic acid decreases, humic acid can easily come into contact with the surface. More importantly, the decreased electrostatic repulsion between humic acid molecules and between the functional groups on the same molecule reduce the lateral repulsion within and between adsorbed chains and allows adsorbed loops and tails to extend further into the solution which allows for a larger adsorbed amount.

2.2 Turbidity removal and zeta potential during coagulation

Through standardized jar testing procedures, it was found that the optimum alum dosage increased from 10 to 20 mg/L based on dissolved organic carbon removal and settled turbidity while humic concentration increased from 0 to 3 mg C/L (data not show). The results of zeta potential of kaolin particle after alum addition are shown in Fig. 4. The zeta potential of uncoated kaolin particle was -30 mV while those of coated kaolin particles shifted toward more negative to -50 mV. After alum addition, the alum dosage to neutralize the surface charge on kaolin particle increased with increasing humic concentration. At the same time, the surface charges on uncoated kaolin particle were gradually neutralized with the result that the zeta potentials of uncoated kaolin particle increased to about 0 mV and the coagulation happened at the 10 mg/L alum. It is believed that the coagulation mechanism is mainly charge neutralization. However, it was found that the zeta potential is -19.5 mV when the turbidity started to be removed to 1.2 NTU at 20 mg/L alum

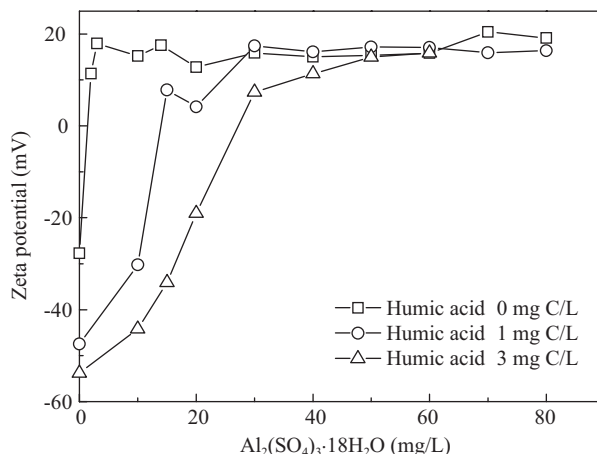


Fig. 4 Effects of humic acid on zeta potential in the coagulation experiments.

and 3 mg/L humic acid. The surface charges were not neutralized at all. The coagulation rates of kaolin particle in the presence of humic acid were faster than that in the absence of humic acid (Fig. 5). It is believed that the coagulation mechanisms of coated kaolin particle is mainly sweep flocculation according to higher alum dosage, faster coagulation rate and increasing alkalinity resulting from humic acid (Gregory, 2006). The removal of humic acid was attributed to the adsorption on kaolin particle and hydroxide precipitate at pH 7.0.

2.3 Floc size and floc recoverability

After the slow stir phase, alum-kaolin flocs had reached a d_{50} floc size of 1475 μm (Fig. 5) for 0 mg C/L humic acid. This was approximately double the size of the alum-kaolin-humic (10 mg C/L) flocs. In all cases, floc size was immediately reduced with an increase in humic acid concentration. The d_{50} size of the flocs after 15 min exposure to high shear was 233 μm for 0 mg C/L humic acid while the flocs were broken into smaller floc sizes of around 114 μm for 10 mg C/L humic acid. As the shear

