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Floc growth kinetics in magnesium hydroxide coagulation process

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ABSTRACT

The population balance modeling (PBM) had been applied to simulate the floc growth with time in magnesium hydroxide coagulation process. Floc number and size distribution were investigated to evaluate the kinetics in a continuous steady experiment. The floc grows fast in rapid mixer and very slow in flocculation basin and sedimentation tank. The experimental data agreed well with the size-dependent model, and the floc formation and growth empirical function was also obtained to understand the relationship between floc formation rate and growth rate under different stages of coagulation. It was also found that floc growth rate increased with the increase of floc size. Although the floc counts in the range of 2–5 μm accounting for about 90%, the setting characteristics of kaolin colloidal suspensions presents good and the turbidity removal efficiency can reach 98%.

Keywords: Magnesium hydroxide; Coagulation; Floc growth; Kinetics; Model

1. Introduction

Coagulation can be described as the formation of larger particles, or flocs, from the small particles in the wastewater [1,2]. The most common coagulants used are hydrolysable metal such as alum and ferric chloride. Floc size and structure, breakage, re-growth, and settling characteristics are the main parameters influencing particle removal efficiency [3,4]. There are many methods available to measure floc physical characteristics and coagulation process such as a nephelometric turbidimeter method [5], laser technique [6,7], and photometric dispersion technique [8]. These measurements are useful in monitoring the initial formation of floc after coagulant addition, the effects of shearing on floc formation, and the rate of re-aggregation of floc after shear induced breakup. The simulation, design, and control of process are dependent on an accurate prediction of the floc size distribution (FSD). There has been an increasing recognition of the importance of growth kinetics in both design and performance assessment of crystallizers or reactors. Population balance modeling (PBM), a mathematical modeling technique used to describe population dynamics, has already been shown to be a valuable tool for understanding the precipitation and flocculation processes [9–13].

In recent years, several authors have investigated the roles of magnesium hydroxide as a potential coagulant or an effective adsorbent for the physicochemical clarification of wastewater [14–17]. The precipitation of magnesium hydroxide has several advantages: it increases the number concentration of

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particles (thereby speeding the flocculation reaction), it enhances the removal of small particles by enmeshment in the forming precipitate or growing the particles to larger sizes by precipitation onto their surfaces, and it facilitates the removal of contaminants [18].

Although there are large amount of data on the characteristics of floc using conventional coagulants, there have been limited studies on the relationship between floc formation and growth process using magnesium hydroxide as the coagulant. There are almost no analysis of the FSD of investigated particles and its change in time. Often, coagulation and flocculation run in a small beaker stirred with a magnetic stirrer or in a jar test. These conditions are far from the real ones existing in industrial-scale unit operations.

The main objectives of this study were to evaluate the magnesium hydroxide coagulation performance, floc characteristics, especially to understand the floc formation and growth processes in a real continuous steady experiment. Evaluation of population balance model for magnesium hydroxide coagulation with FSD data and development of a formation-growth model that provides good fit to the data are better explanations to the experimental results.

2. Materials and methods

2.1. Synthetic test water and coagulant

Kaolin clay (AR. Tianjin Chemical Reagent Co. China) was used for a model suspension. Three hundred grams of kaolin was dispersed in 50L of deionized water with 30 min of 600 rpm blender, and then settled for 30 min. The top suspension was transferred to another 100L tank and the initial turbidity was adjusted to 50 ± 1 NTU by adding deionized water. About 1 M NaOH solution was added to water sample to control the solution pH to 11.5. A pH-meter (PHS-25 Shanghai Jinke industrial Co. China) was used to determine the pH of the solutions. $MgCl_2{\cdot}6H_2O$ (CP. Tianjin Chemical Reagent Co. China) was used to prepare coagulant. About 0.1 M stock Mg^{2+} solutions were prepared with deionized water. The turbidity of the supernatant liquors was measured using a turbidimeter (HACH 2100 N, USA). Zeta potential was analyzed using a Zetasizer Nano ZS (Malvern, UK), and magnesium ion was analyzed with an ICS-1500 (Dionex, USA) ion chromatography system.

