

Effect of kaolin on floc properties for reactive orange removal in continuous coagulation process

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ABSTRACT

Magnesium hydroxide was used as a coagulant for treating reactive orange wastewater in a real continuous process. Effects of kaolin on coagulation performance and floc properties were investigated with controlled experiments through floc size distribution, zeta potential, scanning electron microscopy and Fourier transform infrared spectroscopy. Kaolin had significant influence on magnesium hydroxide-reactive orange floc formation and growth. The results showed that average floc size reached 16.31, 12.88 and 20.50 μm , respectively, in the rapid mixer, flocculation basin and sedimentation tank when kaolin concentration was 10 mg/L and reactive orange initial concentration was 0.25 g/L. The floc size tended to increase with the increase of kaolin suspension to 10 mg/L. All of the flocs under investigation showed that floc breakage led to decreased average floc size and remained stable in the flocculation basin. Reactive orange and kaolin could be removed effectively in the continuous coagulation process. Reactive orange was adsorbed in the surface of magnesium hydroxide through charge neutralization and adsorption.

Key words | floc properties, kaolin, magnesium hydroxide, reactive orange, wastewater treatment

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INTRODUCTION

Reactive dyes are widely used in the textile industry and the residual dyes lead to intensively colored effluents (El-Gohary & Tawfik 2009; Verma *et al.* 2012). Reactive dyes wastewater is usually difficult to biodegrade because of typical characteristics that include high pH value, high chemical oxygen demand and strong color (Riera-Torres *et al.* 2010; Zhou *et al.* 2016). Coagulation has been used for many years as a main treatment or pretreatment process for dye wastewaters due to its low capital cost (Tan *et al.* 2000; Yang *et al.* 2014). Magnesium hydroxide has been shown to be an effective coagulant for the removal of reactive dyes from wastewater (Semerjian & Ayoub 2003; Li *et al.* 2016). Magnesium hydroxide floc formation and growth are the main parameters influencing operational conditions in real industrial scale unit operations. As a cheap and environmentally friendly chemical product, magnesium hydroxide precipitate formation time is short, and the positive superficial charge can attract the negatively charged colloidal flocs very quickly for alkali wastewater (Wei *et al.* 2014; Liu *et al.* 2015). The mechanisms of magnesium hydroxide for color removal may include:

charge neutralization resulting from positively charged $\text{Mg}(\text{OH})_2$ particles, enmeshment by $\text{Mg}(\text{OH})_2$ precipitate and adsorptive coagulating mechanism (Leentvaar & Rebhun 1982; Gao *et al.* 2007; Bouyakoub *et al.* 2011; Zhao *et al.* 2017).

In a real coagulation process, floc formation and physical characteristics will affect the mechanism of pollutant removal (Jiao *et al.* 2017; Li *et al.* 2018). Reactive dyes are soluble and there are some impurities in the wastewater. Kaolin can affect the floc formation and growth in the magnesium hydroxide coagulation process. Although there are some studies on floc properties using magnesium hydroxide as a coagulant in a reactive dyes system, there have been limited studies in a real continuous steady experiment (Ren *et al.* 2017). The floc growth and breakage in the presence of kaolin are still not clear and should be further studied. The main objective of this laboratory study was to evaluate the effect of kaolin on floc properties, especially to understand the floc size distribution (FSD) in the rapid mixer, flocculation basin and sedimentation tank. Furthermore, floc properties and coagulation performance are also assessed.

MATERIALS AND METHODS

Synthetic test water and coagulant

Reactive orange (K-GN) (Jinan Xinxing Textile Dyeing Mill, Shandong, China) was used for a model solution. Artificial water samples with pH 12 were prepared with reactive orange and deionized water to provide concentration of 0.25 g/L. Kaolin clay (AR; Tianjin Chemical Reagent Co., China) was used as an additive with concentrations of 10 and 20 mg/L. The turbidity of the suspension was measured using a turbidimeter (Hach 2100N, USA). A 1 M NaOH solution was added to the water sample to control the solution pH value. A pH-meter (PHS-25 Shanghai Jinke Industrial Co., China) was used to determine the initial pH of the solutions. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (CP; Tianjin Chemical Reagent Co., China) was used to prepare coagulant. Stock solutions of 0.1 M Mg^{2+} were prepared with deionized water. Magnesium ion was analyzed with an ICS-1500 (Dionex, USA) ion chromatography system. The concentration of reactive orange in the solution was analyzed by a UV-visible spectrophotometer (UV2550 Shimadzu, Japan). The reactive orange characteristics for this study are shown in Table 1, where λ_{max} represents maximum absorbance wavelength.