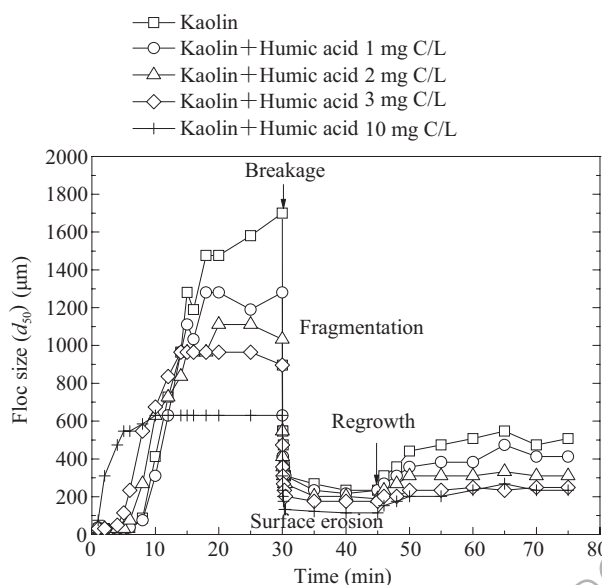


Fig. 5 Flocs sizes during growth-breakage-regrowth process in 15 min breakage.

was reduced again, the flocs begin to regrow; however, the alum-kaolin-humic flocs could not regrow to anywhere near their previous size in all cases. The floc sizes reform to one fourth or one third of initial size known as irreversible breakage. This behavior is different from reversible breakage observed during cyclical breakage and regrowth of activated sludge flocs and latex (Spicer et al., 1998; Chaignon et al., 2002; Jarvis et al., 2005b). For the coagulation of kaolin particles, alum flocs have been shown to have the poorest regrowth, reaching only a third of their previous size after shear, and the extent of recoverability has been seen depending upon the coagulant under investigation and the coagulation mechanism (Jarvis et al., 2005a, 2005b).

The effect of reducing the period of exposure to high shear is shown in Fig. 6. The extent of floc breakage at the reduced shear period of 30 sec was much similar with that at long shear of 15 min for all of the humic acid concentration. At the short shear time, floc regrowth was seen to improve considerably. The alum-kaolin flocs with coagulation mechanism of charge neutralization almost reached the initial size with the floc size of 1280 μm . This behavior is similar with that of latex aggregates formed at a low velocity gradient in salt solutions. The floc sizes re-formed after breakage at high shear decreased with increasing humic acid concentration resulting in a decreasing regrowing capability. It is believed that the differences in floc sizes resulted mainly from steric repulsion between kaolin particles coated with humic acid with the result that the particle can not easily come into contact together (Abu-Lail and Camesano, 2003; Wilkinson and Reinhardt, 2005; Gregory, 2006).

The differing degrees of floc recoverability at long and short shear times were related with the breakage modes. The breakage modes have been classified as surface erosion and large-scale fragmentation. Surface erosion is the removal of small particles from the floc surface resulting in an increase in the small particle size ranges, such as

after 30 sec breakage in Fig. 5. Large-scale fragmentation is the cleavage of flocs into pieces of a similar size without an increase in primary particle concentration, such as during 30 sec breakage in Fig. 5. The breakage modes can be identified by the changes in floc sizes recorded continuously by *in situ* PIV technique with the result that large-scale fragmentation was the main breakage modes at short shear time while large-scale fragmentation and surface erosion coexisted at long shear time. By comparison with the floc sizes after breakage at various shear time, the recoverability of floc at short shear time (large-scale fragmentation) was higher than that at long shear time (large-scale fragmentation and surface erosion).

2.4 Floc structural analysis

In this study, the degree of floc compaction was measured by fractal dimension analysis. The derivation of floc fractal dimension from the power function of dry mass and characteristic length is shown in Fig. 7 for alum-kaolin flocs after 30 min slow stir when the flocs had reached their maximum steady-state size. A total of 15–36 alum-kaolin flocs generated in the coagulation experiments were successfully withdrawn and analysed. The fractal values of alum-kaolin flocs were in the region of 1.7–1.9 for the coagulants under investigation based on the slope of the logarithmic relationship between the dry mass and size. It was proved that the decreased fractal dimension led to the decreasing floc settling velocity in previous study (Zhong et al., 2009). In the meantime, the decreased fractal dimension of alum-kaolin flocs with increasing humic acid concentration indicated that the sweep flocculation gives rise to more loose structures. This does not agree with findings for latex aggregates in the KBr and surfactant system (Tirado-Miranda et al., 1999), which show a trend that charge neutralization leads to an increase in fractal dimension in the presence of organic matter. It seems highly likely that a portion of adsorbed humic acid within alum-kaolin floc should involve in reaction with Al^{3+}