2.2. Floc size distribution analysis

Dynamic floc size was monitored using an IBR particle counter (NASEC, USA) as the coagulation proceeded. Simply inserted the inlet tube into coagulation systems at a flow rate of 60 mL/min and then number of different particle sizes could be calculated with particles/mL at greater than 2 μm. During the continuous coagulation process, samples of flocs were taken from the third flocculation basin and sedimentation tank using a tube with an inner diameter of 5 mm. After transferring the sample onto a flat microscope slide, the morphology of flocs was measured by IX71 digital photomicrography (Olympus, Japan). In this study, FSD was calculated from the numbers of particles range from 2 to 25 μm.

2.3. Apparatus and procedures

A schematic diagram of the experimental apparatus is shown in Fig. 1. The 1 l rapid mixer with an anchor impeller is used for rapid mixing of coagulant with wastewater. The coagulant is added through a measuring pump. For this process to occur, it is necessary to have enough time for small suspended particles to grow larger and heavier flocs that settle out by gravity. The stirring speed was maintained at 300 rpm in rapid mixer and 100 rpm in flocculation basin. Flocculation basin is divided into three parts (3 × 4 L) and sedimentation tank (30 L) is designed for the removal of solid particles. Water sample with pH of 11.5 and initial turbidity of 50 NTU was pumped to rapid mixer with flow of 29 L/h; chemical feed was also pumped to tank 1 of 1 L/h with magnesium concentration 300 mg/L. The total influent flow is 30 L/h and the initial concentration of magnesium ion is 10 mg/L. A continuous steady experiment was carried out at 20 ± 1℃ to justify turbidity removal of magnesium hydroxide coagulation process.

2.4. Theoretical background and model development

Coagulation is also defined as the bringing together of small particles into large particles. Coagulation is used to reduce the number of small, insoluble particles

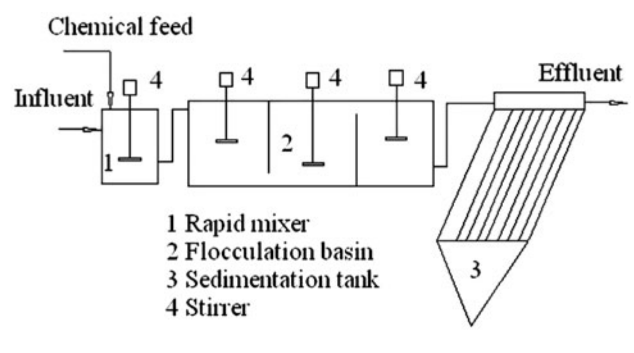

Fig. 1. Experimental apparatus for coagulation.

by attaching them together with different mechanisms which makes it easier to separate them from a suspension. Magnesium hydroxide coagulation process is similar to the precipitation process. When coagulant was added, precipitation process of magnesium hydroxide from simulated water sample with an alkaline such as caustic soda was carried in this experiment. The reaction formula is given as follows:

$$2NaOH + MgCl_2 \rightarrow Mg(OH)_2 \downarrow + 2NaCl$$

The resulting magnesium hydroxide is a gelatinous precipitate, which was found to serve as an efficient coagulant [19]. In coagulation process, there are large amount of impurities such as clay and colloids, while magnesium hydroxide coagulation includes magnesium hydroxide nucleation and combination of kaolin into flocs. Randolph and Larson [20] provided the basis for modeling the particle size distribution in precipitation process. The continuous mixed-suspension mixed-product removal (MSMPR) crystallizer technique using the population balance equation (PBE) has proved the most popular of quantitatively measuring the growth and the apparent nucleation rates. Population balances have also been applied to coagulation processes for the evolution of floc characteristics, floc formation, growth, and aggregation [21,22].

