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Magnesium hydroxide coagulation performance and floc properties in treating kaolin suspension under high pH

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ABSTRACT

Application of magnesium hydroxide as a coagulant for treating kaolin suspension under high pH was studied. The coagulation performance and magnesium hydroxide–kaolin floc properties were investigated under different dosages and pH values. Flocculation index and turbidity removal were then discussed with controlled experiments using intelligent particle dispersion analyzer. Floc size distributions were derived from microscopy and image analysis. The results showed that floc size decreased with increasing coagulant dose. The optimum magnesium ion dose tended to decrease with the increase of initial turbidity and pH value. Higher pH and higher magnesium dose led to rapid floc formation and relatively small flocs. The experiments showed that magnesium hydroxide coagulation process had two stages including fast floc formation and growth of flocs and then the larger flocs break into relative small particles. All of the flocs under investigation showed a limited capacity to regrowth when they had been previously broken. Based on the changes of zeta potential and floc properties, charge neutralization and precipitate enmeshment were proposed to be the main coagulation mechanisms.

Keywords: Magnesium hydroxide; Coagulation; Mechanism; Floc; Flocculation index

1. Introduction

Magnesium hydroxide, a nontoxic and environmentally friendly chemical product, is widely used in industrial wastewater treatment [1–3]. One of the most attractive characteristics of magnesium hydroxide is that it could be recycled and reused [3]. The recoverability of magnesium hydroxide may significantly reduce the chemical costs and may effectively reduce the threat to human being. In recent years, several authors have investigated the roles of magnesium hydroxide as a coagulant for the physicochemical clarification of wastewater [4–6]. Chemical coagulation using magnesium hydroxide has been shown to be an effective alternative to conventional treatments for the removal of color from textile waste effluents. The removal mechanisms may include: charge neutralization, enmeshment of colloidal particles by $Mg(OH)_2$ precipitate, and adsorptive coagulating mechanism [4,6,7].

Coagulation–flocculation can be described as the formation of larger particles, or flocs, from the small particles in the wastewater [8,9]. Floc size, breakage, and settling characteristics are the main parameters

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influencing particle removal efficiency [10,11]. Some of the current floc properties and coagulation processes online monitoring technologies such as nephelometric turbidimeter method [12], laser technique [13,14], and photometric dispersion analyzer [15,16] are widely used. 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 reaggregation of floc after shear-induced breakup. Small particles formed into larger aggregates by coagulation are not uniform in size, and vary over a wide range [17]. Since it is inevitable for flocs to break into small particles which generally reduce the removal efficiency, floc strength and recoverability are important factors as well [15]. Serra et al. [18] found that the larger the shear, the smaller the average aggregate size under steady-state conditions. Yu et al. [19] evaluated the effects of different mixing conditions and additional coagulant on coagulation and floc properties. Increasing the rapid mix time led to a decrease in the final floc size. The surface characteristics of flocs and not just their zeta potential are important in influencing the regrowth of flocs. Additionally, the floc formation and growth rate are recognized as crucial operational parameters in most water treatment processes. A faster floc formation and growth rate means a short coagulation process, therefore, a smaller coagulation tank is required [20].

Although there are large amount of data on the characteristics of floc using conventional coagulants such as aluminum and iron salts, there have been limited studies on floc properties and coagulation performance using magnesium hydroxide as the coagulant. The main objectives of this laboratory study were to evaluate the coagulation performance, especially to understand the floc formation processes and coagulation performance of magnesium hydroxide. Flocculation index (FI) for floc formation and growth of coagulant are determined using intelligent particle dispersion analyzer (iPDA). Furthermore, the effects of coagulant dose, initial turbidity, and pH value on the process are also assessed. In addition, floc properties and magnesium hydroxide coagulation mechanisms were also discussed in this paper.

