Magnesium hydroxide coagulation performance and floc properties in treating high pH reactive orange wastewater
Meile Liu, Jingfang Lu, Lei Wei, Kang Wang and Jianhai Zhao

ABSTRACT
Application of magnesium hydroxide as a coagulant for treating high pH reactive orange wastewater was studied. The coagulation performance and magnesium hydroxide-reactive orange floc properties were investigated under different dosages, feeding modes and pH values. Flocculation index (FI) was then discussed with controlled experiments using an intelligent particle dispersion analyzer and optimum coagulant dose of 150 mg/L (magnesium ion) was obtained for pH value 12. The results showed that the optimum magnesium ion dose tended to decrease with the increase of initial pH value. One time addition feeding mode led to relatively large FI value and higher removal efficiency compared with other addition modes. All of the flocs under investigation showed a limited capacity for re-growth 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.

Key words | coagulation, floc properties, magnesium hydroxide, reactive orange

INTRODUCTION
Reactive dyes have been widely used in the textile industry in recent years because of their bright color and good solubility in water (Riera-Torres et al. 2010; Verma et al. 2012). Most reactive dye wastewater is usually difficult to biodegrade with high pH, high chemical oxygen demand (COD) and strong color due to different dyeing and finishing processes (El-Gohary & Tawfik 2009). Color removal from reactive dyes wastewater by means of cheaper and environmental friendly technologies is still a major challenge. In recent years, investigations have been focused on the treatment of these wastewaters including coagulation, electrolysis, biodegradation, advanced oxidation and adsorption, etc. (Riera-Torres & Gutierrez 2010; Zhao et al. 2012). Coagulation–floculation is a widely used process for color removal. 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 (Tan et al. 2000; Semerjian & Ayoub 2003). The removal mechanisms may include: charge neutralization, enmeshment of colloidal particles by Mg(OH)2 precipitate and adsorptive coagulating mechanism (Leentvaar & Rehun 1982; Gao et al. 2007; Bouyakoub et al. 2011).

Floc properties and settling characteristics are the main parameters influencing particle removal efficiency in real industrial scale unit operations (Wang et al. 2002; Li et al. 2006; Xiao et al. 2010). There are many methods available to measure floc physical characteristics and coagulation processes, such as a nephelometric turbidimeter method (Cheng et al. 2011), laser technique (Gregory & Carlson 2003; Xu et al. 2008) and photometric dispersion technique (Gregory 1985; McCurdy et al. 2004; Yu et al. 2011). 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.

Although there are some studies on the characteristics of floc using magnesium hydroxide as a coagulant, there have been limited studies on floc properties and coagulation performance using magnesium hydroxide as the coagulant in a reactive dyes system. 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 breakage of coagulant are determined using an intelligent particle dispersion analyzer (iPDA). Furthermore, the effects of coagulant dose, feeding modes, and pH values on the
process are assessed. In addition, floc properties and magnesium hydroxide coagulation mechanisms are discussed in this paper.

MATERIALS AND METHODS

Synthetic water and coagulant

Reactive orange (K-GN) purchased from Jinan Xinxing Textile Dyeing Mill (Shandong, China) was used during the experimental process. Artificial water samples with pH between 11.5 and 12.5 were prepared with reactive orange and deionized water to provide a concentration of 0.25 g/L. The reactive orange type, molecular structure and the wavelength of maximum absorbance selected for this study are shown in Table 1. NaOH solution was added to each water sample to control solution pH values. A pH-meter (PHS-25 Shanghai Jinke Industrial Co., Shanghai, China) was used to determine the pH of the solutions. MgCl₂·6H₂O was used to prepare coagulant; 0.1 mol/L stock Mg²⁺ solutions were prepared with deionized water. All reagents used were of analytical grade. Magnesium ion was analyzed with an ICS-1500 ion chromatograph (Dionex, Sunnyvale, CA, USA). The morphology of flocs was measured by IX71 digital photomicrography (Olympus, Tokyo, Japan). The color concentration of dye effluents was measured by UV–visible light spectrophotometer (UV2550 Shimadzu, Tokyo, Japan). Figure 1 shows the correlation between initial absorbance A₀ and the concentration of the water samples. A₀ values increased linearly \( R^2 = 0.999 \) with increasing K-GN concentration of the water samples. With Figure 1, the relationship between the supernatant absorbance A₁ and the concentration of the supernatant can be clearly analyzed. The removal efficiency \( \eta \) can be calculated from the dye absorbance A₀ and A₁.

\[
\eta(\%) = \frac{A_0 - A_1}{A_0} \times 100 \tag{1}
\]

Table 1 | Reactive dye characteristics

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular structure</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive orange (K-GN)</td>
<td><img src="https://example.com/image" alt="Molecular structure" /></td>
<td>476</td>
</tr>
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</table>

Jar test procedures

A schematic diagram of the experimental apparatus is shown in Figure 2. 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, Shenzhen, China) at 20 ± 1°C. The solutions were stirred rapidly at 200 rpm for 60 s during magnesium ion addition, followed by stirring at 40 rpm for 10 min and followed by 20 min of sedimentation before the final concentration of reactive orange was measured. Reactive orange K-GN initial concentration was 0.25 g/L. Different magnesium ion dosages were added to the water sample, throughout the mixing and coagulation periods, an on-line intelligent iPDA was used to monitor the condition of suspensions. The suspension sampled by the iPDA using standard tube of 3 mm internal diameter was then pumped back into the jar with a flow 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 per cent 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.