Floc size distribution and properties analysis

During the continuous coagulation process, samples of flocs were taken from the rapid mixer, the third flocculation basin and sedimentation tank using a tube with an inner diameter of 5 mm. FSD was measured by a Mastersizer 2000 (Malvern, UK). During the slow mixing period in the third flocculation basin, zeta potential was measured by zetasizer Nano ZS (Malvern, UK). The image of flocs in the sample was captured by IX71 digital photomicrography (Olympus, Japan). After sedimentation finished, samples of flocs were taken from below the surface of the suspension. Morphology of sediments was also observed by scanning electron microscopy (SEM FEI, Quanta 200, Czech

Republic) and analyzed by Fourier transform infrared (FT-IR) spectrum analysis (Nicolet iS 10 FT-IR Spectrometer, Thermo Scientific, USA).

Apparatus and procedures

Continuous coagulation experiments were carried out in three steps (Figure 1). For this process to occur, the 1 L rapid mixer was maintained at stirring speed of 300 rpm. The flocculation basin, which was divided into three parts (3×4 L), and sedimentation tank (30 L) were designed for the removal of solid particles. The slow stirring speed was maintained at 80 rpm in the flocculation basin. Water sample with pH of 12 and different concentration of kaolin was pumped to the rapid mixer with flow of 29 L/h, chemical feed was also pumped to the rapid mixer at 1 L/h. The total influent flow was 30 L/h and the initial concentration of magnesium ion was 250 mg/L. A continuous steady experiment was carried out at $20 \pm 1^\circ\text{C}$ to justify reactive orange removal during the magnesium hydroxide coagulation process. The experiment process was similar to that of Zhao *et al.* (2014). In order to obtain a real continuous steady experiment, K-GN removal efficiency remained stable after 1 hour. Then continuous experiments were performed for at least 3 hours and all samples of flocs were taken from the rapid mixer, the third flocculation basin and sedimentation tank every 10 minutes. Each sample was measured three times and the average results were obtained.

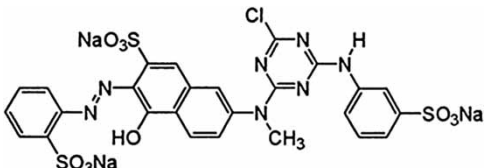
RESULTS AND DISCUSSION

Coagulation behaviors under different kaolin concentration

Floc size distribution in three processes

As previously found (Liu *et al.* 2015; Zhao *et al.* 2017), the dosage of magnesium ion for the jar test experiments was

Table 1 | Reactive orange characteristics

Name	Molecular structure	λ_{max} (nm)
Reactive orange (K-GN)		476

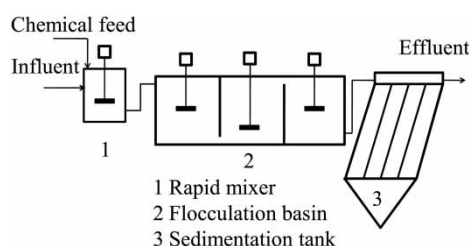


Figure 1 | Experimental apparatus for coagulation of magnesium hydroxide.

