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Fractal characteristics of Al-humic flocs

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ABSTRACT

The characteristics of Al-humic flocs were studied through a series of experiments using microscopic and online optical monitoring techniques. It was verified that Al-humic flocs are of fractal nature and the two-dimensional fractal dimension D_2 derived from image analysis characterizes their morphological properties. At pH 5.0, the structure of Al-humic flocs formed was more compact with higher fractal dimension of 1.43 than that formed at pH 7.0 with lower fractal dimension of 1.17. The difference in floc structure was considered to be related to the different characteristics of hydrolysis and precipitation of aluminum sulfate under these two typical pH values: at pH 5.0 with a low alum dose, the products of aluminum hydrolysis are mainly soluble, while at pH 7.0 at the same alum dose, precipitates form quickly. Alum dose also affected the structure of Al-humic flocs. At pH 5.0 and at a dose to bring about charge-neutralization to $|\zeta| < 10$ mV, flocs formed are more compact with a fractal dimension ranging from 1.43 to 1.49, while at a higher dose when hydrolyzed aluminum precipitates form, flocs are more open and looser with a much lower fractal dimension. During growth, the fractal dimension of the flocs decreased gradually until an equilibrium state was reached. This implies a faster increase of floc volume than the number of primary particles the floc contains.

Keywords: Coagulation; Humic acids; Al-humic flocs; Online monitoring; Fractal dimension; Image analysis

1. Introduction

Coagulation is the most important unit process in water and/or wastewater treatment that brings about aggregation of colloidal particles to form settleable and filterable flocs. The size and the structure of the flocs significantly affect the efficiency of a number of unit processes after coagulation, such as sedimentation, floatation, filtration and sludge dewatering. Fundamental studies on the characteristics of flocs can be traced back to the model of ballistic aggregation proposed [1]. Later on, Lagvankar and Gemmell found an exponential relationship between the density of aluminum hydroxide flocs and their size following Vold's basic theory with comparison with experimental findings [2]. Sutherland pointed out that the ballistic aggregation model would not apply to the aggregation of the particles having certain size distribution and suggested a cluster aggregation model [3], which resulted in flocs with much more open structure than that from the ballistic aggregation model. In the 1970s, sophisticated theoretical and experimental studies were further conducted on the physical properties of flocs. Goodarz-Nia carried out computer simulation of the flocculation process by introducing a

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void ratio into the floc structure and established the concept of multilevel structures of particle aggregation [4]. Based on experimental measurement of floc size and settling velocity, Tambo and Watanabe proposed a floc density function which revealed an exponential decrease of floc density with the increase of aggregate size [5].

A great contribution to the theory of floc structure was made in the early 1980s by Mandelbrot who introduced the basic idea of fractal geometry [6]. The fractal theory provided a completely new theoretical approach to the study on the structure of activated sludge, bacteria growth, aggregation of suspended particles and kinetic studies of flocculation [7]. In a fractal geometrical system, the structure of an object can be characterized by its fractal dimension which, in the case of particle aggregation, indicates the degree of the occupation of the embedding space by the particles comprising the aggregates. A number of studies demonstrated that the fractal dimension would be affected by shearing force and the coagulant dose during flocculation [8]. In general, when an aggregate is formed by the action of a unique mechanism, for example, diffusion limited aggregation, a single fractal dimension is sufficient to characterize its interior structure. However, aggregates occurring naturally may have multilevel structure [9], and the flocs can exhibit different structures. In this case, two or more fractal dimensions can thus be required to characterize the floc structure. Studies on the activated sludge flocs suggested that the differences in the fractal dimension would be due to various types of intermolecular interactions such as DLVO-type interactions, bridging of extracellular polymeric substances by means of divalent and trivalent cations and hydrophobic interactions [10]. Many progresses have been made regarding characterization of the structure of both inorganic and organic aggregates and it has been observed that such particle assemblages often appear to exhibit mass fractal properties.

