Effects of low temperature on floc fractal dimensions and shape factors during alum coagulation

Feng Xiao, Bao-jie Zhang, Jun Ma, Peng Yi and Chong-wei Cui

ABSTRACT

Over 2,000 flocs were involved in the calculations of floc fractal dimensions and floc shape factors to examine the effects of low temperature on floc structures. The 3-D fractal dimension of flocs was found to decrease from 2.48 at 22°C to 2.24 at 2°C, indicating flocs are more compact at the higher temperature. At 22°C, floc fractal dimensions were not significantly affected by flocculation time. However, at the low temperature, 2°C, fractal dimensions were found to increase with flocculation time, indicating that flocs generated at low temperature need more time to be well formed. On the other hand, low temperature did not exert significant influence on floc shape factors. Statistical analyses show that the examined shape factors of the flocs, roundness *R* and smoothness *S*, followed probability rules. Around 80% of flocs have an *R* value ranging from 0.5 to 0.8, and about 75% of flocs have an *S* value in the same range. The mechanism of floc growth during coagulation of kaolinite suspensions is reaction-limited cluster-cluster aggregation (RLCA).

Key words | coagulation, floc, fractal dimension, reaction-limited aggregation, shape factor

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NOTATION

A	floc area (mm^2)
AD	alum dosage ($mg\,l^{-1}$)
D_2	2-D fractal dimension
D_3	3-D fractal dimension
G	velocity gradient (s^{-1})
IT	initial turbidity (NTU)
L	floc size (mm)
P	floc perimeter (mm)
P_e	perimeter of the best-fit ellipse (mm)
R	roundness factor of flocs
S	smoothness factor of flocs
V	floc volume (mm^3)

INTRODUCTION

A coagulation process using aluminium-based coagulant such as alum is commonly applied in the field of water treatment. Enmeshment of contaminants through aluminium hydroxide-floc is a widely used coagulation mechanism (Hillis 2005). Letterman *et al.* (1999) pointed out that formation of voluminous flocs is of great importance for a fast coagulation process.

In the process of coagulation, the snowflake-like floc has an irregular and open structure such that the area of the floc is not filled completely with its mass. In large part as a consequence of the advance in microscopic technology, researchers have focused a great deal of attention on examining the physical morphology of flocs. Tambo & Watanabe (1979) found a non-integral relationship between floc properties and floc size in a series of comprehensive studies at the end of the 1970s. Their finding was influential at that time, and it was later identified as the fractal characteristic of flocs when fractal theory was established and applied to the realm of coagulation. Today, fractal theory has been a powerful tool for researchers to study floc structures. Both the internal structure and the surface of the

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floc exhibit fractal properties (Mandelbrot 1982). According to fractal geometry, power relationships link the surface-geometry parameters:

$$A \propto L^{D_2} \quad (1)$$

$$V \propto L^{D_3} \quad (2)$$

where A is the area of a floc, L the size of a floc, V the volume of a floc; and D_2 and D_3 are the 2-D and 3-D fractal dimensions, respectively. Unlike a Euclidean object, a fractal object has values of $D_2 < 2$ and $D_3 < 3$. Flocs with looser structures have lower fractal dimensions. Furthermore, shape factors are terms commonly applied in this area to quantify the deviation of the shape of a particle from a sphere. For instance, the roundness is a measure reflecting the curvature variations along the grain surface. Smaller distortions of the surface can increase the drag coefficient and thus decrease the settling velocity (Gamenen 2007). As such, a floc with a low smoothness factor S has a relatively jagged shape. Conventional formulae, such as Stokes' law, concerning flocs are usually derived on the assumption that flocs are spherical. In recent years, however, the law has been amended to take account of the shape factor of flocs (Li & Logan 2001). Floc shape factors are involved also in the description of the steady-state size distribution (Jiang & Logan 1991) and frequency of particle collision (Atkinson & Chakraborti 2004).

However, there are no studies to date which report the D_2 and D_3 of flocs formed at low temperatures. As such, the morphology of flocs formed at low temperatures is not well established yet. Therefore, in response to this incomplete understanding of floc structure characteristics at low temperatures, the present paper examines the morphology of hundreds of flocs formed at low temperatures.