chosen as 150 mg/L for pH 12. But in continuous experiments, reactive orange removal efficiency only reached 89% when magnesium ion concentration was 250 mg/L. Continuous experiments under this fixed coagulant were performed to investigate the effects of kaolin clay on coagulation performance and FSD. According to FSD, average floc size significantly increased when kaolin concentration increased in the rapid mixer and flocculation basin. In the sedimentation tank, floc size tended to increase with the increase of kaolin concentration to 10 mg/L. When 20 mg/L kaolin was added to solution, average floc size showed poor ability to aggregate together. Kaolin colloidal suspensions consist of negatively charged particles, and magnesium hydroxide precipitation has a positive superficial charge. This is consistent with the findings that repulsive forces tend to stabilize the suspension and prevent particle agglomeration (Semerjian & Ayoub 2003; Zhao *et al.* 2014). As shown in Figure 2, the average floc sizes 8.06, 16.31 and 15.79 μm were obtained with kaolin concentration 0, 10 and 20 mg/L in the rapid mixer, respectively. For the presence of kaolin, average floc size was almost the same in the rapid mixer. The magnesium hydroxide coagulation process is similar to the precipitation process which includes magnesium hydroxide nucleation and growth. The magnesium hydroxide precipitation process will happen rapidly (Huang *et al.* 2012). As can be seen also in Figure 2, particles smaller than 1 μm accounted for 17.4%, 2.1%, and 4.6% in the rapid mixer with kaolin concentration 0, 10 and 20 mg/L, respectively. It was observed that the percentage of larger particles increased with kaolin clay addition. Kaolin promoted floc formation in the rapid mixing stage. As shown in Figure 3, the average floc size reached 16.31, 12.88 and 20.50 μm in the rapid mixer, flocculation basin and sedimentation tank when kaolin concentration was 10 mg/L.

Effect of different kaolin concentration on removal efficiency

The properties of flocs should play an important role in the magnesium hydroxide coagulation process. Continuous experiments were performed to investigate the effect of kaolin concentration on coagulation performance. As shown in Figure 4, the K-GN removal efficiency after coagulation decreased with the increase of kaolin concentration. The removal efficiency reached 89% and 61% when kaolin concentrations were 0 and 20 mg/L. In order to better understand the coagulation behaviors of magnesium coagulant assisted with kaolin, the effects of different kaolin concentration and turbidity removal relationship were also

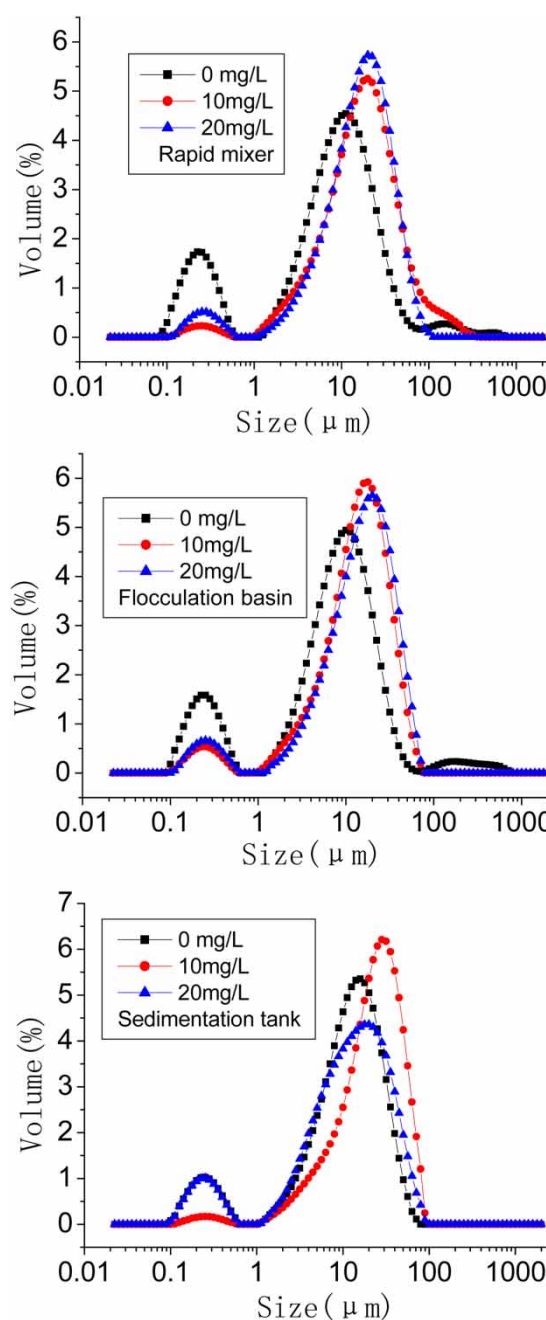


Figure 2 | Floc size distribution with different kaolin concentration for three stages.