For coagulation and flocculation as unit process in water treatment, most of the studies so far conducted are dealing with the aggregation of inorganic colloids such as clay particles under the action of metal coagulants. One of the fundamental approaches in modeling the aggregation process is to take the inorganic particles as basic elements (primary particles) to form flocs. Regarding coagulation of dissolved organic matter, for example, humic substances (HS) as typical natural organic matter in surface water [11], few studies have so far been conducted especially dealing with the morphological characteristics of metal-humic flocs. Because there are originally no primary particles in the solution containing dissolved HS, the interaction between the metal salt (coagulant) and the HS molecules are much different from the interaction between the metal salt and inorganic particles. This in turn affects the morphological characteristics of flocs finally formed. In order to gain knowledge on the physical and morphological aspects of the metal-humic flocs, this paper presents an experimental study using aluminum sulfate (alum) as coagulant for the flocculation of HS. The structure of Al-humic flocs are characterized by using microscopic and online optical monitoring techniques.

2. Materials and methods

2.1. Raw water

The HS for this study were isolated from lake surface sediments in Xi'an, China. Firstly the collected sediment was dissolved in sodium hydroxide (NaOH) solution at $pH > 12$ for 24 h, and then hydrochloric acid (HCl) was added to let the solute precipitate at $pH < 1$ for another 24 h. The precipitates so obtained are humic acids [12]. Raw water for the experiment was prepared by dissolving the isolated HS in distilled water. The dissolved solution was then filtered by a 0.45 μm membrane filter to remove the suspended matter. According to liquid chromatographic analysis, the molecular weight of the dissolved organic matter in the raw water was estimated as several hundred to twenty thousand Dalton which is believed to be representative of natural humic matter in surface waters. Further information on the MW (molecular weight) analysis of the extracted HS is provided in the authors' former paper [13].

2.2. Experiment setup and procedure

Fig. 1 shows the experimental setup for this study. The system consists of a cubic jar equipped with a speed-adjustable stirrer, a flocculation monitor (PDA2000, Rank Brothers, UK) with a peristaltic pump, a microscopic camera, and a personal computer with data acquisition units. In each experimental run, the jar stirrer was filled with 800 ml of raw water with an initial dissolved organic carbon (DOC) concentration as 10 mg l^{-1} or UV absorbance at 254 nm (UV_{254}) as 0.15 cm^{-1}. 0.1 mol l^{-1} HCL and NaOH was used for adjusting the pH required ($pH = 5.0$ and 7.0). Sodium bicarbonate ($NaHCO_3$) solution was pre-injected at a dose of 10 mg l^{-1} for adding alkalinity to 1 mmol l^{-1}. Aluminum sulfate

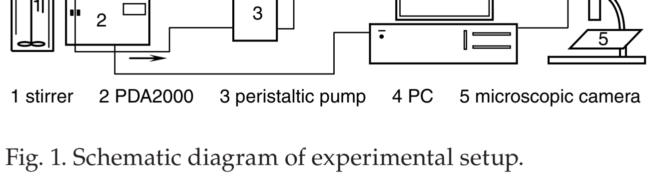

Fig. 1. Schematic diagram of experimental setup.

($Al_2(SO_4)_3 \bullet 18H_2O$) was added at required dose, together with a predetermined amount of 0.1 mol l^{-1} NaOH solution to restore the pH to the required value (pH = 5.0 and 7.0). The approximate dosage of NaOH was determined through calculations and then the deviation was reduced through experiments. The stirrer was operated at preset condition as: rapid mixing (200 rpm) for 1 min, slow mixing (20 rpm) for 30 min and quiescent settling for 60 min. Water temperature was kept at about 25°C.

Zeta potential of the destabilized suspension was analyzed at the end of rapid mixing using a ZC-2000 zeta potential analyzer (Microtech Nichion Co., Japan). At given intervals, a small amount of the suspension was gently collected from the jar using a glass tube of 3.5 mm inner diameter, and then moved on to a cell mounted on the microscopic camera for image analysis of the particles in the suspension. Because the sampling tube was sufficiently large and the cell was previously filled with distilled water, no breakage or further growth would happen with the sampled particles during image analysis under careful operation.

