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Effects of operational conditions on the floc formation time and rate in magnesium hydroxide coagulation process

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ABSTRACT

Feasibility of using magnesium hydroxide as coagulant for treating high pH wastewater was studied. The floc formation kinetics and minimum dose were investigated with a laser particle analyzing system under different experimental conditions. Floc formation time tended to decrease with the increase of coagulant dose, turbidity, temperature and pH value. A pseudo first-order mathematical model was developed to estimate the floc formation rate. The experimental data agreed well with the pseudo first-order equation. It was also found that when pH value reached 11.5, floc formation rate is not significantly influenced by initial turbidity. The relationship between floc formation rate coefficient and temperature is in agreement with the Arrhenius equation. Based on the changes of residual turbidity and zeta potential, charge neutralization is believed to be the main coagulation mechanism.

Keywords: Magnesium hydroxide; Coagulation; Floc formation time; Coagulation kinetics

1. Introduction

Magnesium hydroxide, a valuable chemical product, is widely used in many applications, such as industrial wastewater treatment [1,2], carbon dioxide capture [3,4] and as a flame retardant in polymeric materials [5,6]. One of the most attractive characteristics of magnesium hydroxide is its nontoxic and environmentally friendly nature. It was also found that magnesium hydroxide could be recycled and reused in treating low concentration of heavy metals contaminated wastewater [7]. The recoverability of magnesium hydroxide may significantly reduce the chemical costs and may effective reduce the threat to human being. In recent years, several authors have investigated the roles of magnesium hydroxide as a potential coagulant and an effective adsorbent for physic-chemical clarification of wastewater [3,8–10]. Chemical coagulation using magnesium chloride has been shown to be an effective alternative to conventional treatments for the removal of color from textile waste effluents. The color removal mechanisms may include: charge neutralization resulted from positively charged $Mg(OH)_2$ particles to destabilize dyes [8], and adsorptive coagulation by $Mg(OH)_2$ precipitates [10,11].

Coagulation-flocculation can be described as the formation of larger particles, or flocs, from the small particles

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in the wastewater [12,13]. Floc size and structure, breakage, re-growth and settling characteristics are the main parameters influencing particle removal efficiency [14,15]. There are many methods available to measure floc physical characteristics and coagulation processes such as a nephelometric turbidimeter method [16], laser technique [17,18] and photometric dispersion technique [19]. 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 processes of magnesium hydroxide precipitation and the floc formation and growth are important in understanding the coagulation mechanism and the wastewater treatment performance.

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 setting characteristics using magnesium hydroxide as coagulant. The main objectives of this laboratory study were to evaluate the coagulation performance, especially to understand the initial floc formation processes of magnesium hydroxide. Floc formation time and minimum coagulant dose were determined using a laser particle analyzing system. In this paper floc formation process is analyzed and the kinetics of floc formation is discussed. Furthermore, the effects of coagulant dose, initial turbidity, temperature, and pH value on the process are also assessed. In addition, the relationships between the coagulant dose and the zeta potential and residual turbidity are determined.

2. Experimental methods

2.1. Materials and methods

Artificial water samples with pH between 11 and 12 were prepared with kaolin and deionized water to provide turbidity of 5–20 NTU. Five grams of kaolin (Tianjin Chemical Reagent Co.) was added to 1 l deionized water and stirred for 30 min at 600 rpm. After settling for 60 min, supernatant was decanted and saved as stock solution. NaOH solution was added to each water sample to control solution pH values. A pH-meter (PHS-25 Shanghai Jinke industrial Co.) was used to determine the pH of the solutions. $MgCl_2 \cdot 6H_2O$ was used to prepare coagulant. 0.1 M stock Mg^{2+} solutions were prepared with deionized water. Working solution was prepared by placing 25-ml stock solution (0.1 M) with deionized water in a 250-ml volumetric flask. All reagents used were of analytical grade. A Hach 2100 N tubidimeter was used for turbidity measurements. 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.

