The strength and fractal dimension characteristics of alum–kaolin flocs

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Abstract

Flocs generated by various shear forces exhibit different characteristics of size, strength and structure. These properties were investigated by employing a continuous optical monitoring and a microscope with CCD camera to directly monitor aggregation under six different shear intensities. The floc structure was characterized by the fractal dimension. The results showed that the flocculation index (FI) decreased from 1.16 at 20 rpm to 0.25 at 250 rpm and the floc size decreased from 550 μm to 150 μm, meantime, the FI value showed a good correlation with floc size. In order to determine the floc strength, two methods were used. One was the strength factor, ranging from 18.3% to 62.5%, calculated from FI curve, and the other was a theoretical value between 0.005 N/m² and 0.240 N/m², estimated by calculation. The floc strength increased with the G value in both cases. Furthermore, the fractal dimension increased with G and its value was between 1.30 and 1.63. The relation between fractal dimension and strength was also obtained.

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1. Introduction

Coagulation is a well-established process in water treatment and mineral processing operations to remove suspended particles by flocculating small particles into larger aggregates (Baltar and Oliveira, 1998; Hogg, 2000). The most common coagulant used in water treatment is aluminum sulfate, as a result of its effectiveness in treating a wide range of water types and its relatively low cost. Meanwhile, many polymeric flocculants were used in the mineral processing (Glover et al., 2004; Ersoy, 2005). Generally, the aggregates formed by coagulation are known as flocs, which are defined as highly porous aggregates, with irregular shape and composed of smaller primary particles (Huang, 1994). The properties of flocs, such as size, structure and strength, influence the efficiency of separation and purification operation. Therefore, the understanding of properties of flocs is important in study of coagulation.

1.1. Fractal dimension

Flocs, generated under water treatment or mineral processing, have been shown to be fractal (Chakraborti et al., 2000; Glover et al., 2004) and it has been considered that the flocs properties, such as density and
settling velocity, are non-integral functions of size, but exhibit the fractal nature with fractional power. Generally, the most important characteristics of fractal flocs are self-similar and scale invariant (Gregory, 1997; Jiang and Logan, 1991; Johnson et al., 1996). Fractal theories for flocs provide an original method to describe the structure of particles aggregates (Lee et al., 2002). Many investigations have studied the structure of aggregates by describing fractal geometry (Gregory, 1998; Tang, 1999; Waite et al., 2001; Wu et al., 2002; Bushell et al., 2002; Li et al., 2006).

Fractal dimensions can be described as one of the significant properties of fractal aggregates. Mass fractals may be summarized by the relationship between their mass $M$, a characteristic measure of size $L$, and the mass fractal dimension $D_f$:

$$ M \propto L^{D_f} $$

(1)

For Euclidean objects, $D_f$ is usually an integer (Waite, 1999). But for fractal objects, the values of $D_f$ are non-Euclidean dimensionality. Compact aggregates have a higher fractal dimension, while aggregates with loose structures have a lower fractal dimension. Experimental measurement of fractal dimensions of aggregates is not straightforward, and the methods available are indirect.

1.2. Floc strength

In addition to fractal dimension, floc strength is another important parameter to describe floc properties (Hermawan et al., 2004). The floc strength is interrelated with the number and strength of the interparticle bonds (Bache et al., 1999). Therefore, a floc will break if the stress applied on its surface is larger than the bonding strength within the floc (Boller and Blaser, 1998). However, there is no straightforward technique to experimentally characterize the floc strength (Jarvis et al., 2005). Researchers (Francois, 1987; Yeung and Pelton, 1996; Leentvaar and Rebhun, 1983) found a correlation between floc size and the strength for a given shear rate. The relation on a log–log scale between the average velocity gradients $G$ in the flocculator and the floc size of the suspension in equilibrium with that $G$ yields a measure for the floc strength:

$$ d = CG^{-\gamma} $$

(2)

values of $\gamma$ and $\log C$ can be found from the a log–log plot of floc size against the average velocity gradients:

$$ \log d = \log C - \gamma \log G $$

(3)

where $d$ is the floc size and $C$ is a constant, determined by the method used for floc size measurement; $\gamma$ is an exponent of floc size, the steeper the slope $\gamma$, the more prone the flocs are to break into smaller sizes under increasing shear rate, and thus, the $\gamma$ value is considered as an indicator of floc strength (Jarvis et al., 2005). Bache et al. (1999) gave the values of slope, which varied between 0.44 and 0.64, for alum–humic flocs under low alkalinity conditions. Francois (1987) concluded that the values of $\gamma$ were around 0.5 for all types of floc formed by alum–kaolin under different aluminum sulphate dosage.