2.3. Image analysis

With the picture of flocs captured by the microscopic camera connected to the PC, the diameter and fractal dimension of the flocs were obtained by image analysis using a computer program. Firstly the projected area of each floc was measured, and then the diameter of the equal-circle-area was calculated. For evaluating the fractal dimension at each sampling time, the maximum length of each particle appeared on the picture was also measured. According to the theory of fractal geometry [6], there exists a relation between the projected area A and the maximum length L as:

$$A \propto L^{D_2} \tag{1}$$

where D_2 is the two-dimensional fractal dimension ($D_2 = 2$ for non-fractal objects). By plotting A against L on a logarithmic paper, D_2 was evaluated from the slope of the linear relationship.

3. Results and discussion

3.1. Morphological characteristics of Al-humic floc at pH 5.0 and 7.0

Figs. 2 and 3 shows the relation of projected area A of the flocs with their maximum length L on logarithmic coordinates where the fractal dimension of flocs was derived, together with the images of typical flocs after 30 min mixing at two pH values. Through a series of

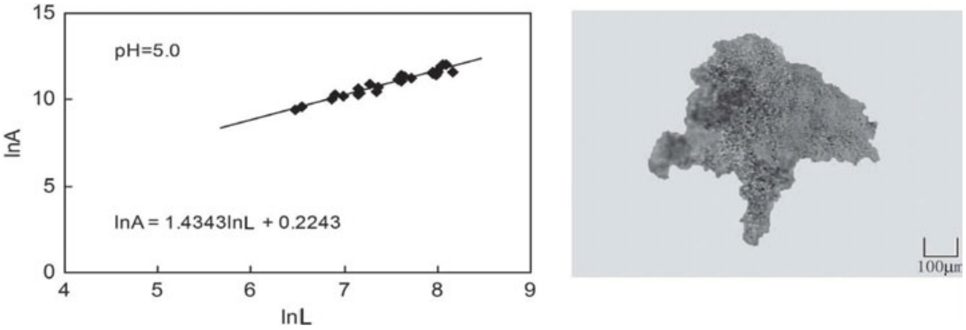

Fig. 2. Morphological characteristics of Al-humic floc at pH 5.0.

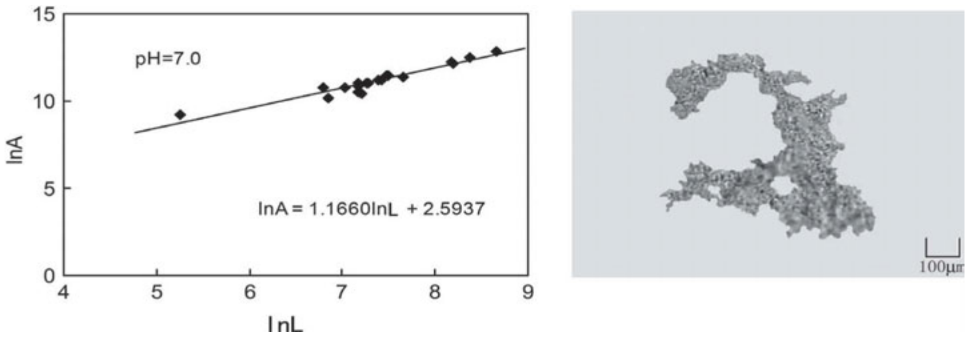

Fig. 3. Morphological characteristics of Al-humic floc at pH 7.0.

the coagulant dosing experiments and in the same high organic matters removal condition, the alum dose was 0.17 mg-Al mg^{-1}-TOC (the initial value of TOC equal to the value of DOC mentioned above) at pH 5.0 and 0.68 mg-Al mg^{-1}-TOC at pH 7.0, both being the optimum doses under the given pH values. As can be seen from these figures, the flocs formed at pH 5.0 appear more compact with a fractal dimension of 1.43, while those at pH 7.0 appear looser and more porous with a lower fractal dimension as 1.17.