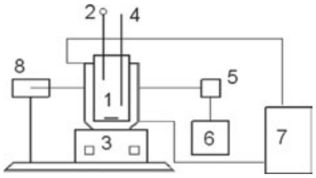

Fig. 1. Experiment apparatus for determination of floc formation (1-reactor; 2-feed tube; 3-magnetic stirrer; 4-thermometer; 5,6,8-laser system; 7-constant temperature bath).

2.2. Apparatus and procedures

2.2.1. Floc formation determination apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. The 0.25 l glass reactor is placed in a water bath to maintain a constant temperature within ±0.2°C. Coagulant solution is added at the beginning of each run, and a magnetic stirrer is employed to provide rapid mixing to ensure even distribution of the coagulant throughout the reactor. When the floc size approaches 635 nm (wavelength of the laser light), light scattering and diffraction occurs that weakens the light transmission. The online laser system detects the floc formation time through the change of laser intensity.

2.2.2. Jar testing

Based on the results of floc formation experiments, additional coagulation experiments were carried out on a jar test apparatus with 1-l beakers. The pH of the water was adjusted to 11.5 with a 0.1 M NaOH solution. Different coagulant dose were added to the water sample with initial turbidity of 10 NTU at 20°C. After magnesium coagulant was added, the solutions were stirred rapidly at 300 rpm for 30 s, followed by slow mixing at 80 rpm for 20 min and then 30 min sedimentation before finial turbidity of the supernatant was measured. During the slow mixing period, sample (10 ml) was withdrawn and analyzed immediately for zeta potential.

3. Theoretical background and model development

Coagulation, defined as the bringing together of small particles into large particles, is a very complicated process involving a series of physical–chemical interactions. Addition of coagulant causes colloidal particles to destabilize. Precipitates form by reaction between coagulant and water aggregates with destabilized pollutant particles to form flocs, which are then removed by gravity separation. The initial floc formation time and the rate of floc formation are important factors for the coagulant selection and coagulation process design and operation. Magnesium hydroxide coagulation process is similar to the nucleation process. The classical theory of homogeneous nucleation indicates that when the solution is supersaturated the monomers in solution start to coagulate and form clusters. If the size of a cluster exceeds a critical size, a nucleus forms and the subsequent growth of nucleus leads to crystal formation [20]. In this study, magnesium hydroxide coagulation includes magnesium hydroxide nucleation and combination of kaolin into flocs.

The floc formation rate may depend on several variables, such as temperature (T), Alkalinity, pH value, coagulant dose and relative supersaturation (S), which is defined as:

$$S = \frac{C}{C^*} \tag{1}$$

where, C (mg l^{-1}) is the coagulant dose and C^* (mg l^{-1}) is the minimum coagulant concentration that can cause the floc formation. The floc formation rate J, defined as number of flocs formed per volume per time (# $(m^3 \cdot s)^{-1}$), was found inversely proportional to the floc formation time or induction period t_{ind} (s) [20]:

$$J = \mathrm{K} t_{\mathrm{ind}}^{-1} \tag{2}$$

where K (# m^{-3}) is a rate coefficient. Among other factors, degree of supersaturation is the most important factor to affect the floc formation time, which decreases with increase of supersaturation. The relationship between induction period and supersaturation has been studied by different researchers [20–22]. Conventionally, two ways are used to interpret the experimental data of induction period and supersaturation. One is the empirical expression [21]:

$$\ln(t_{\mathrm{ind}}) = k - n \ln(S) \tag{3}$$

This model suggests a linear relationship between $\ln(t_{ind})$ and $\ln S$, where the slope refers to the nucleation rate order. The other model is the based on the classical nucleation theory that predicts a linear relationship between $\ln(t_{ind})$ and $(\ln S)^2$. The equation can be written as [20]:

$$\ln t_{\mathrm{ind}} = \frac{A}{T^3 (\ln S)^2} + B \tag{4}$$

where A and B are constants, and T is the absolute temperature (K). Although the above two models have been widely used in simulating nucleation rate in crystal formations, application of these equations to the magnesium coagulation data resulted in limited success. In coagulation process, there are large amount of impurities, such as clay and colloids. These particles may act as nuclei of $Mg(OH)_2$ precipitates and floc formation. The heterogeneous and complex nature of the coagulation process requires different approach in model simulation. Based on the experimental results from this study, the following model is proposed to simulate the relationship between induction period and relative supersaturation:

$$\frac{dt_{\mathrm{ind}}}{dS} = -\frac{1}{kS^n} \tag{5}$$

where k is the rate coefficient (s^{-1}) and n is the rate order. When n is assumed to be 1, Eq. (5) can be simplified to a pseudo first-order reaction. After integration, the induction period function is obtained as:

$$t_{\mathrm{ind}} = B - \frac{\ln S}{k} \tag{6}$$

where B is an integration constant and is related to minimum coagulant dose and corresponding induction time. This model was used to interpret magnesium hydroxide coagulation experimental data and to explain the impact of initial turbidity, pH and temperature on floc formation.

4. Results and discussion

4.1. Effects of turbidity on minimum dose of coagulant

To investigate the effects of turbidity on minimum dose of magnesium coagulant, a laser system was used to detect floc formation. Coagulant was added to the sample water drop by drop till initial floc formation was observed as rapid change in laser light transmittance occurred. Fig. 2 shows the effect of turbidity on minimum dose under pH of 11, 11.5 and 12, at temperatures of 20°C and 25°C. The parallel experiments show that the average relative deviation is 0.67% and 1.2%, respectively. The minimum dose of magnesium ion decreased as initial turbidity increased. The two diagrams show the same trends that at the same pH lower minimum dose is required at higher turbidity. When the initial turbidity was 10 NTU and pH 11.5, minimum dose of coagulant was 3.72 mg l^{-1}. At the same pH value and temperature, when the initial turbidity was increased to 20 NTU, the minimum dose reduced to 2.88 mg l^{-1} (Fig. 2(a)). At higher temperature, the minimum dose of magnesium decrease at the same conditions. Lower minimum dose of magnesium was observed at higher pH levels. This is likely due to lower magnesium hydroxide solubility at higher pH.

4.2. Effects of turbidity on floc formation time

In order to better understand the coagulation behaviors of magnesium coagulant, the floc formation time with respect to magnesium dose was investigated under different initial turbidities at 20°C. As shown in

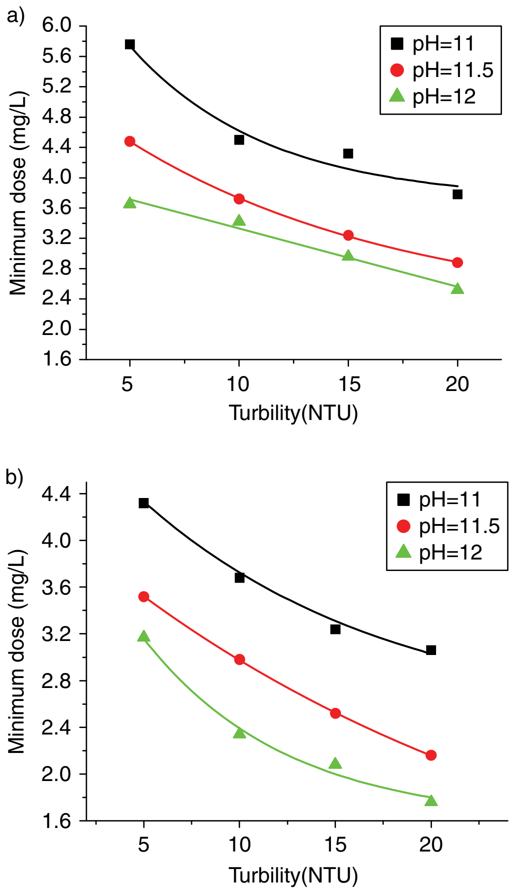

Fig. 2. Effects of turbidity on minimum dose of coagulant, (a) at 20°C and (b) at 25°C.