investigated. The changes of kaolin concentration and turbidity removal are shown in Table 2. It can be seen that the turbidity removal efficiency increased with the increase of kaolin concentration. When kaolin concentration reached 20 mg/L, the turbidity removal was 95%. Magnesium hydroxide can act as a charge neutralization species. Although K-GN removal decreased, turbidity removal increased with kaolin concentration increasing. Kaolin will not only act as

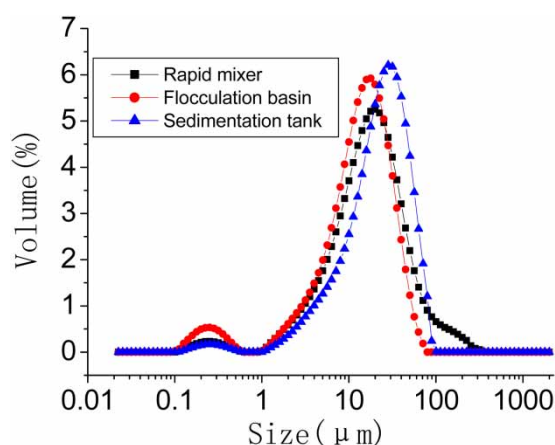


Figure 3 | Floc size distribution for three stages with 10 mg/L kaolin.

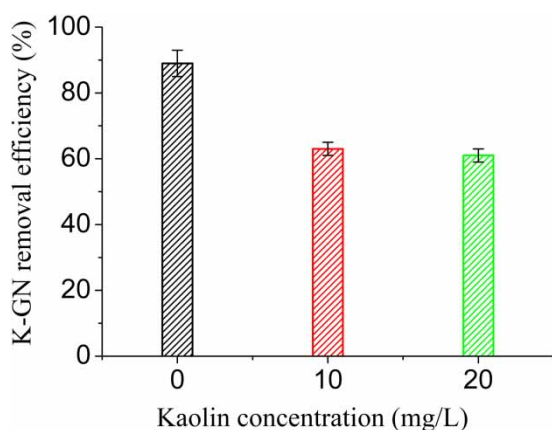


Figure 4 | Effects of kaolin concentration on K-GN removal.

Table 2 | Kaolin concentration and turbidity

Kaolin (mg/L)	Initial turbidity (NTU)	Final turbidity (NTU)	Turbidity removal (%)
10	46	5	87
20	60	2.5	95

a nucleation-promoting agent for magnesium hydroxide nucleation and floc formation, but also adsorbed magnesium hydroxide particles. This is different from the findings of our previous study (Li *et al.* 2016) of reactive red and reactive yellow dyes removal in jar test. Magnesium hydroxide could remove both K-GN and kaolin effectively.

Zeta potential under different kaolin concentration

There are three stages in the coagulation process including rapid mixing, slow mixing and sedimentation. During the slow mixing process, the flocs are broken into relatively

smaller flocs and remain in steady state. Zeta potential is important in terms of the impact on steady state floc size. Floc properties impact significantly on the overall removal efficiency (Sharp *et al.* 2006). In order to explore mechanisms of reactive orange removal using magnesium hydroxide as coagulant in the presence of kaolin, the effect of different kaolin concentration on the zeta potential is presented in Table 3. K-GN concentration was 0.25 g/L and magnesium ion was 250 mg/L with pH 12. Zeta potentials with kaolin concentration 20 mg/L were -3.42 , -3.66 and -2.72 mV in the rapid mixer, flocculation basin and sedimentation tank, respectively. It is likely that higher turbidity removal efficiency during the coagulation process caused zeta potential near 0 mV. This is consistent with the findings of turbidity value which are shown in Table 2. Based on this observation, it can be reasoned that charge neutralization is one of the mechanisms for destabilization and removal of turbidity. This is also consistent with the findings of our previous study (Zhao *et al.* 2014). Similar results were also found in the magnesium hydroxide coagulation process in which magnesium precipitates served as effective coagulant at high pH levels (Semerjian & Ayoub 2003; Ayoub *et al.* 2014). The process of coagulation is complex and may involve several mechanisms. According to removal mechanisms in the literature (Gao *et al.* 2007; Bouyakoub *et al.* 2011; Zhao *et al.* 2017), charge neutralization and adsorptive coagulating mechanism should be suitable for the coagulation process.