2. Materials and methods

2.1. Synthetic water and coagulant

Five grams of kaolin was dispersed in 1 L deionized water with 30 min at 600 rpm, and then the suspension was transferred to a measuring cylinder and allowed to settle for 60 min. The top 500 mL was decanted as the stock solution. Synthetic water samples with pH between 11 and 12 were prepared with kaolin stock solutions and deionized water to provide turbidity of 5–20 NTU. About 0.1 M NaOH solution was added to each water sample to control the solution pH values. $MgCl_2 \cdot 6H_2O$ was used to prepare coagulant and 0.1 M stock Mg^{2+} solutions were prepared with deionized water. All reagents (Tianjin Chemical Reagent Co.) used were of analytical grade. The precipitation process of magnesium hydroxide from simulated water sample under high pH was carried out in this experiment. The reaction formula is given as follows:

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

The resulting magnesium hydroxide precipitate was found to serve as an efficient coagulant because of the adsorptive surface area and a positive superficial charge.

2.2. Jar test procedures

A schematic diagram of the experimental apparatus is shown in Fig. 1. Coagulation experiments were carried out on a program-controlled jar test apparatus with 1-L beakers (ZR4–6, Zhongrun Water Industry Technology Development Co. Ltd., China) at 20 ± 1˚C. The solutions were stirred rapidly at 200 rpm for 60s during magnesium ion addition, followed by stirring at 60 rpm for 10 min and followed by 30 min of sedimentation before final turbidity was measured. The pH of the water was adjusted to 11–12 with 0.1 M NaOH solution. Different magnesium ion doses were added to the water sample with initial turbidity 5–20 NTU. Throughout the mixing and coagulation periods, an online iPDA was used to monitor the condition of suspensions. The suspension sampled by the iPDA using standard tube of 3 mm internal diameter

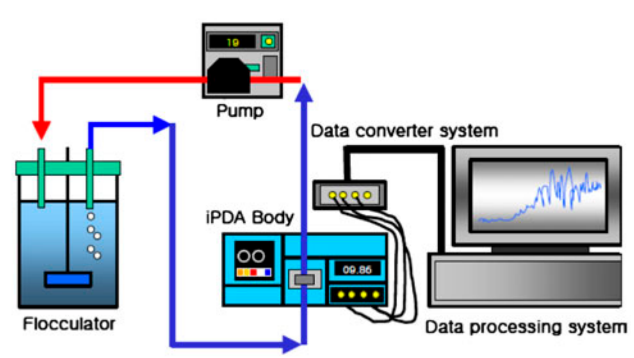

Fig. 1. Experiment apparatus for coagulation of magnesium hydroxide.

was then pumped back into the jar with a flowing rate of 20 mL/min. In this method, the average transmitted light intensity (dc value) through the flowing sample and the root mean square (rms) value of the fluctuating component are measured. The ratio (*R*) between the rms and the average transmitted light intensity (10 rms/dc) provides a sensitive measure of particle aggregation and *R* value is often termed the FI. Very small changes in the state of aggregation of a suspension can lead to changes of several percent or more in the FI output. A higher FI value suggested a bigger size of flocs. The instrument is much better suited to the early detection of the floc formation.

2.3. Analytical methods

A pH meter (PHS-25 Shanghai Jinke Industrial Co.) was used to determine the pH of the solutions. The turbidity of the supernatant liquors was measured using a turbidimeter (HACH 2100N, USA). Zeta potential can be analyzed by zetasizer Nano ZS (Malvern, UK), ICS-1500 (Dionex, USA) was used to analyze magnesium ion. Floc size was measured by IBR particle counter (NASEC, USA). Floc formation and growth can be detected by iPDA (iPDA, EcoNovel Company Ltd., Korea). The morphology of flocs was measured by IX71 digital photomicrography (Olympus, Japan).