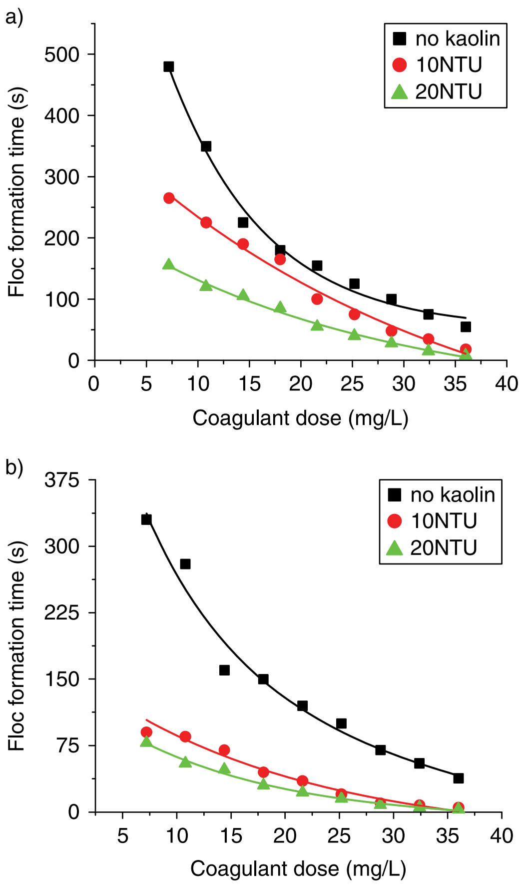

Fig. 3. Effects of turbidity on floc formation time, (a) pH = 11 and (b) pH = 11.5.

Fig. 3, floc formation time decreased with the increase of coagulant dose under all test conditions. It can also be seen that at higher turbidity, the floc formation time was shorter at the same coagulant dose. The experiments show that the average relative deviation is 1.7% and 2.1% under pH of 11 and 11.5, respectively.

At pH value of 11 and magnesium ion dose of 10.8 mg l^{-1} (Fig. 3(a)), when there was no kaolin in the water sample, the floc formation time was 350 s. When the turbidity was increased to 10 NTU and 20 NTU by addition of kaolin, the floc formation time reduced to 225 s and 120 s, respectively. According to the classical nucleation theory [20], homogeneous nucleation induction time is larger than that of heterogeneous nucleation [23]. In this experiment, kaolin acts as a nucleation-promoting agent for magnesium hydroxide nucleation and floc formation. Increasing kaolin addition resulted in reduced induction time of floc formation. The impact of pH can be seen by comparing Fig. 3(a) and (b). Floc formation time was significantly shortened at pH 11.5. More discussion of pH impact is presented in the following section.

4.3. *Effects of pH on floc formation time*

Precipitation of magnesium hydroxide under alkaline conditions may be explained by the following chemical reaction:

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

The resulting magnesium hydroxide, a gelatinous precipitate, was found to serve as an efficient coagulant or flocculent aid [24]. Similar results were also found in lime–magnesium wastewater treatment process in which magnesium precipitates served as effective coagulants at high pH levels [2]. It was also reported that pH higher than 11 is required to achieve effective particle removal using magnesium as coagulant [25]. Fig. 4 shows that an increase in pH upon alkalization at 20°C resulted in shorter floc formation time at the same magnesium dose. The differences are more significant between pH 11 and 11.5 and at low magnesium doses. The experiments show that the average relative deviation is 1.9% and 2.1%, respectively. When magnesium dose was greater than 10 mg l^{-1}, difference in floc formation