For a continuous coagulation process, the PBE can be written as:

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} + \frac{Q}{V} n = B - D \tag{1}$$

where n, (#/μm mL), is the population density per suspension volume (V), Q is the total volumetric flow rate, (L/h), and B and D represent the birth and death density functions, respectively, accounting for particle aggregation and breakage in the suspension. G, (μm/h), is growth rate and L, (μm), is floc size. Under the conditions of constant suspension volume and negligible particle birth and death, Eq. (1) can be simplified to:

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} + \frac{n}{t} = 0 \tag{2}$$

where $t = V/Q$, (h), is the mean retention time in the reactor. Eq. (2) requires a boundary condition and a initial condition. The initial condition is:

$$n(L, 0) = 0 \tag{3}$$

and boundary condition n (0, t) is the primary floc population density. The n^0, (#/μm mL), can be related to the primary floc formation rate and growth rate by

$$n(0, t) = n^0 = B^0/G \tag{4}$$

where B^0, (#/mL h), is the primary floc formation rate. Under steady state condition, the population balance Eq. (2) may be solved analytically when G is known.

$$\frac{d(Gn)}{dL} + \frac{n}{t} = 0 \tag{5}$$

Unfortunately, no generally agreed theoretical description has been proposed and resort is therefore currently made to empirical methods. When floc growth rates exhibit such as size dependence, the relationship between the FSD and the coagulation kinetics becomes more complicated. In this case, using the population balance Eq. (5) to estimate the coagulation kinetics requires the knowledge of size-dependent growth function. Abegg et al. [23] had also proposed a semi-empirical equation as ASL model.

$$G(L) = G_0(1 + aL)^b \tag{6}$$

where G_0, (μm/h), is the primary floc growth rate, and a and b are the coefficient. Using this proposed model with Eq. (5), the size-dependent growth function is obtained as:

$$\ln n = \ln n^0 + \frac{1}{1-b} - b \ln(1 + aL) - \frac{(1 + aL)^{1-b}}{1-b} \tag{7}$$

where $a = 1/(G_0 t)$, when $b = 0$, Eq. (6) will be size-independent growth function, when $b > 0$, the growth rate increases with increasing of floc size, and when $b < 0$, growth rate decreases with the increase of floc size.

3. Results and discussion

3.1. Turbidity removal during coagulation

A continuous experiment was carried out under the conditions of initial turbidity of 50 NTU and pH 11.5 to determine the turbidity removal during magnesium hydroxide coagulation process. As shown in Fig. 2, with time, the residual turbidity decreases at first stage and then remains about 1.9 NTU. It can also be seen that at 100 min, the coagulation process reaches a steady state. The coagulation behavior indicates magnesium hydroxide is an effective chemical for turbidity removal with efficiency of 98%. Process of coagulation is complex and may involve several mechanisms such as charge neutralization, adsorption, and sweep flocculation to achieve destabilization, which allows particle agglomeration and enhances

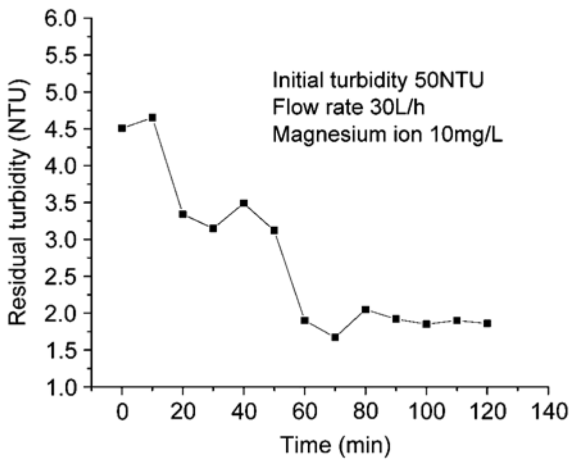

Fig. 2. The residual turbidity changes with time.

subsequent particle removal. The zeta potential of original kaolin suspension was −40.6 mV and the final zeta potential reached to −10.8 mV. $Mg(OH)_2$ provides a large adsorptive surface area and a positive electrostatic surface charge, enabling it to remove the negatively charged colloidal particles through charge neutralization and an adsorptive coagulating mechanism [15]. In order to detect the floc properties, formation, and growth rate of magnesium hydroxide, subsequent experiments will be carried out in a steady state condition of stable removal efficiency.