MATERIALS AND METHODS

Test solution

Experiments were performed using deionized water containing $1 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ HCO_3^-, $2 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ Cl^-, $2 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ Na^+, and $1 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ K^+ as the test solution. Different initial turbidities (3.3, 9.3 and 16.5 NTU) were realized by dispersing kaolinite particles in the solution. The particles in the suspension had a mean diameter of 0.5 μm with a narrow size distribution (Xiao *et al.* 2009). Turbidity was measured by a portable turbidimeter (2100P Portable Turbidimeter, HACH Company, USA). All reagents used were of analytical grade, and the solution pH was ~7.8. The test solution was stored in a closed glass container for 12 hours to allow the equilibration of all the components. The experiments were conducted at a low temperature of 2°C and at an ambient temperature of 22°C. The low temperature was controlled by a thermostat (model: THD-0515, Ningbo, China).

Jar test

A jar test was used to simulate the coagulation and sedimentation processes. The study was conducted with a program-controlled tester with two cylindrical beakers (model TA2-I, Wuhan, China). Before the jar test, a beaker containing 1 l of the test solution was kept in the thermostat for 3 hours to reach a predetermined low temperature, which was maintained during the jar test. Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) was used as the coagulant in this study. A known amount of alum was added to the test solution, and the tester immediately triggered the stirrer to mix the solution for 1 min at 150 rpm (velocity gradient $G = 85\,\mathrm{s^{-1}}$) and then at 40 rpm ($G = 10\,\mathrm{s^{-1}}$) for different lengths of time, according to the experiment, followed by quiescent sedimentation for 30 min.

Floc image analysis

The steps for capturing a floc image have been described previously (Xiao *et al.* 2009). The floc dimensions were obtained by processing the floc image using Scion Image software (Scion Image 4.03, Scion Corporation, USA) showing the projected area, perimeter, and the longest length of a selected region. The software calculated a best-fit ellipse with the same area as a floc. The size of the floc was defined as its longest length.

Floc fractal dimensions and shape factors

Fractal theory has received much attention among environmental communities, because flocs generated in a water

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treatment process are fractal objects (Chakraborti *et al.* 2000; Jarvis *et al.* 2005). Floc fractal dimensions were calculated by Equations (1) and (2). The floc volume V was defined as the volume obtained by rotating the ellipse around its major axis, assuming that the thickness of the floc is normal to the viewing direction (Jiang & Logan 1991; Chakraborti *et al.* 2000).

Floc shape was described by two shape factors, roundness, R, and smoothness, S.

$$R = \frac{4A}{\pi L^2} \quad (3)$$

$$S = \frac{P_e}{P} \quad (4)$$

where P and P_e are the perimeters of a floc and its best-fit ellipse.

R describes how much a floc varies from a circle. A line has a value of R or S equal to zero, whereas $R = S = 1$ for a circle. For a fractal object, the value of R or S ranges from 0 to 1.

RESULTS AND DISCUSSION

Effects of low temperature on fractal dimensions of flocs

The fractal dimensions of flocs relate so closely to their inherent characteristics and express them so powerfully that active discussion on the fractal dimensions has continued for decades, as presented in Table 1. However, we are not aware of any report on the 2-D or 3-D fractal dimensions of alum flocs formed at low temperatures; and the question of whether flocs formed at low temperature are more compact has not been addressed.

It is well known that the fractal dimension was quantified on the basis of regression analysis. The more flocs involved, the more accurate the result. The dimensions of more than 2,000 flocs were analysed in this study. Figures 1 and 2 show that the fractal dimensions of flocs (D_2 and D_3) were affected by the low temperature to a certain extent. The decrease of temperature from 22°C to 2°C reduced D_2 from 1.67 to 1.52 and D_3 from 2.48 to 2.24, suggesting more irregular and less compact flocs at the low temperature.