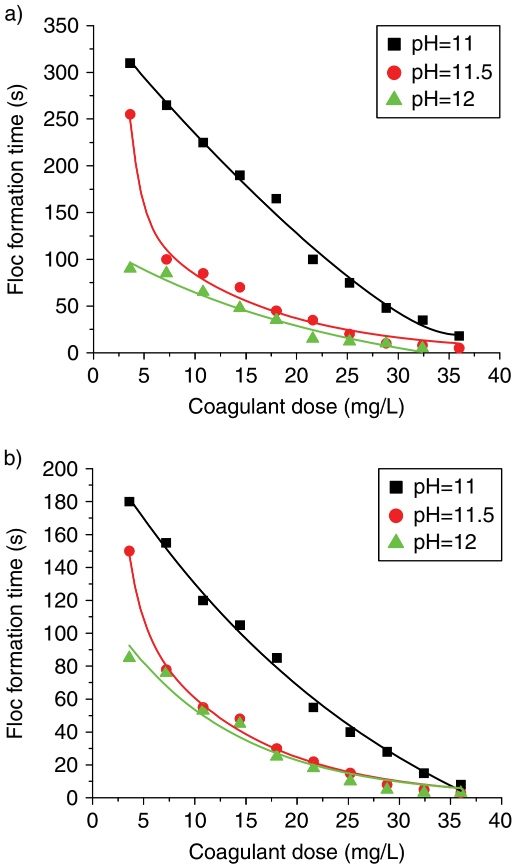

Fig. 4. Effects of pH value on floc formation time with initial turbidity of (a) 10 NTU and (b) 20 NTU.

time between pH 11.5 and pH 12 became less significant. The differences in floc formation time with initial turbidities of 10 NTU and 20 NTU can be seen by comparing Fig. 4(a) and (b). As mentioned above, higher turbidity with higher pH value always cause shorter floc formation time. When the turbidity is 10 NTU at the same magnesium dose of 10.8 mg l^{-1} with pH 11 and 12, the floc formation times are 225 s and 65 s, respectively.

4.4. Effects of temperature on floc formation time

Like most chemical reactions, the rate of magnesium hydroxide precipitation increases as the temperature is raised. As shown in Fig. 5, when magnesium dose was 10.8 mg l^{-1}, increasing reaction temperature from 10°C to 25°C resulted in a decreasing trend of floc formation time. At pH 11.5 (Fig. 5(a)), temperature impact on floc formation time was more significant, changing from 245 s at 10°C to 70 s at 25°C. At pH 12 (Fig. 5(b)), however, temperature had less impact on floc formation time. It is also noticed that when temperature was at 20°C or higher, the difference in floc formation time between pH 11.5 and 12 was less noticeable. The experiments show that the average relative deviation is 1.2% and 1.5%, respectively. As partly described before, higher turbidity and higher pH value can lead to fast floc formation. It appears that the magnesium hydroxide nucleation and floc formation rate in suspension is fast at higher temperatures.

4.5. Floc formation kinetics

The kinetic model developed in Section 3 was used to estimate floc formation rate under the following experimental conditions: temperature 20°C and 25°C; pH 11, 11.5 and 12; and initial turbidity 10 and 20 NTU. The relative supersaturation, S, was calculated based on the minimum dose and actual magnesium coagulant concentration under specific experimental conditions. According to Eq. (6), when t_{ind} is plotted against ln S, a linear curve will be formed and the floc formation rate coefficient k can be determine from the slope of the straight line. Experimental results with best fitted lines are presented in Fig. 6. The values of k and coefficient of determination (R^2) obtained from linear regression analysis are shown in Table 1. The model provided excellent fits to the experimental results with R^2 values ranging between 0.94 and 0.99. The k values represent the floc formation rate under different experimental conditions.