3. Results and discussion

3.1. Coagulation behaviors under different coagulant dosage

3.1.1. Effects of initial turbidity

Jar test experiments ware performed to investigate the effects of initial turbidity on turbidity removal under different magnesium coagulant doses. Magnesium ion was added to the tested water with pH value of 11.5 and magnesium hydroxide precipitate served as an efficient coagulant for particle removal. Fig. 2 shows the effects of magnesium coagulant dose on turbidity removal under different initial turbidity values from 5 to 20 NTU, at a temperature of 20˚C. The turbidity removal efficiency after coagulation increased first and then decreased with the increase of coagulant dosage, but the optimum coagulant dose of magnesium ion decreases as the initial turbidity increases. From Fig. 2, the highest turbidity removal efficiency reaches 84, 85, and 80.5% with optimum coagulant dose 18, 14.4, and 7.2 mg/L for initial turbidity of 5, 10, and 20 NTU, respectively. When magnesium hydroxide is formed, the coagulation demands a process that destabilizes particles and a

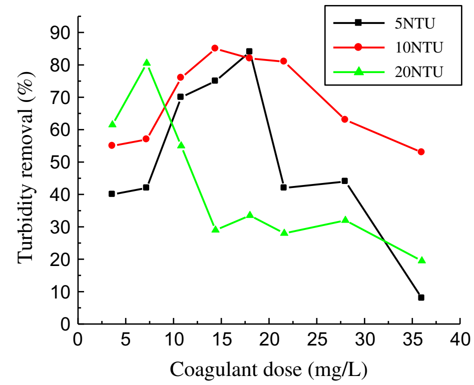

Fig. 2. Effects of coagulant dose on turbidity removal under different initial turbidity levels.

transport process that brings the particles into contact with each other. At higher initial turbidity, the concentration of negative kaolin particles is higher, low amount of coagulant will be needed to form flocs. This may be related to the formation of magnesium hydroxide precipitate and the coagulation mechanism, which will be discussed in the following section.

3.1.2. Effects of pH value

The pH of the solution can be a key parameter in the choice of the magnesium hydroxide coagulation technology. In order to investigate the effects of pH on magnesium hydroxide coagulation performance, the test water pH was adjusted to different levels (from 11 to 12) and the initial turbidity was fixed at 10 NTU. If pH is lower than 11, magnesium hydroxide flocs are not easy to form and the removal efficiency is low [21]. When pH is higher than 12, the pH adjustment systems after coagulation process are also needed if this process is used in practice. The changes of turbidity removal with different coagulant doses are shown in Fig. 3. The pH value had a significant influence on turbidity removal with different coagulant doses. However, the variations of turbidity removal with pH were rather complicated. When pH values were 11 and 11.5, the turbidity removal experienced increase and subsequent decrease with increasing coagulant dose, while magnesium dose of 14.4 mg/L resulted in the highest value of turbidity removal. This is consistent with the findings of Elmaleh et al. [21] who showed that increasing pH promoted treatment efficiency. When pH reached 12, the results showed that turbidity removal was high at low coagulant dose. Increasing coagulant dose led to low turbidity removal when magnesium ions exceeded 14.4 mg/L at pH 12. Furthermore, in terms of turbidity removal, coagulation was found to be very sensi-

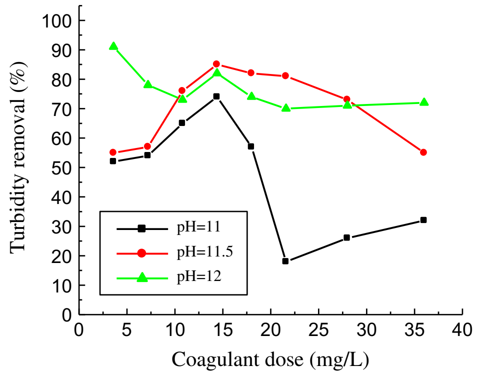

Fig. 3. Effects of coagulant dose on turbidity removal at different pH levels.

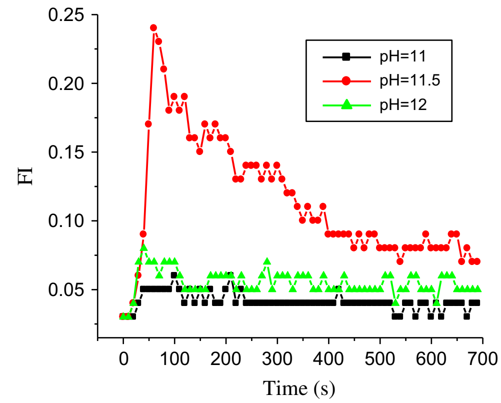

Fig. 4. Effects of pH value on FI in different coagulation processes.

tive to the change of pH at the same coagulant dosage. At low coagulant dose, higher pH led to higher turbidity removal. Magnesium hydroxide can act as charge neutralization species. With further coagulant dose increasing, large amount of magnesium hydroxide was formed and when the precipitation forms in large quantities, colloidal particles would be effectively removed by enmeshment in the forming precipitate rather than by traditional charge neutralization. Although it is difficult to draw a conclusion about these differences in turbidity removal, the properties of magnesium hydroxide precipitate and combined flocs should play an important role in the coagulation process.