In order to compare flocs of different strengths obtained at various shear rates, the floculation index (FI) was used by Gregory (2003) to indicate floc strength. According to Francois (1987) and Yukselen and Gregory, (2004), the breakage and regrowth of flocs were indicated by a ‘strength factor’ and a ‘recovery factor’:

$$ \text{Strength factor} = \frac{\text{FI}_3}{\text{FI}_1} \times 100\% $$

(4)

$$ \text{Recovery factor} = \frac{\text{FI}_1 - \text{FI}_2}{\text{FI}_1} \times 100\% $$

(5)

FI$_1$, FI$_2$ and FI$_3$ are the floculation index of initial, broken and re-formed flocs individually. The resistant ability of a floc against rupture by a certain velocity gradient is given by strength factor. Meanwhile, the recovery factor shows how sensitive the aggregating capacity of the ruptured flocs after breakage.

The theoretic method for floc strength calculation was elucidated by Bache et al. (1999). The average strength per unit area at the plane of rupture was defined as $\sigma$ (N/m$^2$) and could be calculated as

$$ \sigma = \frac{4\sqrt{3} \rho_w \varepsilon^{3/4} d}{3 \nu^{1/4}} $$

(6)

where, $\rho_w$ is the density of water (kg/m$^3$), $\varepsilon$ is the local rate of energy dissipation per unit mass (m$^2$/s$^3$) and $\nu$ is the kinematic viscosity. Furthermore, the average $\bar{\varepsilon}$ was selected to substitute for $\varepsilon$, $\bar{\varepsilon}$ could be calculated by

$$ \bar{\varepsilon} = \nu \cdot G^2 $$

(7)

Although a number of methods have been employed for the determination of floc strength and fractal dimension, there is limited literature for investigating the relation between fractal dimension and floc strength. The main objective of this investigation was to compare the breakage of flocs upon exposure to different levels of shear intensities, the fractal characteristics and strength of flocs formed by coagulation based on aluminum salts. Jar tests were conducted with focus on the
relation between fractal dimensions and strength of flocs.

2. Experimentals

2.1. Kaolin suspension

Kaolin was applied as a model suspension. The stock suspension of kaolin was prepared in deionized water, which was similar to Yukselen and Gregory (2004). The solid concentration of suspension was determined gravimetrically to be 137 g/L. The average size of the particles in suspension was close to 5 μm, measured by a laser diffraction instrument (Mastersize 2000, Malvern, UK).

An 800 mL tap water sample was used in the jar test and the kaolin concentration in the suspension was 50 mg/L. The pH of this suspension was kept at 7.5 by adding 0.1 mol/L HCl or NaOH and zeta potential was about −17.5 mv (Zetasizer 2000, Malvern, UK). Moreover, the turbidity of the suspension was closed to 50 NTU (Turbidimeter 2100N, Hach, USA).

2.2. Coagulant

Aluminum sulfate (Al₂(SO₄)₃ · 18H₂O, analytic reagent) was used as ‘alum’ coagulant and 0.1 mol/L alum solutions were prepared with deionized water as stock solution.

2.3. Dynamic monitoring

Coagulation experiments were carried out on a speed-adjustive jar test with 50 × 40 mm flat paddle impellers and a 1-L beaker at pre-set rotary speeds and the stirring time. A photometric dispersion analyzer (PDA2000, Rank Brothers Ltd, Cambridge, UK) was employed to monitor floc aggregation kinetics. A sample from beaker was circulated through transparent plastic tubing of 3 mm inner diameter by a peristaltic pump at a flow rate of 25 mL/min. The peristaltic pump was located after the PDA instrument to minimize potential floc breakup caused by the pump. The ratio value obtained by PDA is called the Flocculation Index (FI) and was taken every 5 s for the duration of jar test. The FI values are strongly correlated with suspended particles size and always increase as particles grow larger (Gregory and Nelson, 1986; Gregory and Chung, 1995).

2.4. Fractal dimension calculation

Image analysis to calculate the two-dimensional fractal dimensions was used (Chakraborti et al., 2000; Kim et al., 2001); the two-dimensional fractal dimension is defined by a power law relation between projected area (A) and the characteristic length of the aggregate, l.

\[ A \sim l^{D_2} \]  

where \( D_2 \) is the two-dimensional fractal dimension (Chakraborti et al., 2000; Kilps et al., 1994). Image analysis of suspended particles was done by microscope with high solution CCD camera (B2 series, Motic, USA). A pipette with 5 mm inner diameter was used to sample flocs and then the flocs were moved to a cell under the microscope for image analysis. This sampling method minimizes disturbance of the fragile floc particles and preserves the natural state of floc samples (McCurdy et al., 2004). The pictures of flocs were captured by CCD camera and then were analyzed by image analysis software (Mivnt, DaHeng, China). In this work, the long axis of the fitted ellipse, which is fitted to the particles image such that the moment of inertia of the ellipse and the image are equal, was taken as the characteristic length and considered as floc size. The two-dimensional fractal dimension was calculated by regression analysis of the logarithm of the projected area versus the logarithm of the long axis of the fitted ellipse as suggested by Eq. (8).