3.2. Characteristics of aluminum precipitation at pH 5.0 and 7.0

In order to understand the action of aluminum coagulant at pH 5.0 and 7.0, the process of hydrolysis and precipitation of aluminum ions was monitored using the PDA2000 device with alum being dosed to a "HS free" solution and jar-tester being operated following the procedure described in Section 2.2. In this way the "flocs" monitored by the device are in fact precipitates of hydrolyzed aluminum. As shown in Fig. 4, the output signal of the PDA2000 device is expressed as flocculation index (FI curve), and the variation of the FI curve with mixing time reveals the process of aluminum hydrolysis and precipitation [11]. At pH 5.0 with a low alum dose of 2.7 mg-Al l^{-1}, no precipitated aluminum particles are detected in the whole period of agitation. As alum dose increases to 5.4 mg-Al l^{-1}, slight increase of the FI value is noticed after mixing for 20 min, indicating the formation of small particles of aluminum precipitates. Contrarily, at pH 7.0 with a low alum dose of 2.7 mg-Al l^{-1}, formation of tiny particles is noticed from the beginning of mixing and after 10 min particle growth becomes more apparent. At higher alum dose of 5.4 mg-Al l^{-1}, larger aluminum precipitate form quickly.

3.3. Mechanism of aluminum precipitation and flocculation

As alum is added to a solution, the Al^{3+} ions will be hydrolyzed to form various species. This process depends on both Al^{3+} concentration and pH of the solution. Generally speaking, at lower pH the main hydrolyzed species of aluminum will be less polymerized ones such as Al^{3+} and Al(OH)$^{2+}$ with higher electric charge density. In this case, almost no precipitates can be detected (alum dose 2.7 mg-Al l^{-1} and pH = 5.0 in Fig. 4) unless alum dose is doubled and mixing lasts for longer time (alum dose 5.4 mg-Al l^{-1} and pH = 5.0 in Fig. 4). At higher pH, precipitated aluminum hydroxides such as amorphous Al(OH)$_3$ will form easily. In this case, precipitates appear quickly (alum dose 2.7 mg-Al l^{-1} and pH = 7.0 in Fig. 4) and large "alum flocs" are detected as alum dose is doubled (alum dose 5.4 mg-Al l^{-1} and pH = 5.0 in Fig. 4). We estimate that the formation duration of the alum flocs is in proportion to the coagulant dosage, beacase it is easier for alum ions to aggregate, if the amount of the alum ions increase [14].

It is believed that at pH 5, charge-neutralization and co-precipitation will be the main interactions between the highly-charged soluble aluminum species and HS molecules, while at pH 7 adsorption or sweep flocculation will occur between the precipitated aluminum hydroxides and HS molecules [15]. The former case results in Al-humic flocs with more compact structure (Fig. 2) and the latter case results in Al-humic flocs with more open structure (Fig. 3). Gorczyca and Ganczarcayk reported similar results when they used alum and an organic polymer to coagulate mineral suspensions [16]. They measured the fractal dimension of flocs (two-dimensional) as about 1.8 and 1.6 at pH 5.3–6.3 and pH 7.5 respectively. Chakraborti et al. [17] and Li and Ganczarczyk [18] also noticed the difference in the morphological characteristics between flocs formed by charge neutralization and sweep flocculation.