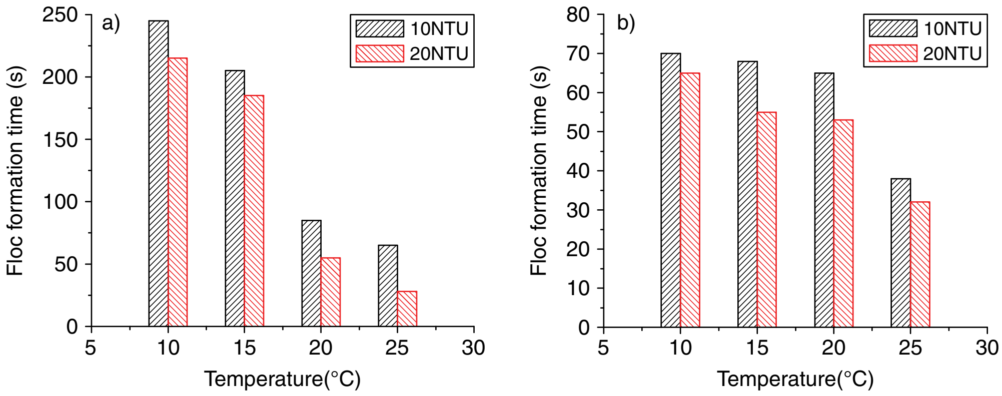

Fig. 5. Effects of temperature on floc formation time, (a) pH = 11.5 and (b) pH = 12.