Another variable, initial turbidity, however, was not found to exert significant influence on floc fractal

Table 1 | Fractal dimensions of alum flocs examined by different approaches

Fractal dimensions of alum flocs					
D_2	D_3	Temperature (°C)	Type of water used for alum coagulation	Method used for obtained fractal dimensions	Source of data
1.98	2.60	N/A	DI water with polystyrene particles (pH = 7.0–7.2)	Image analysis: microscope equipped with a video camera	Spicer & Pratsinis 1996
1.58–1.62	2.25–2.40	20	DI water with kaolinite particles (pH = 8)	A log-log plot of floc velocity ∝ floc diameter $^{D_3-1}$	Adachi & Tanaka 1997
1.77–1.89	2.39–2.51	22	DI water with montmorillonite particles (pH = 3.2)	Image analysis–digital CCD camera	Chakraborti *et al.* 2000
1.65–1.96	2.12–2.93	22	Lake water (pH: N/A)		
N/A	2.46–2.59	21	Tap water with clay particles (pH = 7.2)	A log-log plot of floc velocity ∝ floc diameter $^{(D_3-1.4)/1.4}$	Turchiuli & Fargues 2004
N/A	2.00–2.40	N/A	Reservoir water (pH = 7.9)	Scattered light	Ho & Newcombe 2005
1.52 ± 0.02	2.24 ± 0.04	2	DI water with kaolinite particles (pH = 8.0)	Image analysis: microscope equipped with a video camera	This study
1.67 ± 0.02	2.48 ± 0.04	22			

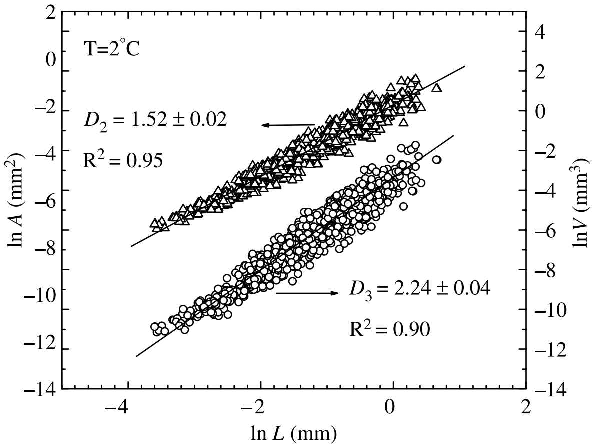

Figure 1 | Fractal dimensions of flocs formed at 2°C (alum dosage = 30 mg l^{-1}).

dimensions (see Figures 3 and 4). Flocculation time did not affect fractal dimensions significantly at 22°C (see Figures 3 and 4). Figures 3 and 4 indicate that the physical properties of floc were quite independent of scale at 22°C, since the floc was relatively small in the initial stage of flocculation. Serra & Casamitjana (1998) reported that the fractal dimensions of aggregates did not change significantly during aggregation. However, at the low temperature, 2°C, both D_2 and D_3 increased with flocculation time: D_2 increased from 1.3 at 8-min flocculation to 1.6 at 20-min flocculation, and D_3 increased from 1.9 to 2.3. It had been found that low temperature greatly reduced the coagulation rate (Xiao *et al.* 2009). The increase in floc fractal dimensions with flocculation time, as observed in this study, indicates that flocs

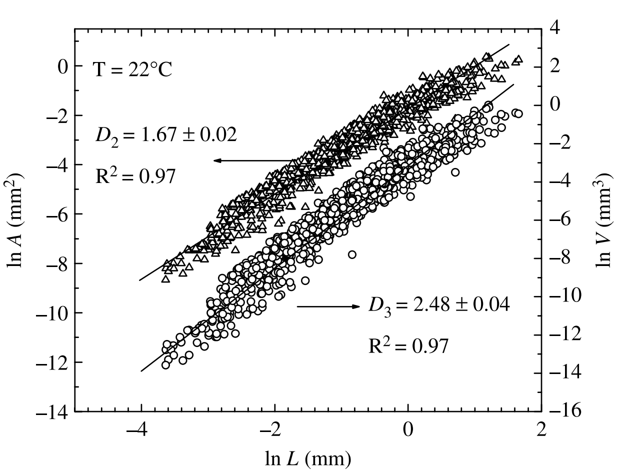

Figure 2 | Fractal dimensions of flocs formed at 22°C (alum dosage = 30 mg l^{-1}).