3.2. Floc characteristics

There are three stages in coagulation process including rapid mixing, flocculation, and sedimentation. Many smaller particles and colloids forming larger ones can be removed more efficiently based on floc size and characteristics. To investigate the FSD in these three process units, an IBR particle counter was used to detect floc size and floc number. Magnesium ion was added to the tested water through measured pump and the concentration was 10 mg/L. At a high pH value 11.5, the precipitation of magnesium hydroxide and coagulation process will occur with the initial turbidity of 50 NTU. The experimental results of FSD in different process units under steady state are shown in Fig. 3. It was found that a gradual increase in floc size during three coagulation processes. Small particles such as 2 μm accounted for 50.6, 47.6, and 45.9% in rapid mixer, flocculation basin, and sedimentation tank, respectively (Fig. 3(a)). The percentage of 7–10 μm particles increased from 6.38 to 8.07% and 9.59% in these three stages. It was observed that the percentage of larger particles increased and such phenomenon was more obvious in sedimentation tank. The FSD had the same shape and almost the same range from 2 to 25 μm; flocs grew and aggregated to form relatively large particles in the coagulation process. In addition to shifting to larger sizes, the total number of particles decreased during the coagulation experiments. Floc counts in the range of 2–5 μm accounting for about 90% at three units were shown in Fig. 3(b). It can be seen that final floc size is not too large with the dominant value at 5 μm. Although there are relatively smaller flocs exist in coagulation system, the flocs have good settling properties and can be removed easily.

Percentage distribution by number for each unit helped to understand floc behavior in coagulation system. However, percentage distribution was usually limited to explain flocs properties. To gain further insight into the floc characteristics, image analysis was used to predict the floc properties. During the slow mixing period in flocculation basin and sedimentation tank, samples of flocs were taken from below the surface of the suspension. The image of flocs in the

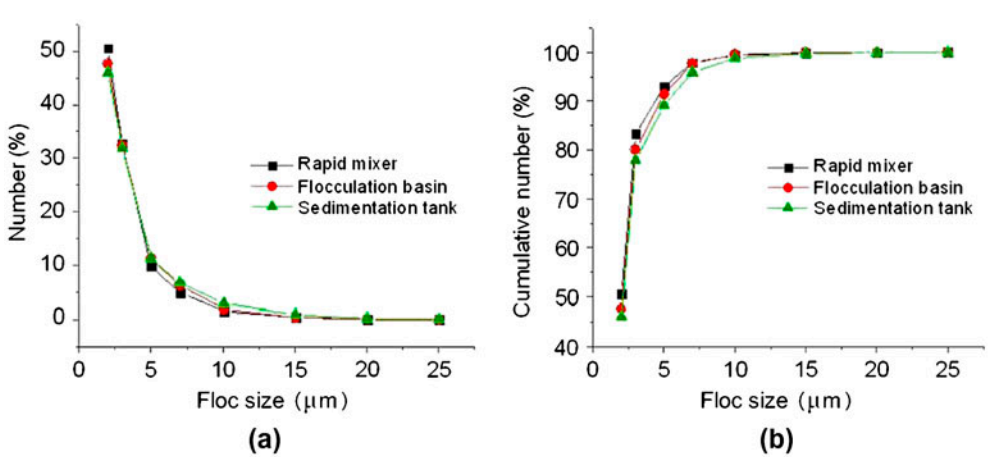

Fig. 3. FSD for three stages: (a) number percentage and (b) cumulative percentage.