Floc and sediments characteristics

Floc image analysis

The FSD can provide information about the distribution of particle size of flocs, and the removal efficiency is commonly used to estimate coagulation performance. To gain further insight into the floc characteristics, image analysis was used to predict the floc properties. Samples of coagulation floc were withdrawn below the surface of the suspension in the flocculation basin (third basin). Addition

Table 3 | Zeta potential in different process units

Kaolin (mg/L)	Zeta potential (mV)		
	Rapid mixer	Flocculation basin	Sedimentation tank
0	-9.2	-8.99	-3.82
10	-15.2	-13.8	-4.42
20	-3.42	-3.66	-2.72

of kaolin with different concentration resulted in different floc properties. Figure 5 clearly indicates that the average size of flocs in the presence of kaolin was higher than that without kaolin. This is consistent with the findings of FSD value which are shown in Figures 2 and 3. The floc size of magnesium hydroxide–reactive orange is lower $10\text{ }\mu\text{m}$. When kaolin concentration is 20 mg/L , the floc size can reach $15\text{ }\mu\text{m}$ (Figure 5(c)). Magnesium hydroxide has a positive superficial charge, which attracts the negatively charged

reactive orange and kaolin in the coagulation process. The resulting magnesium hydroxide is a gelatinous precipitate, which was found to serve as an efficient coagulant (Ayoub *et al.* 2000).

FT-IR spectral analysis and SEM

In order to confirm the existence of functional groups responsible for coagulation of reactive orange, the FT-IR spectra of magnesium hydroxide and coagulation flocs are shown in Figure 6. In the IR spectrum of the magnesium hydroxide, the peak at $3,700\text{ cm}^{-1}$ was assigned to the free O-H stretching vibration mode of the hydroxyl functional groups. The two peaks of the spectra between $1,650\text{ cm}^{-1}$ and $1,416\text{ cm}^{-1}$ were attributed to the bending vibration of Mg-OH and OH bond in crystal structure, respectively (Wu *et al.* 2008). The peak at $2,360\text{ cm}^{-1}$ was an interference peak. The peak in the $1,637\text{ cm}^{-1}$ region was ascribed to the stretching vibration of C=C and the stretching vibration of C-OH led to the peak at $1,050\text{ cm}^{-1}$. The FT-IR spectra showed that reactive orange K-GN was adsorbed on the magnesium hydroxide surface during the coagulation process.

The surface and morphology of magnesium hydroxide coagulation flocs with and without kaolin, determined by SEM images, are illustrated in Figure 7. According to the SEM image analysis (Figure 7(b)), significant changes observed in the surface morphology of dye-loaded sediments indicate an uneven, irregular surface with a molecular cloud of reactive orange. No more aggregation occurred due to the strong repulsion between positively charged particles of magnesium hydroxide (Li *et al.* 2006). Figure 7(c) indicates that magnesium hydroxide–kaolin flocs aggregated together in coagulation system.