3.4. Effect of alum dose on the structure of Al-humic flocs

It is found that compaction rate of the flocs will increase with the increasing dosage of coagulant and then decrease at pH 5.0. Moreover, this phenomenon will not occur at pH 7.0. Therefore, a series of

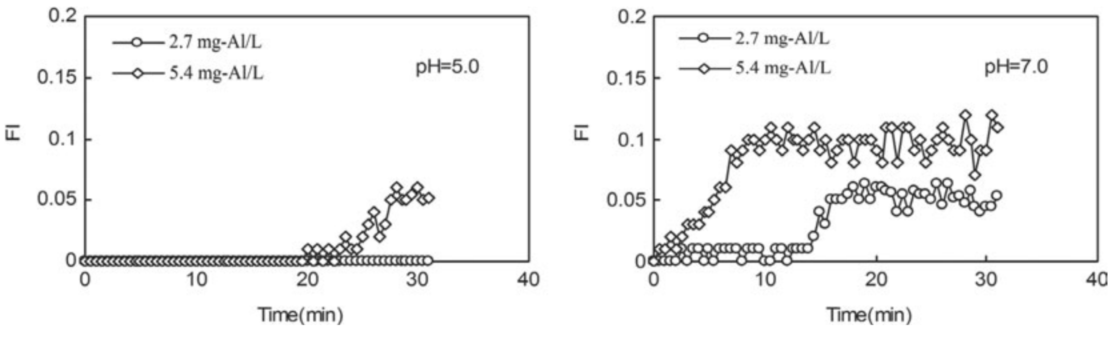

Fig. 4. FI curves of Al hydrolysis at pH 5.0 and 7.0.

experiments was conducted for investigating the morphological characteristics of Al-humic flocs under different alum doses at pH 5.0. As shown in Fig. 5, with lower alum dose from 0.07 to 0.27 mg-Al mg^{-1}-TOC, the fractal dimension of flocs estimated from the lnL–lnA plot ranges from 1.43 to 1.49, while as alum dose increases to 0.54 and 0.68 mg-Al mg^{-1}-TOC, the estimated fractal dimension decreases to 1.31 and 1.22, respectively, showing a tendency for flocs to become more open in their structure with increasing alum dose. The image of typical flocs (Fig. 5) also provides evidence of the change in floc structure.