3.2. Coagulation behaviors with time under fixed coagulant dose

Just as mentioned above, when magnesium ion was added to the sample water, an increase in pH upon alkalization will result in the precipitation of magnesium hydroxide. In order for the treatment process to operate efficiently, NaOH should be used to increase the pH of the original wastewater to pH 11.0–11.5 [21]. The working behavior of the iPDA is generally discussed here. During the fast coagulation period, voluminous flocs are formed, and thus the increase in floc size primarily results from the enmeshment of particles by flocs. Fig. 4 shows that an increase in pH upon alkalization at initial turbidity of 10 NTU will result in shorter floc formation time at the same magnesium dose of 14.4 mg/L. At a higher pH of 12, the reaction is very fast and FI reaches it first peak in 40 s. Whereas pH values are 11 and 11.5, the FI peak times are 100 s and 60 s, respectively. The primary nucleation process of magnesium hydroxide will affect the floc formation time of colloids in the simulated water samples. Higher pH value always causes rapid nucleation of magnesium hydroxide and shorter floc formation time. On the other hand, higher pH ($\geqslant$11.5) also causes small particles of magnesium hydroxide to precipitate. As shown in Fig. 4, the average FI of pH 12 is smaller than that of pH 11.5 and the flocs had relatively smaller size in higher pH. However, the average FI of pH 11 is smaller than that of pH 12 and 11.5. Because flocs are not easy to form when pH is 11 and when pH reaches to 11.5, floc formation time is short and 14.4 mg/L magnesium ion is the optimum dose for this pH value. Nucleation and precipitation of magnesium hydroxide should affect the floc properties significantly. In addition, although the flocs will break during the process, the final FI value is the highest for pH 11.5.

3.3. Zeta potential and particle removal

The iPDA does not indicate the settlement of flocs, but tells the growth rate of flocs. The residual turbidity of the settled water product is commonly used to estimate the performance of the coagulation process. To explore the potential mechanism of colloidal particle removal using magnesium hydroxide as coagulant, zeta potential variation and particle removal as a function of coagulant dose at pH 11.5 was examined. The zeta potential of original kaolin suspension was less than −22.5 mV and the initial turbidity was 10 NTU. As Fig. 5 indicates, zeta potential increases from negative zone to positive zone with the increasing magnesium dose from 7.2 to 15.5 mg/L, the residual turbidity decreases at the first stage with a lower magnesium dose and then increases with the increase in magnesium dose. The lowest turbidity of less than 1.5 NTU was achieved with magnesium dose between 14.4 and 17.9 mg/L. At higher magnesium dose, on the other hand, magnesium hydroxide itself may

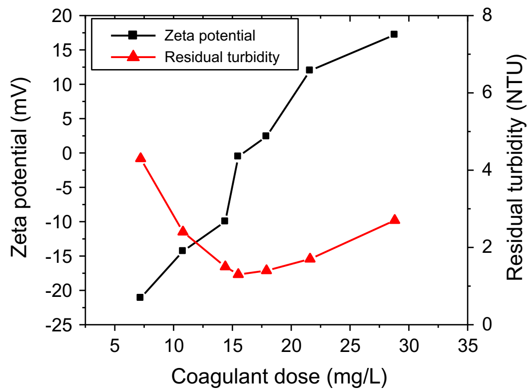

Fig. 5. Curves of zeta potential and residual turbidity with varying magnesium doses at pH 11.5.

cause the residual turbidity increases. The impact of magnesium dose on turbidity removal may be explained by the change in zeta potential. It was near the concentration of zeta potential reversal that the highest turbidity removal efficiency was achieved. Based on this observation, it can be reasoned that charge neutralization is one of the mechanisms for destabilization and removal of kaolin particles. The process of coagulation is complex and may involve several mechanisms such as charge neutralization, patch aggregation, and sweep flocculation to achieve destabilization, which allows particle agglomeration and enhances subsequent particle removal. More evidence can be seen from the following floc size distribution and floc images.