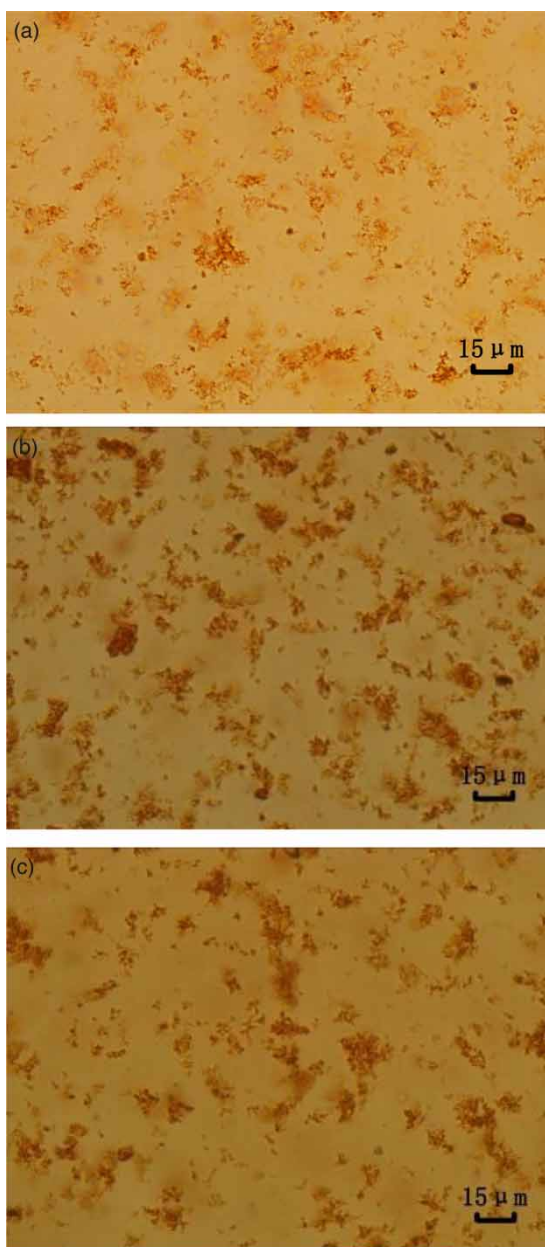


Figure 5 | Floc image analysis: (a) without kaolin, (b) 10 mg/L kaolin, (c) 20 mg/L kaolin.

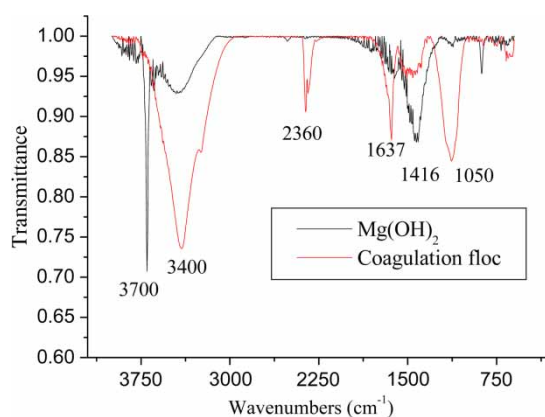


Figure 6 | IR spectrum of $\text{Mg}(\text{OH})_2$ and coagulation floc.