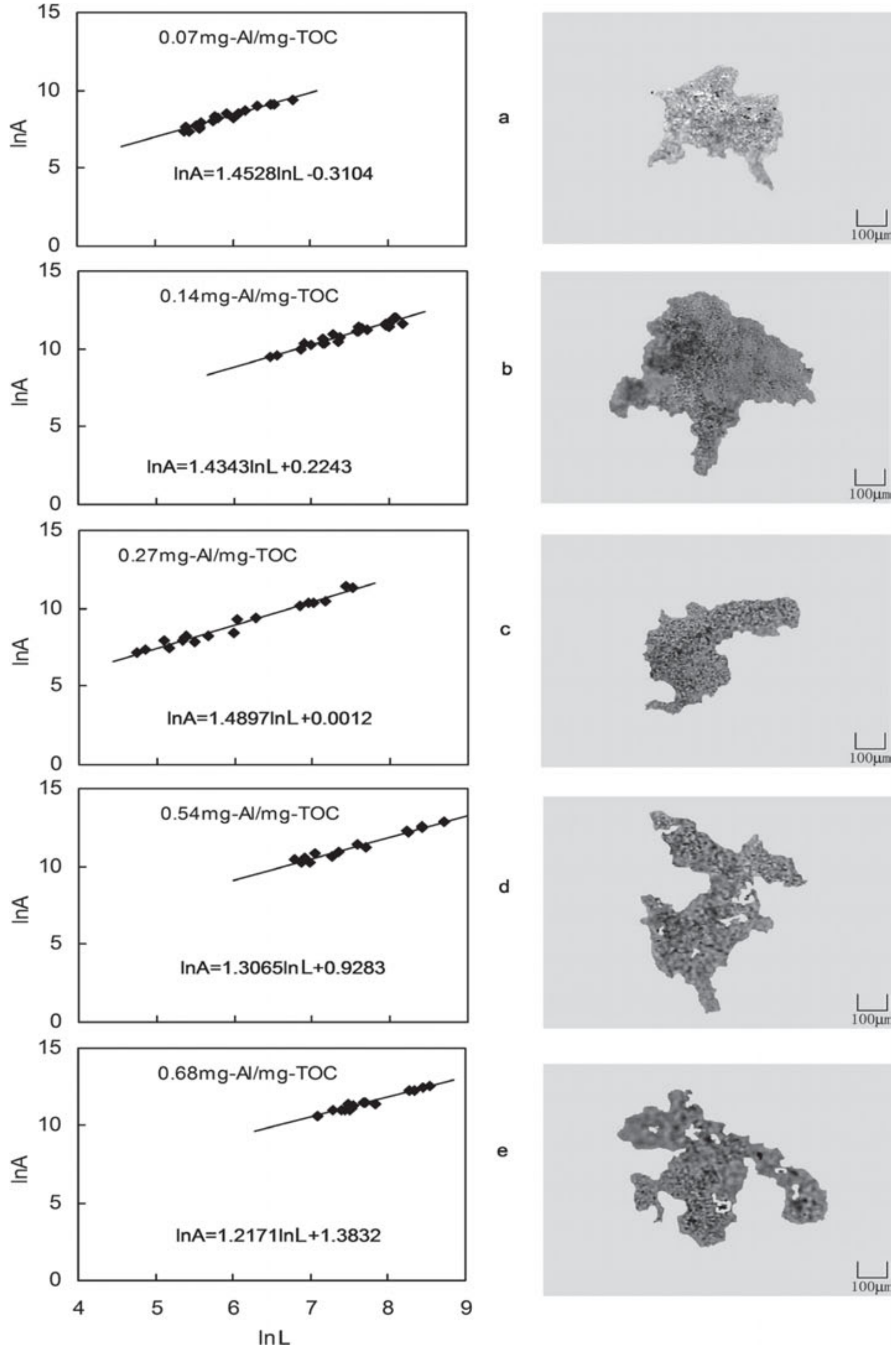

Fig. 5. Effect of alum dose on Al-humic flocs at pH 5.0.

The zeta potential of the Al-humic flocs formed under each alum dose was measured and the result is shown in Fig. 6. The original ζ value of the HS is about −27 mV. As alum dose increases, charge neutralization occurs and the ζ value increases. The alum dose to attain a complete charge neutralization, that is, ζ = 0 is about 0.17 mg-Al mg^{-1}-TOC. As alum dose further increases, charge reversal occurs and ζ value turns to be positive. It finally reaches a value about 15 mV at an alum dose over 0.5 mg-Al mg^{-1}-TOC. Comparing this result with the fractal dimension and floc image shown in Fig. 5, it is understood that a compact structure of Al-humic flocs is attainable at an alum dose corresponding to $|\zeta| < 10$ mV (a, b and c in Fig. 5). In this range, charge neutralization and co-precipitation may play the main role in bringing about Al-humic coagulation. As alum is overdosed there is an apparent decrease in the fractal dimension of Al-humic flocs (d and e in Fig. 5). From the appearance of the flocs and the ζ value measured, it is considered that sweep coagulation may play the main role in Al-humic coagulation at high alum dose. In this case, Al-humic flocs formed are more open and looser in their structure.

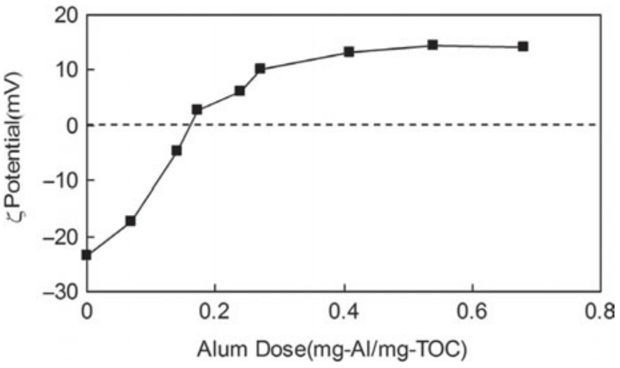

Fig. 6. Variation of zeta potential at different alum dosage.