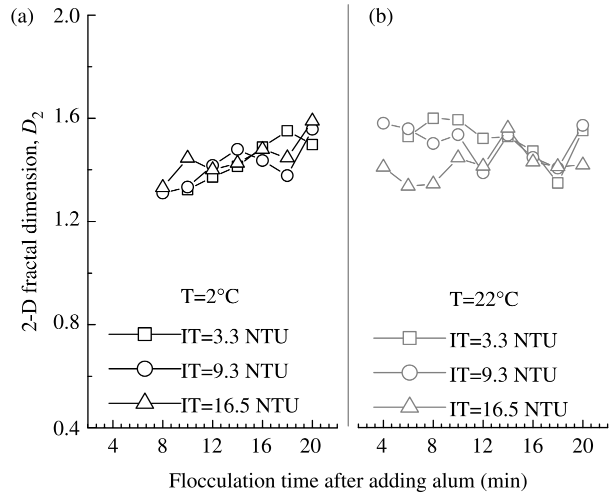

Figure 3 | 2-D fractal dimension of flocs as a function of flocculation time (alum dosage = 30 mg l^{-1}, IT refers to initial turbidity, the practice is remained in following discussion).

produced at the low temperature need more time to become well formed. The floc fractal dimensions shown in Figures 1 and 2 are obtained from all the flocs formed at different flocculation times. Therefore, some parts of the fractal dimensions in Figures 3 and 4 are smaller than the value determined from Figures 1 and 2, while other parts are larger. Figure 5 shows the floc images captured in different cases. In this study, over 2,000 flocs were involved in the calculation of fractal dimensions and shape factors. Therefore, it is impossible to judge from Figure 5 alone that flocs formed at a low temperature have a more irregular shape.

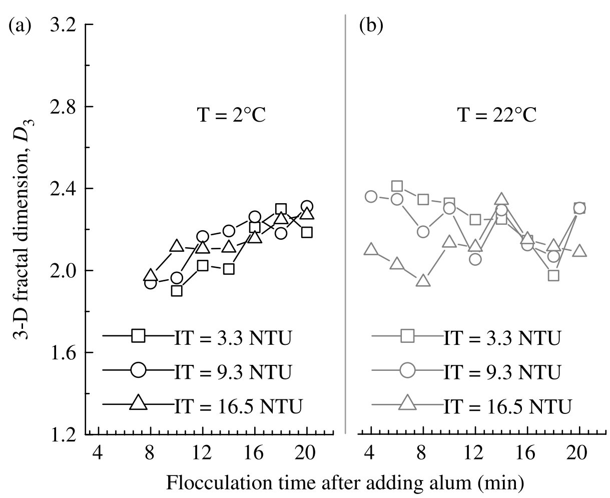

Figure 4 | 3-D fractal dimension of flocs as a function of flocculation time (alum dosage = 30 mg l^{-1}).

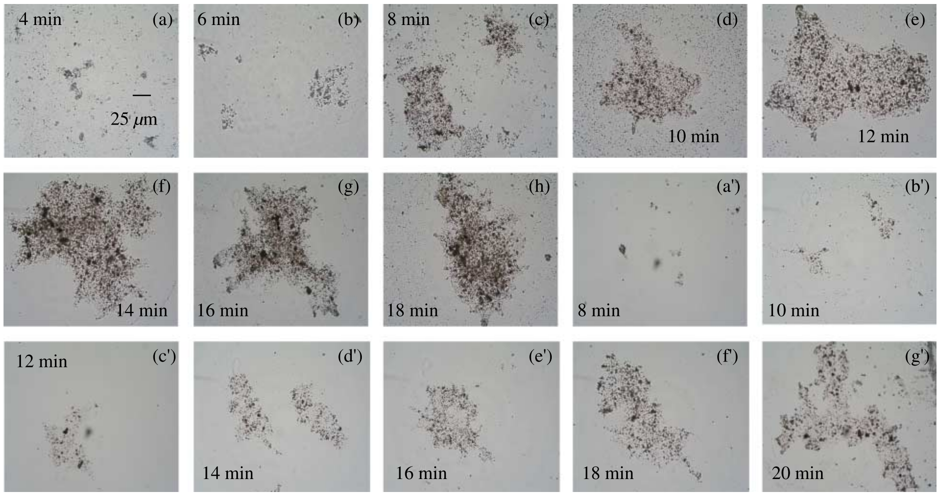

Figure 5 | Images of the flocs (200X magnification) formed at different times during the 30 mg l^{-1} alum flocculation of test water with initial turbidity = 3.3 NTU. (a)–(h) from 4 min to 18 min, 22°C; (a′)–(g′) from 8 min to 20 min, 2°C.