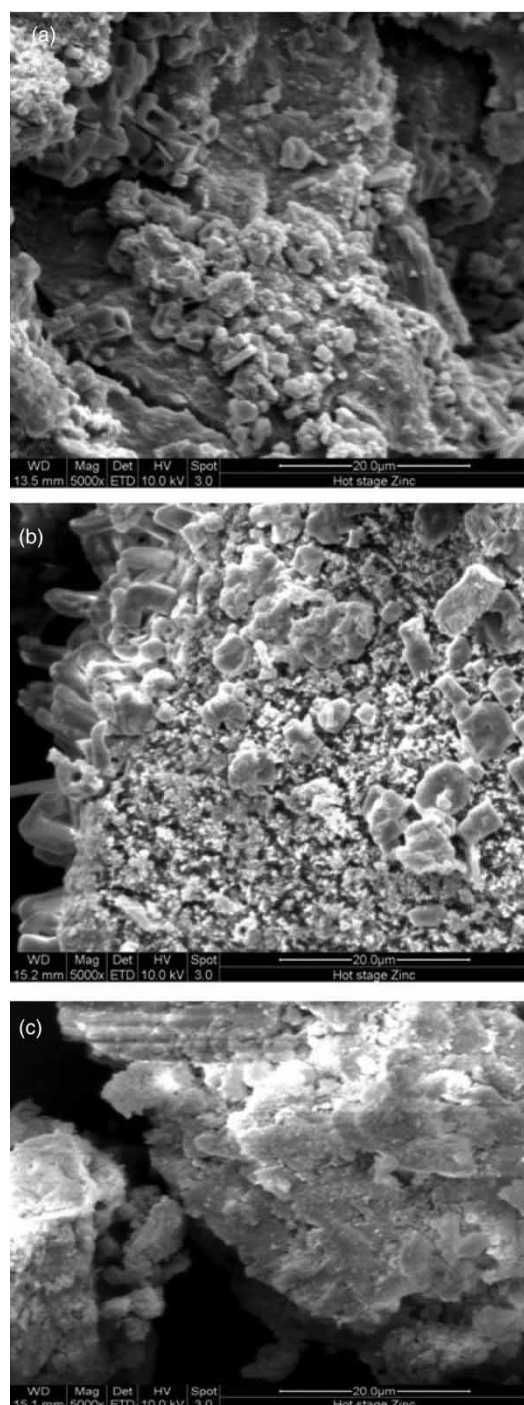


Figure 7 | SEM images of $\text{Mg}(\text{OH})_2$ and sediments: (a) $\text{Mg}(\text{OH})_2$, (b) after coagulation, (c) after coagulation with 10 mg/L kaolin.

CONCLUSIONS

In this research, magnesium hydroxide continuous coagulation performance and floc properties in the presence of

kaolin were investigated. Kaolin clay with the whole coagulation process plays a significant role in floc formation and growth. The final average floc size reached $20.5\ \mu\text{m}$ in the sedimentation tank under the conditions of wastewater flow of 30 L/h, kaolin 10 mg/L and pH 12. Reactive orange removal efficiency reached 89% and 63% for kaolin concentration 0 and 10 mg/L, respectively. Flocs were formed rapidly in the rapid mixer and grew relatively large and the floc size remained relatively stable in the flocculation basin; then the flocs aggregated together in the sedimentation process. During the coagulation process, reactive orange and kaolin removals were mainly through charge-neutralization and adsorptive mechanisms according to the zeta potential and floc properties analysis. Reactive orange K-GN was adsorbed on the surface of magnesium hydroxide in the coagulation process.

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REFERENCES

- Ayoub, G. M., Merhebi, F., Acra, A., Fadel, M. E. & Koopman, B. 2000 [Seawater bittern for the treatment of alkalized industrial effluents](#). *Water Research* **34** (2), 640–656.
- Ayoub, G. M., BinAhmed, S. W., Al-Hindi, M. & Azizi, F. 2014 [Coagulation of highly turbid suspensions using magnesium hydroxide: effects of slow mixing conditions](#). *Environmental Science and Pollution Research* **21** (17), 10502–10513.
- Bouyakoub, A. Z., Lartiges, B. S., Ouhib, R., Kacha, S., El Samrani, A. G., Ghanbaja, J. & Barres, O. 2011 [MnCl₂ and MgCl₂ for the removal of reactive dye Levafix Brilliant Blue EBRA from synthetic textile wastewaters: an adsorption/aggregation mechanism](#). *Journal of Hazardous Materials* **187** (1–3), 264–273.
- El-Gohary, F. & Tawfik, A. 2009 [Decolourisation and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor \(SBR\) process](#). *Desalination* **249** (3), 1159–1164.
- Gao, B. Y., Yue, Q. Y., Wang, Y. & Zhou, W. Z. 2007 [Color removal from dye-containing wastewater by magnesium chloride](#). *Journal of Environmental Management* **82** (2), 167–172.
- Huang, X., Wu, T., Li, Y., Sun, D., Zhang, G., Wang, Y., Wang, G. & Zhang, M. 2012 [Removal of petroleum sulfonate from aqueous solutions using freshly generated magnesium hydroxide](#). *Journal of Hazardous Materials* **219–220**, 82–88.
- Jiao, R., Fabris, R., Chow, C. W. K., Drikas, M., Leeuwen, J., Wang, D. & Xu, Z. 2017 [Influence of coagulation mechanisms and](#)