3.5. Dynamic properties of Al-humic flocs

Under the condition of alum dose as 0.17 mg-Al mg^{-1}-TOC at pH 5.0, continuous measurement of floc diameter and fractal dimension was conducted during the 30 min mixing for flocculation. As shown in Fig. 7, the average diameter of flocs d_f increases quickly in the first 10 min and almost reaches an equilibrium size about 0.4 mm after 15 min stirring time. The fractal dimension of the flocs D_2 at the beginning is about 1.8 and it decreases gradually as floc size d_f increases. When d_f approaches its equilibrium value, D_2 reaches its final value as about 1.4.

The above mentioned result indicates an interesting fact that the structure of Al-humic flocs undergoes a significant change during their growth. Similar phenomena have also been noticed in Chakraborti's experimental study of flocculation of an initially monodisperse suspension of latex microspheres [19]. He found the two-dimensional fractal dimension of the flocs formed ranging from 1.94 to 1.48 corresponding to the compactness of floc structure, and pointed out that a change in fractal dimension would be associated with particle growth accompanied with a change in floc morphology. Wu et al. investigated the structure of kaolinite clay sludge and activated sludge using light-scattering and free-settling methods [9]. They noticed a change in the fractal dimension of the aggregates, and suggested that naturally occurring aggregates possess a multilevel structure.

The mass M of a floc with fractal geometry is related to its characteristic length L and can be expressed as:

$$M = cL^{D_3} \quad (2)$$

where D_3 is the three-dimensional fractal dimension of the floc and c is a coefficient.

Let's go back to the Euclidean geometric system where the volume of the floc V is:

$$V = aL^3 \quad (3)$$

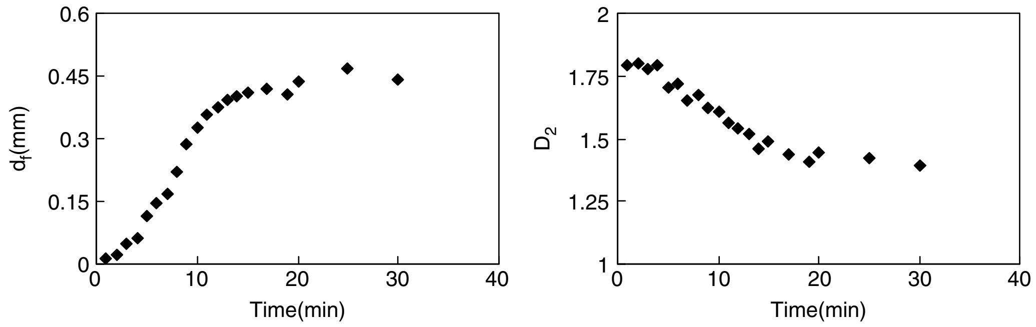

Fig. 7. Variation of average diameter and fractal dimension with time.

where a is the shape factor of the floc (for a spherical particle $a = \pi/6$). Assuming that the floc contains N primary particles with a shape factor b and characteristic length L_0, the void ratio of the floc ε can be written as:

$$\varepsilon = \frac{V - V_0}{V} = \frac{aL^3 - NbL_0^3}{aL^3} = 1 - N\frac{b}{a}\left(\frac{L_0}{L}\right)^3 \tag{4}$$