3.4. Coagulation performance and floc characteristics

3.4.1. FI and floc size distribution

Since magnesium ion concentration had significant effects on the coagulation process and turbidity removal, additional experiments were conducted at coagulant doses of 7.2, 14.4, and 21.6 mg/L under the conditions of pH 11.5 and initial turbidity of 10 NTU. As shown in Fig. 6(a), coagulant dose impact on floc formation time was more significant. Increasing coagulant dose resulted in a decreasing trend of floc formation time. When magnesium dose was 7.2 mg/L, the maximum FI value was achieved at 90 s, changing from 60 s at 14.4 mg/L to 30 s at 21.6 mg/L. Then, FI decrease with experimental time went on. We found that coagulation of kaolin particles can be taken as a two-phase process, involving the fast growth of flocs and then the larger flocs break into relatively small particles. All of the flocs under investigation showed a limited capacity to regrowth when they had been previously broken. Fig. 6(a) also shows that the lower

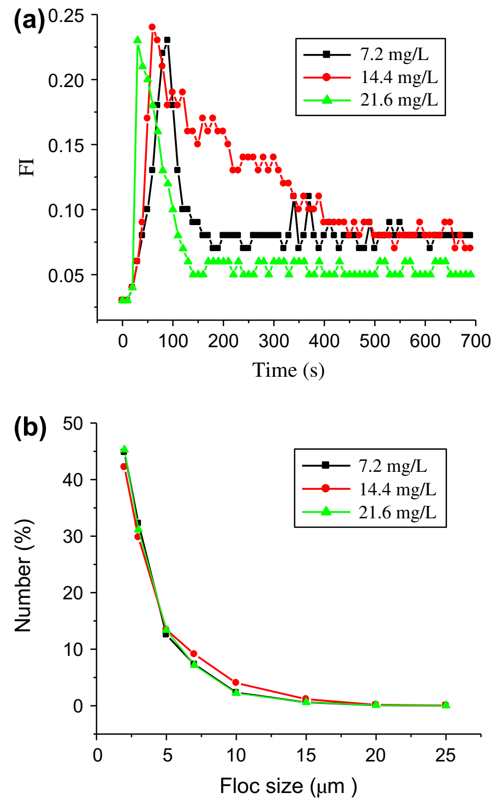

Fig. 6. FI and floc size distribution with different coagulant doses.

coagulant dose led to relatively higher FI. These results can also be easily understood in combination with the floc size analysis. Floc size was monitored using an IBR particle counter and floc size distribution can be calculated from the number of particles ranging from 2 to 25 μm (Fig. 6(b)). The experimental results showed small particles with size such as 2 μm account for 44.8, 42.2, and 45.3% with different coagulant doses of 7.2, 14.4, and 21.6 mg/L, respectively. The parallel experiments show that the average relative deviation is 1.2%. The percentage of 7–10 μm particles changed from 2.33 to 4.04% and 2.24% with coagulant dose increase. It was observed that the floc size distribution had the same shape and almost the same ranging from 2 to 25 μm. Although flocs grew and aggregated to form relatively large particles in the coagulation process, the floc size was not very large compared with other coagulation process using conventional coagulants such as alum [19]. The flocs have good settling properties and can be removed easily. Magnesium hydroxide coagulation process is different from conventional coagulation processes due to high alkalization from 11 to 12. The reaction rate is very fast and large amount of nuclei are formed.