sample was captured by IX71 digital photomicrography. As shown in Fig. 4, it clearly indicates that the average size of flocs in sedimentation tank was slightly larger than that of in flocculation basin. Some of the flocs have regular shapes and some aggregate together to form more compact flocs. Normally, the characteristic of a formed floc depends strongly on the coagulant. Kaolin colloidal suspensions consist of negatively charged particles and magnesium hydroxide precipitation has a positive superficial charge. Magnesium hydroxide can attract the negatively charged colloidal particles, but there is no more aggregation occurred for sedimentation process. Maybe positively charged particles of magnesium hydroxide with strong repulsion prevent particles to aggregate together. The resulting repulsive forces tend to stabilize the suspension and prevent particle agglomeration [2,24]. The mechanism is most likely attributed to charge neutralization.

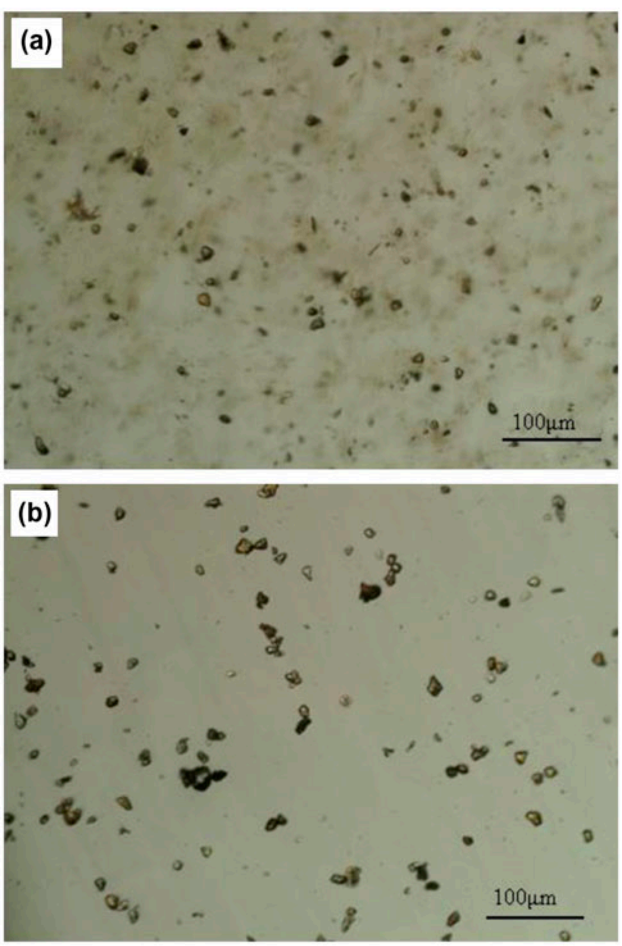

Fig. 4. Images of the flocs: (a) flocculation basin and (b) sedimentation tank.

3.3. Floc growth rate

According to the FSD and Eq. (7), these parameters such as a, b can be obtained by nonlinear fitting method (Table 1). Fig. 5 is the ln(n)–Floc size plot which shows the nonlinear fitting results and experimental data of three process units. The experimental data agreed well with the ASL model.

By calculating, the parameters and the growth rate function are obtained. For flocs in rapid mixer, the size-dependent growth function is:

$$\ln n = 17.65 - 0.627\ln(1 + 2.548L) - 2.68\ln(1 + 2.548L)^{0.373}$$

In flocculation basin, the floc growth function is:

$$\ln n = 15.51 - 0.406\ln(1 + 1.093L) - 1.68\ln(1 + 1.093L)^{0.594}$$

and for flocs in sedimentation tank, the function can be written as:

$$\ln n = 14.16 - 0.516\ln(1 + 1.154L) - 2.07\ln(1 + 1.154L)^{0.484}$$

Since the parameter $b > 0$, the growth rate increases with increasing the floc size.