- floc formation on filterability. *Journal of Environmental Science* **57**, 338–345.
- Leentvaar, J. & Rebhun, M. 1982 Effect of magnesium and calcium precipitation on coagulation–flocculation with lime. *Water Research* **16** (5), 655–662.
- Li, T., Zhu, Z. & Wang, D. S. 2006 Characterization of floc size, strength and structure under various coagulation mechanisms. *Powder Technology* **168** (2), 104–110.
- Li, H., Liu, S., Zhao, J. & Feng, N. 2016 Removal of reactive dyes from wastewater assisted with kaolin clay by magnesium hydroxide coagulation process. *Colloids and Surfaces A Physicochemical and Engineering Aspects* **494**, 222–227.
- Li, R., Gao, B., Sun, J. & Yue, Q. 2018 Coagulation behavior of kaolin-anionic surfactant simulative wastewater by polyaluminum chloride-polymer dual coagulants. *Environmental Science and Pollution Research* **25**, 7382–7390.
- Liu, M., Lu, J., Wei, L., Wang, K. & Zhao, J. 2015 Magnesium hydroxide coagulation performance and floc properties in treating high pH reactive orange wastewater. *Water Science and Technology* **71** (9), 1310–1316.
- Ren, P., Nan, J., Zhang, X. & Zheng, K. 2017 Analysis of floc morphology in a continuous-flow flocculation and sedimentation reactor. *Journal of Environmental Science* **57**, 338–345.
- Riera-Torres, M., Gutierrez-Bouzan, C. & Crespi, M. 2010 Combination of coagulation–flocculation and nanofiltration techniques for dye removal and water reuse in textile effluents. *Desalination* **252** (1–3), 53–59.
- Semerjian, L. & Ayoub, G. M. 2003 High-pH–magnesium coagulation–flocculation in wastewater treatment. *Advances in Environmental Research* **7** (2), 389–403.
- Sharp, E. L., Jarvis, P., Parsons, S. A. & Jefferson, B. 2006 The impact of zeta potential on the physical properties of ferric-NOM flocs. *Environment Science and Technology* **40** (12), 3934–3940.
- Tan, B. H., Teng, T. T. & Mohd Omar, A. K. 2000 Removal of dyes and industrial dye wastes by magnesium chloride. *Water Research* **34** (2), 597–601.
- Verma, A. K., Dash, R. R. & Bhunia, P. 2012 A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management* **93** (1), 154–168.
- Wei, L., Zhao, J., Xu, C. & Liu, M. 2014 Experimental analysis of magnesium hydroxide-reactive orange floc formation time and rate in coagulation process. *Journal of the Taiwan Institute of Chemical Engineers* **45** (5), 2605–2609.
- Wu, X. F., Hu, G. S., Wang, B. B. & Yang, Y. F. 2008 Synthesis and characterization of superfine magnesium hydroxide with monodispersity. *Journal of Crystal Growth* **310** (2), 457–461.
- Yang, Z., Li, H., Yan, H., Wu, H., Yang, H., Wu, Q., Li, H., Li, A. & Cheng, R. 2014 Evaluation of a novel chitosan-based flocculant with high flocculation performance, low toxicity and good floc properties. *Journal of Hazardous Materials* **276**, 480–488.
- Zhao, J., Li, W., Jiao, X., Lai, Y. & Guo, X. 2014 Floc growth kinetics in magnesium hydroxide coagulation process. *Desalination and Water Treatment* **52** (22–24), 4334–4341.
- Zhao, J., Shi, H., Liu, M., Lu, J. & Li, W. 2017 Coagulation-adsorption of reactive orange from aqueous solution by freshly formed magnesium hydroxide: mixing time and mechanistic study. *Water Science and Technology* **71** (9), 1310–1316.
- Zhou, Q., Chen, F., Wu, W., Bu, R., Li, W. & Yang, F. 2016 Reactive orange 5 removal from aqueous solution using hydroxyl ammonium ionic liquids/layered double hydroxides intercalation composites. *Chemical Engineering Journal* **285**, 198–206.

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