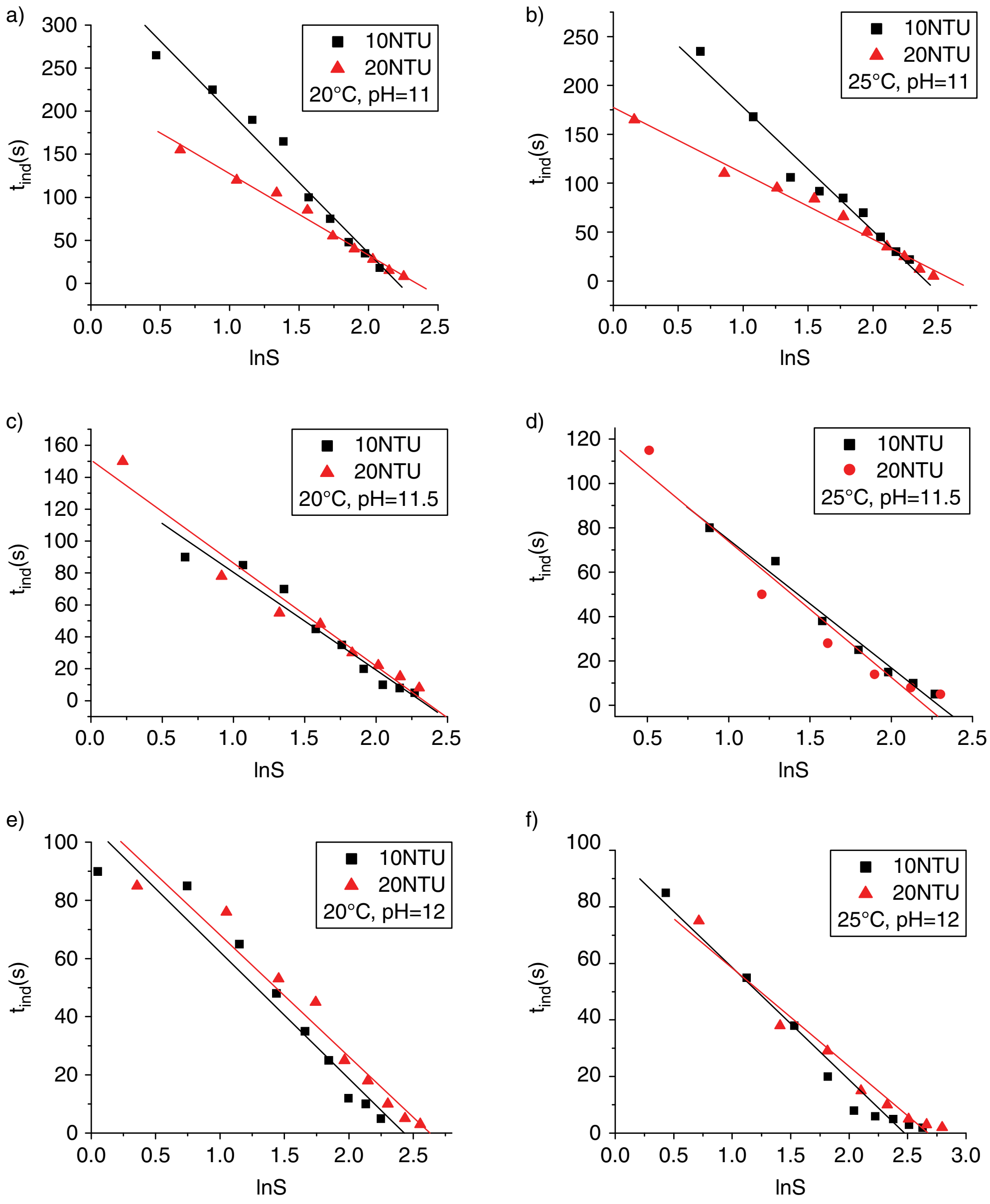

Fig. 6. Induction period as a function of ln *S* in different conditions.

Table 1
Operational conditions and floc formation coefficient

Initial turbidity (NTU)	pH	Floc formation coefficient					
		T = 20°C			T = 25°C		
		$k \times 10^3$ (s^{-1})	B	R^2	$k \times 10^3$ (s^{-1})	B	R^2
10	11	6.08	363.7	0.971	7.92	303.8	0.969
	11.5	16.34	141.4	0.956	19.27	124	0.962
	12	22.99	105.8	0.941	27.55	98.18	0.955
20	11	10.56	222.1	0.987	14.81	177.6	0.983
	11.5	16.53	150.7	0.96	19.23	116.9	0.904
	12	23.92	109.9	0.959	28.78	93.19	0.964

Higher k value means faster floc formation or shorter floc formation time. From Table 1, it can be seen that k value is most sensitive to solution pH. As pH increased by 1 unit, from 11 to 12, k value increased by two- to threefolds with more impact observed under lower initial turbidity. When pH value reached to 11.5 or higher, the impact of turbidity on coefficient became less significantly. At 20°C and pH 11.5, is 1.634×10^{-2} s^{-1} and 1.653×10^{-2} s^{-1} for initial turbidity of 10 NTU and 20 NTU, respectively. Both of the experimental and theoretical results show that the floc formation time decreases with increasing relative supersaturation at constant temperature.

A positive impact of temperature on floc formation rate can also be seen from Table 1. To obtain more conclusive understanding of the temperature effect, additional experiments were conducted at temperatures of 10°C and 15°C under the conditions of pH 11.5 and initial turbidity of 20 NTU. The Arrhenius equation (Eq. (7)) is used to evaluate the relationship between k and temperature:

$$\ln k = \ln A_0 - \frac{E}{RT} \tag{7}$$

where A_0 is Van't Hoff-Arrhenius coefficient (variable units), E is activation energy (J mol^{-1}), R is the universal gas constant (8.314 J $(mol \cdot K)^{-1}$), and T is absolute temperature (K). When temperature change is limited to a relatively small range, the simplified form of Arrhenius equation, Eq. (8), is often used:

$$k_{T_2} = k_{T_1} \theta^{(T_2 - T_1)} \tag{8}$$

where θ is temperature coefficient, $k_{T1}$and k_{T2} are k values at temperature T_1 and T_2, the unit of T_1 and T_2 can use degree Centigrade (°C). According to Eq. (8), when ln k is plotted versus T, a linear curve will be formed and θ can be determine from the slope of the straight line. As shown in Fig. 7, slope of the linear line equals to ln θ, and θ can be determined as 1.043.