Although there appears to be an increased growth rate with increasing floc size, the changes of growth rate is different in three process units. The growth rate of flocs in the three process units is calculated and the trends are shown in Fig. 6. It shows apparently that floc size has significant influence on floc growth rate in rapid mixer. The growth rate is much more than that in flocculation basin and sedimentation tank. When magnesium ion was added to the sample water, a higher pH upon alkalization will result in the precipitation of magnesium hydroxide. The primary nucleation rate of magnesium hydroxide will affect the floc formation of colloids in the simulated water samples. Coagulation of kaolin particles can be taken as a two-phase process, involving the rapid growth of tiny flocs in rapid mixer and then the slow growth into relatively larger flocs in flocculation basin and

Table 1
Parameters of size-dependent growth rate model

Process unit	$G(L) = G_0(1 + aL)^b$			
	G_0	a	b	R^2
Rapid mixer	11.776	2.548	0.627	0.996
Flocculation basin	2.288	1.093	0.406	0.997
Sedimentation tank	0.867	1.154	0.516	0.997

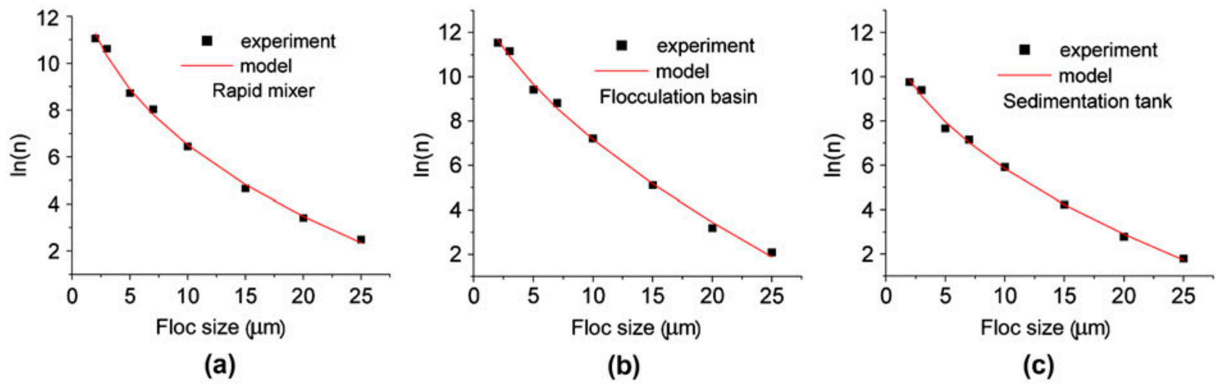

Fig. 5. Comparison of simulated and experimental size distributions of three process units.

sedimentation tank. Although the retention time was short (2 min) in rapid mixer, the magnesium hydroxide was formed quickly and flocs grew rapidly during the first stage. In the next flocculation and sedimentation processes, the growth slowed down although the growth rate increased with increasing the floc size. The three steps of coagulation may be distinguished: fast aggregation during first 2 min, slow aggregation from 2 to 26 min, and finally sedimentation. In general, therefore, time extension in the flocculation and sedimentation process had little impact on floc growth.

3.4. Floc formation-growth kinetics

To understand the relationship between floc formation rate and growth rate under different stage of coagulation, an empirical kinetics model was developed to estimate floc formation-growth rate. The primary floc formation rate B^0 and growth rate G were represented by the empirical expression:

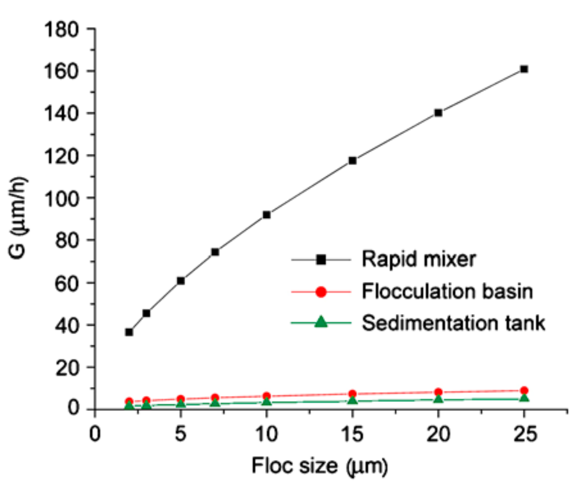

Fig. 6. Floc growth rate with different size in three process units.