2.5. Floc strength

The strength factor was used to determine the floc strength, indirectly. As comparing, floc strength was also directly calculated by Eq. (6) for theoretical value.

2.6. Procedure

0.1 mmol/L alum was added at the beginning of rapid mixing. At this dosing point, the zeta potential of the alum–kaolin flocs was closed to zero, and thus, could be considered as charge neutralization point.

Flocs were formed at different shear conditions in a series of jar test to examine the flocs structure and strength. Mixing at 250 rpm for 1 min was followed by floc growth phase at 20 rpm, 40 rpm, 80 rpm, 100 rpm, 150 rpm, and 250 rpm for 15 min, respectively. A broken phase was introduced by mixing at 400 rpm for 1 min, and then, the re-growth phase was performed by changing the rotary speed to 20 rpm, 40 rpm, 80 rpm, 100 rpm, 150 rpm, and 250 rpm for 15 min, respectively. All of the experiments were carried out 20±3 °C.
3. Results and discussion

3.1. Flocculation index and floc size

Flocculation index (FI) values at different shear intensities were shown in Fig. 1. Different FI curves were presented at various shear rates. At a lower rotary speed, a higher FI value was observed. When the rotary speed was 20 rpm for floc growth, FI value was about 1.16, and which was the highest at the six shear rates. On the contrary, the lowest FI value was close to 0.25 at 250 rpm. Therefore, the results showed that larger flocs with higher FI values formed at lower shear intensity.

Flocculation index was directly proportional to floc size as shown in Fig. 2. In this paper, floc size was measured by image analysis and the size of long axis of the fitted ellipse substituted for which of floc. Moreover, the FI values in Fig. 2 were average FI at different rotary speeds. The results showed a high degree of correlation with $R^2$ value 0.94 between FI and floc size, and the similar conclusion was drawn by McCurdy et al. (2004). Increased FI corresponded to an increase in average floc size under all of these shear rate conditions. It was concluded that FI value monitored by PDA could be used as a reliable indicator of aggregate size development.

Floc size was close to 150 $\mu$m as the FI value of 0.25 at 250 rpm, and grew up to 550 $\mu$m with FI value of 1.16. Generally, the floc size was inversely proportional to hydraulic gradient. The log–log curves of floc size decreasing with $G$ value were shown in Fig. 3. Floc size decreased sharply with the increase of $G$. Because floc size is a balance between growth and

![Fig. 1. The curves of flocculation index at six different rotary speeds and which were 20 rpm, 40 rpm, 80 rpm, 100 rpm, 150 rpm, and 250 rpm individually.](image-url)
breakage, flocs that formed at higher shear intensity, would have higher strength with stronger bonds to resist the shear force.

3.2. Floc strength and fractal dimension

As Eq. (3) describes, $\gamma$, calculated from the slope of log–log curve, is the stable floc size exponent dependent upon floc break-up mode and the size of eddies that causes the breakage. The slope $\gamma$ was 0.37 in Fig. 3 and less than those reported by other researchers (Francois, 1987; Bache et al., 1999; Jarvis et al., 2005), it might be attributed to the $\gamma$ value that deeply depended on the methods for floc size measurement. In view of the fact, the steeper the slope $\gamma$, the more prone the flocs are to break into smaller sizes with increasing shear force, and thus, the $\gamma$ value is considered as an indicator of floc strength.

A comparison of floc strength between six different shear intensities was listed in Table 1. Two indicators were used to indicate the floc strength, one was strength factor calculated from FI curves as Eq. (4) and the other was theoretic method for floc strength calculation by Eq. (6). However, these two different strength values were directly proportional to each other as shown in Fig. 4, moreover, both two strength values increased with the $G$ value. The range of strength factor was from 18.3% to 62.5%, meanwhile, the theoretical values of floc strength were between 0.005 N/m² and 0.240 N/m², and the range of strength values, calculated by Eq. (6), was close to the study by Bache et al. (1999). By referring to Table 1, it is apparent that the flocs with highest strength were formed at 250 rpm as compared with the flocs with lowest strength formed at 20 rpm. Floc strength calculations showed that flocs at high $G$ value were smaller but with higher strength. It turned out that floc strength depended on the hydraulic condition significantly; correspondingly, it was also interrelated with the number and strength of the interparticle bonds. At high hydraulic shear force, the weak bonds would be broken, therefore, the larger