However, in this figure, the flocs appear less compact at lower temperature. Their thickness appears to be attenuated at the low temperature, too. Furthermore, as reported by Morris & Knocke (1984), a negative correlation exists between floc size and temperature (see Figure 5).

Image-processing software, such as the Scion Image software used in this study or the NIH image software used by other researchers, can calculate a best-fit circle or ellipse with the same area as a floc. The length of the diameter of the best fitting circle or the major axis of the best fitting ellipse is usually termed the equivalent length (Chakraborti *et al.* 2000). Controversy may arise when applying Equations (1) and (2) to obtain the fractal dimensions, because the equivalent length can easily be taken as L in the regression analysis of Equation (1) or (2). It will actually have the 3-D dimension of the best fitting circle or the ellipse if ln$V$ is regressed on ln[equivalent length] in Equation (2). As confirmed by MicroExcel (MicroExcel 2003, Microsoft Company, USA), the result is usually <3, which disguises itself as the 3-D fractal dimension. A similar error will happen in the regression analysis between ln$A$ and ln[equivalent length] to obtain the 2-D fractal dimension. For instance, if the major axis of the best-fit ellipse is taken as L in Equations (1) and (2), D_2 and D_3 at 22°C are, respectively, 1.96 and 2.92, instead of 1.67 and 2.48 as shown in Figure 2.

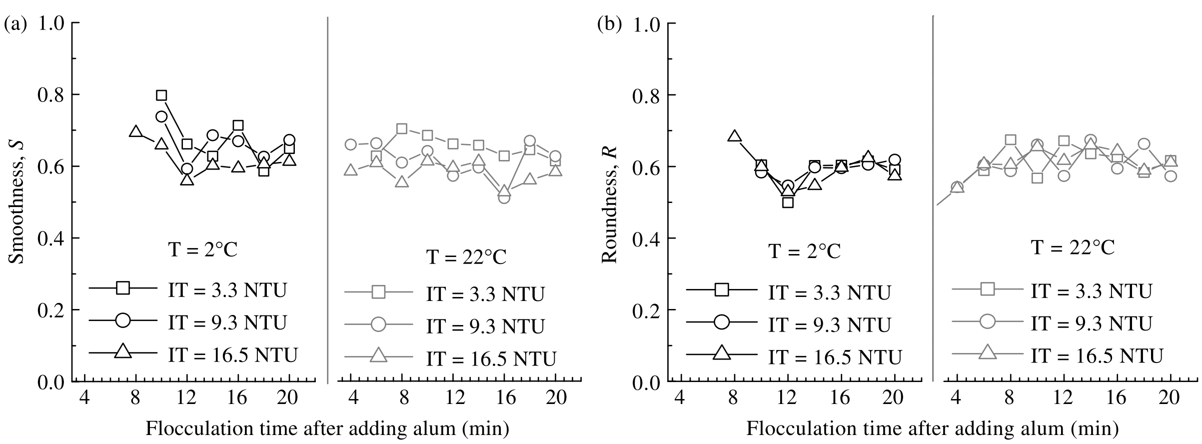

Figure 6 | Variation of floc shapes as a function of flocculation time.