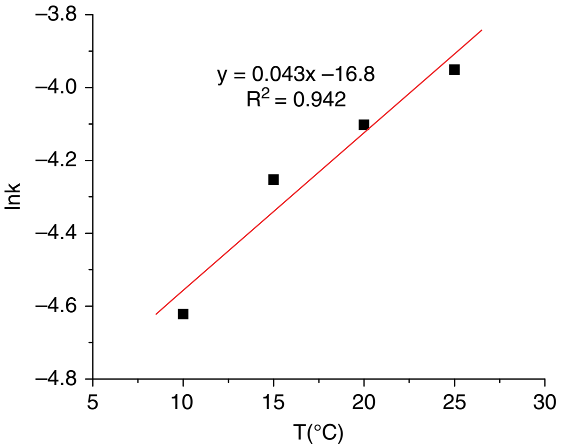

Fig. 7. Arrhenius plot of temperature on coefficient k at pH 11.5, 20 NTU.

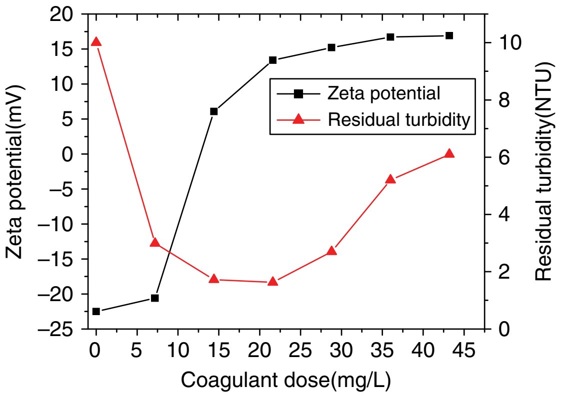

Fig. 8. The curves of zeta potential and residual turbidity varying with magnesium dose.

4.6. Zeta potential and particle removal

Jar tests were carried out under the conditions of initial turbidity of 10 NTU and pH 11.5 to determine the relationship between magnesium dose and residual turbidity. To explore the potential mechanism of colloidal particle removal using magnesium hydroxide as coagulant, zeta potential at different magnesium doses was measured. As shown in Fig. 8, addition of magnesium salt as coagulant resulted in significant turbidity removal. Lowest turbidity of less than 1.7 NTU was achieved with magnesium dose between 14.4 mg l^{-1} and 21.6 mg l^{-1}. Further increase of magnesium concentration, however, caused residual turbidity to increase. The impact of magnesium dose on turbidity removal may be explained by the change in zeta potential. The kaolin suspension used in this study had a zeta potential of −22.5 mV or less. Zeta potential increased with increase of magnesium dose. When magnesium concentration was increased from 7.2 mg l^{-1} to 14.4 mg l^{-1}, zeta potential changed from negative to positive. It was near the concentration of zeta potential reversal that highest turbidity removal efficiency was achieved. Based on this observation, it can be reasoned that charge-neutralization is a main mechanism for destabilization and removal of kaolin particles. Magnesium hydroxide has a positive superficial charge, which attracts the negatively charged colloidal particles, thus inducing agglomeration.

5. Conclusions

Effects of operational conditions on the floc formation time and rate in magnesium hydroxide coagulation process were studied in this paper. The experimental results show that laser system can be very useful to detect the minimum dose and floc formation time. The floc formation time of magnesium coagulant tended to decrease with the increase of coagulant dose, temperature, pH value and turbidity.

The pseudo first-order coagulation model developed in this study is a suitable one to interpret the effects of various operating variables on the floc formation rate. Higher temperature, turbidity and pH value can cause higher floc formation rate. When pH value reached to 11.5 or higher, the impact of turbidity on floc formation rate coefficient *k* became less significantly. The relationship between *k* and temperature is in agreement with the Arrhenius equation.

In terms of coagulation performance, charge neutralization is suggested to be the main mechanism.

Acknowledgements

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