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**Table 1**

<table>
<thead>
<tr>
<th>Rotary speed (rpm)</th>
<th>$G$ value (s)</th>
<th>Floc strength (N/m²)</th>
<th>Strength factor (%)</th>
<th>Fractal dimension $D_2$ (±0.05)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.5</td>
<td>0.005</td>
<td>18.3</td>
<td>1.30</td>
<td>0.90</td>
</tr>
<tr>
<td>40</td>
<td>11.3</td>
<td>0.017</td>
<td>20.7</td>
<td>1.34</td>
<td>0.86</td>
</tr>
<tr>
<td>80</td>
<td>29.1</td>
<td>0.053</td>
<td>21.4</td>
<td>1.41</td>
<td>0.90</td>
</tr>
<tr>
<td>100</td>
<td>39.7</td>
<td>0.077</td>
<td>23.9</td>
<td>1.45</td>
<td>0.94</td>
</tr>
<tr>
<td>150</td>
<td>67.7</td>
<td>0.131</td>
<td>47.2</td>
<td>1.55</td>
<td>0.94</td>
</tr>
<tr>
<td>250</td>
<td>134.6</td>
<td>0.240</td>
<td>62.5</td>
<td>1.63</td>
<td>0.92</td>
</tr>
</tbody>
</table>

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Fig. 2. The relationship between flocculation index and floc size.

Fig. 3. The relationship between the change in floc size and an increase in velocity gradient $G$ value.

Fig. 4. The relationship between strength factors calculated from FI curves and the theoretic values by using Eq. (6).
Floc would be divided into several parts and the floc size decreased simultaneously. However, the strong bonds still existed in the residual small parts of original floc, and thus, the smaller floc with strong bonds might have the high strength to resist the increasing shear force.

Despite the fact that floc size decreased with shear rate, the fractal dimensions increased with $G$. Flocs formed at a low $G$ value ($4.5 \text{ s}^{-1}$) were large and had a fractal dimension of 1.30 whilst floc size decreased and the fractal dimension was increased to 1.60 when the flocs were formed at a much higher $G$ value ($134.6 \text{ s}^{-1}$). Due to floc structure determined by shear force, there was a tight relationship between floc structure and fractal dimension. Therefore, the fractal dimensions could be used to explain the floc structure variation. Specifically, densely packed aggregates had a higher fractal dimension, while lower fractal dimension resulted from large, high branched and loose bound structures. As the shear with low intensity was introduced, the flocs formed with more open structure, as a result, the fractal dimensions were low. On the contrary, the more dense flocs at the high intensity shear force had higher fractal dimensions because the relative open structure was destroyed by strong shear force, and thus the final flocs reformed with higher fractal dimension instead of branched and loose bound structure. More compact structure indicates that primary particles may have more attachments with one another or repulsive force between these particles is minimized. In summary, coagulation increases the average floc size, but decreases the average compactness.

A linear relation of log–log curves between fractal dimensions and strength was shown in Fig. 5. Both the theoretical strength values and strength factor calculated by FI curves were directly proportional to fractal dimensions in log–log curves. As evidenced in Fig. 5a, the slope was 15.36 in comparison with that of 5.64 in Fig. 5b. The distinction between two slopes was ascribed to the various methods for floc strength measurement and the absolute value of slope was relatively not significant. But, if floc strength was calculated on a uniform method to compare the characteristics of various flocs, the slope for log–log curves of floc strength and fractal dimension would be significant and useful. When a floc has a higher slope, its strength would decrease more sharply with the decrease in fractal dimension. It could be concluded that the floc, with higher slope of log–log linear relation between strength and fractal dimension, would be weaker due to the increase in floc size. With fractal dimensions of different flocs taken into consideration, if the slope was higher, the flocs with higher strength would be formed at the same fractal dimension. Therefore, the larger flocs could resist higher shear force intensity and thus the performance of separation process was improved.

4. Conclusions

Floc size, structure and strength are significant operational parameters in particles separation. The evolution of floc size, structure and strength was monitored by a photometric dispersion analyzer and a microscope with image analysis. The experimental results show that there was a fundamental difference in the alum–kaolin flocs that were generated at various shear force. During turbulent shear flocculation, large floc structures were shown to be more open than smaller flocs. Small and dense flocs with high strength and fractal dimension were formed at high shear force. Furthermore, the FI value recorded by PDA was closely related to floc size measured by particle image analysis. The relation between floc strength and floc dimensions and floc structure was demonstrated.
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