If the density of the primary particle is ρ_0, then the density of the floc ρ can be written as:

$$\rho = (1 - \varepsilon)\rho_0 = N\frac{b}{a}\rho_0\left(\frac{L_0}{L}\right)^3 \tag{5}$$

and the mass of the floc can be calculated as:

$$M = \rho V = Nb\rho_0 L_0^3 \tag{6}$$

Comparing Eq. (5) with Eq. (1), the fractal dimension of the floc can be expressed as:

$$D_3 = 3\frac{\log(KN)}{\log(L^3)} \tag{7}$$

where $K = \frac{b}{c}\,{}_0L_0^3$ is a constant. The critical condition for $D_3 = 3$, that is, a floc of non-fractal structure, is:

$$\log(KN) = \log(L^3) \tag{8}$$

Comparing Eq. (8) with Eq. (5), we get:

$$\rho = \frac{c}{a} \tag{9}$$

This gives us an important conclusion that a floc of non-fractal structure will have a constant density. However, it is not the condition for any real flocs as has been verified by many studies. If we consider the floc to be of fractal nature, then its fractal dimension should be less than 3, so the following inequality holds:

$$\log(KN) < \log(L^3) \tag{10}$$

Eq. (10) indicates that the cubic power of the characteristic length of the floc L, which is proportional to the floc volume V, may increase quicker than the number of the primary particles it contains.

During particle growth, if the fractal dimension of the growing floc D_3 is constant, then from Eq. (6) the volume of the floc L^3 should be proportional to the number of primary particles N in it. This is a condition when every addition of a primary particle into the growing floc brings about an increase of the same volume, including the substantial volume and the void volume. However, if the floc has a multilevel structure [9], then floc growth will be accompanied by an addition of higher level void volume into the floc, which may not be proportional to the number of newly added primary particles but often with a quicker increase in floc volume than the particle number.

In this experiment, as alum is dosed into the HS solution with pH pre-adjusted to 5.0, aluminum hydrolysis and interactions between aluminum species and HS molecules will occur at the beginning stage to bring about the formation of small Al-humic precipitates. As shown in Fig. 7, these small precipitates are of relatively high fractal dimension ($D_2 = 1.8$). Then these small precipitates will grow possibly by mutual collision and aggregation in a stepwise way and/or continuous precipitation of solutes from the HS solution. It is apparent that the structure of the flocs is changing in the process of floc growth, as is indicated by the change of their fractal dimension shown in Fig. 7. When the growth process ultimately reaches an equilibrium state, there is no further change in both the average floc size d_f and the fractal dimension D_2. The Al-humic flocs finally formed ($D_2 = 1.4$) is much looser in their structure than the small precipitates at the beginning.

4. Conclusions

From the experimental results described in the former sections, conclusions can be drown as followings:

1. Al-humic flocs are of fractal nature and the two-dimensional fractal dimension D_2 derived from image analysis characterizes their morphological properties. At pH 5.0, the structure of the flocs formed is more compact with higher fractal dimension of 1.43 than that formed at pH 7.0 with lower fractal dimension of 1.17.
2. Aluminum sulfate shows different characteristics of hydrolysis and precipitation under slightly acidic and neutral conditions. The PDA online monitoring result shows that at pH 5.0 with a low alum dose, the products of aluminum hydrolysis are mainly soluble matter, while at pH 7.0 at the same alum dose, precipitates form quickly. This difference in aluminum hydrolysis/precipitation implies different mechanisms of HS coagulation: at pH 5.0 charge-neutralization and co-precipitation will be the main interactions between soluble aluminum species and HS molecules and at pH 7.0 the main interactions will be adsorption or sweep flocculation.

3. Alum dose also affects the structure of Al-humic flocs. Under pH 5.0 and at a dose to bring about charge-neutralization to $|\zeta| < 10$ mV, flocs formed are more compact with a fractal dimension ranging from 1.43 to 1.49, while at a higher dose when hydrolyzed aluminum precipitates form, flocs are more open and looser with a much lower fractal dimension.
4. Al-humic flocs undergo a dynamic change in their morphological properties. As flocs grow, their fractal dimension decreases gradually until an equilibrium state is reached. The decrease of fractal dimension implies a faster increase of floc volume than the number of primary particles the floc contains. This might be the case for flocs of multilevel structure which is growing in a stepwise way with higher level void water being added to the floc at each aggregation step.

Acknowledgements

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