$$B^0 = kG^m \tag{8}$$

The overall rate coefficient k and m would be expected to depend on the many variables, such as temperature, hydrodynamics. Using the Eq. (8), the floc formation and growth function is obtained as:

$$\log B^0 = \log k + m \log G \tag{9}$$

This suggests a straight line for $\log B^0$ against $\log G$, where the slope m refers to the floc formation-growth rate order. As mentioned above, the floc growth rate increases with increasing floc size and the large percentage of 2 µm flocs in coagulation system. Floc size of 2 µm was used to calculated the growth rate. The values of B^0 and G obtained from the analysis of FSD are shown in Table 2. The coefficient log k and m are 5.10 and 1.64, respectively.

Fig. 7 is $\log B^0$ against $\log G$ plot which shows the straight line for experimental results. The floc formation and growth empirical function was obtained to understand the relationship between floc formation rate and growth rate under different stages of coagulation.

$$\log B^0 = 5.10 + 1.64 \log G$$

Table 2
Data of floc growth kinetics at different time

Process unit	T (h)	n^0 (#/µm mL)	G (µm/h)	B^0 (#/mL h)
Rapid mixer	1/30	3.18×10^6	36.57	3.75×10^7
Flocculation basin	2/5	1.01×10^6	3.67	2.31×10^6
Sedimentation tank	1	1.79×10^5	1.61	1.55×10^5

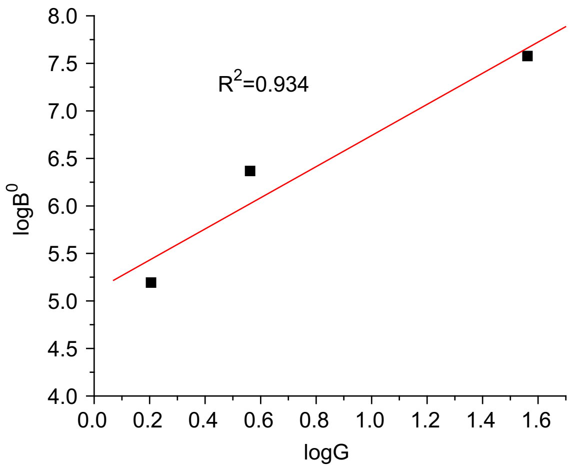

Fig. 7. plot of $\log B^0$ against $\log G$.

4. Conclusions

This study investigated the coagulation of kaolin suspensions using magnesium hydroxide as coagulant. A suitable population balance model was applied to describe the floc growth kinetics in coagulation process. We found that coagulation of kaolin particles in the real situation can be taken as a two-phase process, involving the rapid growth of tiny flocs in rapid mixer and then the slow growth into relatively larger flocs in flocculation basin and sedimentation tank. It should be noted that for different wastewater samples, the optimum conditions were different, therefore, the floc growth kinetics equation could be changed according to the actual situation. Further research will be carried out to evaluate coagulation process in practical application.

In summary:

(1) It is shown that the ASL size-dependent model was developed to systematically investigate the suitability of different size dependence of kinetics to describe the experimental results. Such that model can be used to predict the magnesium hydroxide coagulation process.

(2) Floc growth rate increases with the increase of floc size whereas the growth rate is different in three coagulation stages. The floc formation and growth empirical function is also obtained to understand the relationship between floc formation rate and growth rate under different stage of coagulation.

(3) This study provides more detailed experimental data of flocs for rapid mixing, flocculation, and sedimentation operations. For the given coagulation conditions, floc size was measured by IBR particle counter including three stages. Although the floc counts in the range of 2–5 μm accounting for about 90%, the fast settling floc leads to higher turbidity removal efficiency.

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