3.4.2. Floc images

The percentage distribution usually is limited to explain flocs properties. To gain further insight into the floc characteristics, image analysis was used to predict the floc properties. Samples of flocs were taken from below the surface of the suspension. The image of flocs in the sample was captured by IX71 digital photomicrography. Fig. 7 clearly indicates that the average size of flocs in the kaolin–magnesium hydroxide system with low coagulant dose was slightly higher than that of high coagulant doses. 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. Magnesium hydroxide has a large adsorptive surface area and a positive superficial charge, which attracts the negatively charged colloidal particles, thus inducing adsorption and agglomeration [2,22]. Fig. 6(b) shows some aggregates and small particles existing in the coagulation system. It is likely that, during the process of floc breakage and regrowth, more small flocs are incorporated into larger ones even though the average size of the regrown flocs is smaller. However, as mentioned, too much of coagulant dose will lead to small particles, there is no more aggregation occurred due to the strong repulsion between positively charged particles of magnesium hydroxide. The resulting repulsive forces tend to stabilize the suspension and prevent particle agglomeration [9]. According to removal mechanisms in references, charge neutralization, enmeshment of colloidal particles by $Mg(OH)_2$ precipitate and adsorptive coagulating mechanism should be suitable for this process. But through the previous research, we cannot determine which mechanisms are the dominating ones. The coagulation behavior indicates that the mechanisms are charge neutralization and precipitate patch coagulation at lower magnesium dose. Large coagulant dose enhances the removal of small particles by enmeshment in forming the precipitate. The adsorptive coagulation mechanism and proportion of adsorptive mechanism are still not clear and should be further studied in future. From this experiment, it can be seen that charge neutralization and precipitate enmeshment must be the main mechanisms.

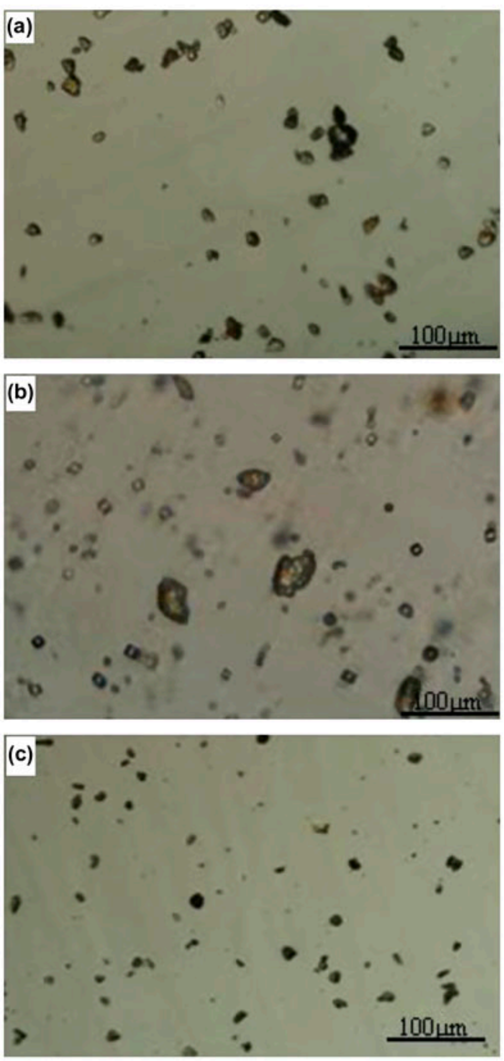

Fig. 7. Images of the flocs: (a) 7.2 mg/L, (b) 14.4 mg/L, (c) 21.6 mg/L.

4. Conclusions

In this research, magnesium hydroxide coagulation performance and the floc properties under different conditions were investigated. From investigations, we come to the following conclusions:

(1) The optimum magnesium coagulant dose tended to decrease with the increase of initial turbidity and pH value.
(2) FI value showed that an increase in pH will result in shorter floc formation time at the same magnesium dose. Flocs formed at a high pH with significant precipitation of magnesium hydroxide was relatively small.
(3) Floc formation time and floc size tended to decrease with the increase of coagulant dose. The coagulation process involves fast formation and growth of flocs and then the larger flocs break into relative smaller particles. All of the flocs under investigation showed a limited capacity to regrowth when they had been previously broken.

(4) The experimental results show that mechanisms involved in magnesium hydroxide coagulation are charge neutralization and precipitate enmeshment.

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