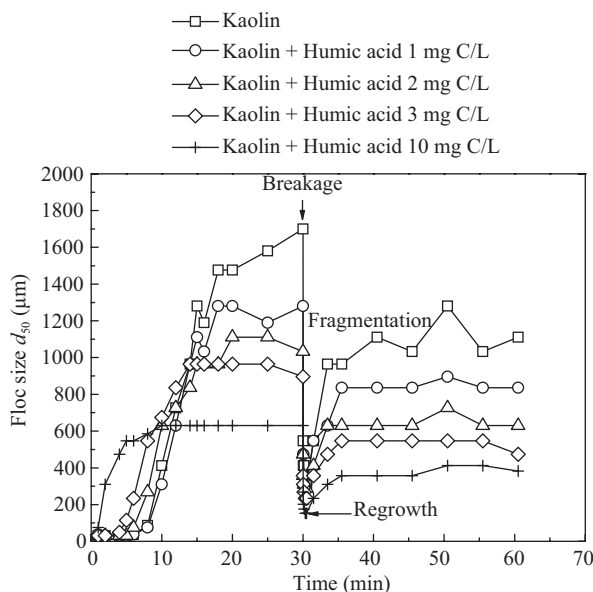


Fig. 6 Flocs sizes during growth-breakage-regrowth process in 30 sec breakage.

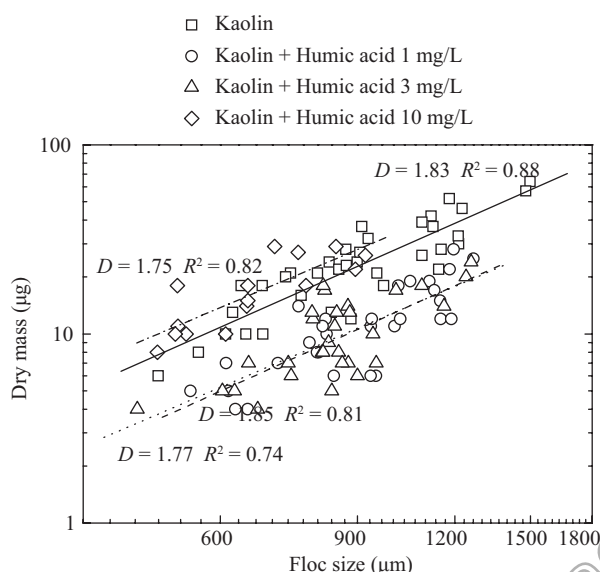


Fig. 7 Fractal dimensions of alum-kaolin flocs at various humic concentrations.

to form the network structures, leading to more loose structures, and the others of adsorbed humic acid should provide increased repulsion, leading to decreasing floc sizes.

3 Conclusions

(1) Surface characteristics of kaolin particles were controlled by adsorbed layer of humic acid. The adsorbed amount of humic acid on kaolin surface increased with increasing ionic strength and decreasing pH. The adsorption of humic acid on kaolin particle resulted in more negatively charged surface. (2) The optimum alum dosage increased from 10 to 20 mg/L with increasing humic acid concentration. The coagulation mechanisms were mainly charge neutralization for kaolin only and sweep flocculation for kaolin and humic acid. (3) PIV was able to identify the breakage modes and continuously record the floc size as a non-intrusive tool. The stable floc sizes of alum-kaolin flocs decreased with increasing humic acid concentration from 0–10 mg/L. Floc recoverability depended on the breakage modes and humic acid concentration. (4) The fractal dimensions of alum-kaolin flocs decreased with increasing humic acid concentration resulting in smaller settling velocity.

Acknowledgments

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