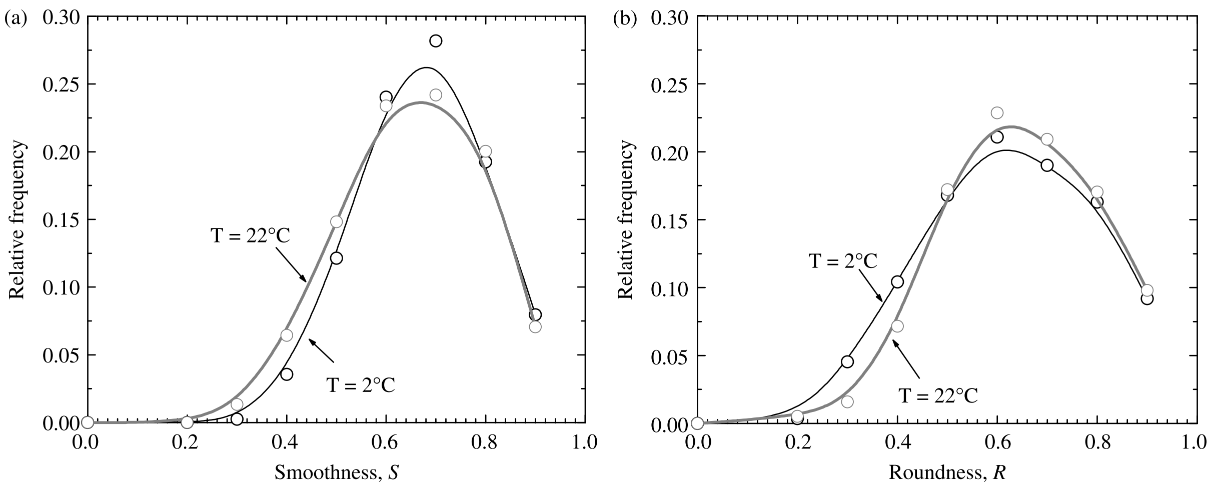

Figure 7 | Distribution of floc shape factors.

The present study focuses on the effects of low temperature on floc structure; the effects of other variables, such as solution pH and coagulant dosage, can be found elsewhere (Kim *et al.* 2001).

Floc growth mechanisms at low temperature

Examining the fractal dimensions during coagulation can reveal the mechanism of floc growth. Two important theories, particle-cluster aggregation (PCA) and cluster-cluster aggregation (CCA), have been put forward to explain the growth of flocs (Meakin 1988). In the PCA model, aggregates grow by entrapping particles, whereas in the CCA model, growth results from clusters joining together. The CCA model was suggested to best describe the coagulation process (Li & Logan 2001). Further, concerning CCA, two limiting regimes have been proposed: the reaction-limited cluster-cluster aggregation (RLCA) and the diffusion-limited cluster-cluster aggregation (DLCA) (Weitz *et al.* 1984; Lin *et al.* 1990). In RLCA, collision does not necessarily evoke attachment, and aggregation requires many encounters between pairs of clusters. DLCA assumes aggregation comes from the random walk trajectories of clusters acting as collectors, and every collision leads to an irreversible attachment. In RLCA, flocs are compact and have D_3 values in the range 2.0–2.5 (Meakin 1988). On the other hand, DLCA generates open flocs, with D_3 of $\sim$1.80 (Meakin 1988). From Figures 1 and 2, coagulation processes at 2°C and 22°C lead to a structure within the range 1.90–2.22 and 1.94–2.39, respectively, which agrees well with the RLCA model. The floc-growth mechanism during coagulation is not influenced by the low temperature.

Floc shapes during coagulation at low temperature

It can be assumed that irregular flocs exist in a variety of shapes. Nevertheless, the morphology of a floc is not unimportant. Serra & Casamitjana (1998) found that floc shape factors did not depend on the shear rate. However, researchers still do not know whether there is no dependence between the floc shape factors and the variables, such as temperature, initial turbidity and the flocculation time. In the present study, the examined shape factors of the flocs were found to follow the probability rule of statistics. Figure 6 shows that S and R were not affected significantly by temperature, initial turbidity and flocculation time. Furthermore, from Figure 7, out of 2,000 flocs, around 80% have an S value ranging from 0.5 to 0.8, and about 75% of flocs have an R value in the same range. Each point in the plots of Figure 6(a) and (b) represents the average value of a shape factor under a certain setting.

CONCLUSIONS

From what has been discussed, some points can be emphasized:

(1) The 3-D fractal dimension of flocs was found to decrease from 2.48 at 22°C to 2.24 at 2°C, indicating flocs are more compact at the higher temperature.
(2) While flocculation time exerted little effect on floc fractal dimensions at 22°C, at the low temperature, 2°C, fractal dimensions were found to increase with the flocculation time, indicating that flocs at low temperature need a longer time to become well formed.
(3) The floc fractal dimensions were scale-invariant and changed little with initial turbidity.
(4) The averaged values D_3 of flocs during the coagulation indicate that the flocs came mostly from the reaction-limited cluster-cluster aggregation (RLCA). The decrease in temperature from 22°C to 2°C did not change floc growth mechanism.
(5) The shape of flocs, in terms of smoothness S and roundness R, can be expressed statistically. Flocs with S and R in the range 0.5–0.8 account for 80% and 70% of the total flocs in the solution, respectively.
(6) In terms of roundness R and smoothness S, the morphology of flocs formed in coagulation processes was not affected by ambient variables such as temperature, initial turbidity or flocculation time.

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