RESULTS AND DISCUSSION

Coagulation behaviors under different coagulant dosage

Jar test experiments were performed to investigate the effects of coagulant dose on coagulation performance and removal efficiency. Figure 3 shows the effects of magnesium coagulant dose on reactive orange removal under different initial pH levels from 11.5 to 12.5. The removal efficiency after coagulation increased with the increase of coagulant dosage at higher pH value. When pH was 11.5, the highest removal efficiency was 32% under coagulant dose 210 mg/L. When the pH value reached 12 and 12.5, the impact of coagulant dose on removal efficiency became less significant with coagulant dose higher than 150 mg/L. Removal efficiency reached 98% and remained stable when increasing magnesium ion concentration to 270 mg/L. 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; Zhao et al. 2004).

To ascertain the optimum dosage for K-GN removal under higher pH levels from 12 to 12.5, coagulation optimization tests were performed and an on-line iPDA was used to detect floc formation. According to iPDA, a higher FI value means large floc size. As shown in Figure 4, the higher FI values were obtained with optimum coagulant dose 150 mg/L and 90 mg/L for initial pH values of 12 and 12.5, respectively. Figure 4(b) also shows that the FI values are low at low coagulant dose from 60 to 120 mg/L. When increasing coagulant dose to 150 mg/L, the FI reaches higher values and remains stable for slow mixing periods. Then FI values decreased with the increase of coagulant dosage. As mentioned, the variation of the iPDA output FI actually reflects the change in floc size. During the slow mixing process under different magnesium concentration conditions, the flocs were broken into relatively smaller flocs and remained 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). To explore the potential mechanism of color removal using magnesium hydroxide as coagulant, zeta potential at different magnesium doses was measured.

As shown in Figure 5, addition of magnesium ion resulted in significant increase of zeta potential. When magnesium ion concentration was increased from 60 to 210 mg/L, zeta potential changed from negative to positive. However, charge neutralization cannot be the only mechanism of destabilization. According to K-GN removal and FI values, in lower magnesium ion concentration, charge neutralization maybe the main coagulation mechanism. Large coagulant dose enhances the removal of K-GN by enmeshment in the forming precipitate and adsorption. In practice it is not easy to distinguish between the precipitation and adsorption process. Electrical charge or colloidal properties of the magnesium hydroxide-reactive orange flocs would be greatly affected. Magnesium hydroxide has a positive superficial charge, which attracts the negatively charged reactive dye. Higher pH value always caused rapid nucleation of magnesium hydroxide. Nucleation and precipitation of magnesium hydroxide should affect the floc properties significantly. Based on this observation, it can be reasoned that charge neutralization and precipitate enmeshment are the main mechanisms for destabilization and removal of reactive orange.

Coagulation behaviors under fixed coagulant dosage

Effects of pH value

The pH of the solution can be a key parameter in the choice of magnesium hydroxide coagulation technology. To investigate the effects of pH on the coagulation process, the test
water pH was adjusted from 11.5 to 12.5 and magnesium ion concentration was fixed at 150 mg/L. Figure 6 shows that an increase in pH upon alkalization resulted in shorter floc formation time and higher FI value at the rapid mixing stage. The differences are more significant between pH 12 and 12.5. At a higher pH of 12.5, the reaction is very fast and FI reaches its first peak in 70 s. When pH value is 12, the FI peak time is 150 s. The magnesium hydroxide coagulation process is similar to the precipitation process which includes magnesium hydroxide nucleation and combination of reactive orange into flocs. Nucleation and precipitation of magnesium hydroxide should affect the floc properties significantly. The pH value had a significant influence on floc formation time with fixed coagulant dose. The process of Mg\(^{2+}\) conversion to Mg(OH)\(_2\) is as follows (Huang et al. 2012):

\[
\text{Mg}^{2+} + \text{OH}^- \rightleftharpoons \text{Mg(OH)}^+ \tag{2}
\]

\[
\text{Mg(OH)}^+ + \text{H}^+ \rightleftharpoons \text{Mg}^{2+} + \text{H}_2\text{O} \tag{3}
\]

\[
\text{Mg(OH)}^+ + \text{OH}^- \rightleftharpoons \text{Mg(OH)}_2 \tag{4}
\]
When pH value is higher, the resulting magnesium hydroxide is a gelatinous precipitate, which was found to serve as an efficient coagulant (Ayoub et al. 2000). The pH adjustment systems after the coagulation process are also needed if this process is used in practice.

Addition of magnesium ion with different pH resulted in different floc properties. Figure 7 clearly indicates the average size of flocs in the magnesium hydroxide-reactive dyes system. Some of flocs aggregated together to form more compact ones. The size of some aggregations can reach 15 μm. At a higher pH of 12.5, the reaction is very fast and floc formation rate is higher. Whereas when pH value is 11.5, the flocs are not easy to form (Figure 7(a)). This is consistent with the findings for the FI value which are shown in Figures 4 and 6. The magnesium hydroxide coagulation process is similar to the precipitation process. When coagulant was added to higher pH value solutions, the precipitation process of magnesium hydroxide happened rapidly. Flocs grew and aggregated to form relatively large particles in the coagulation process when pH value was 12.

**Effects of feeding mode**

Just as mentioned above, when magnesium ion was added to high pH solution, chemical reaction rate was very fast. The magnesium hydroxide precipitation process depends on many parameters, and the supersaturation locally at the feed point as well as globally in the whole tank is of key importance (Lindberg & Rasmuson 2000). A series of jar tests were conducted to investigate the effect of feeding mode on coagulation performance. One time addition, dropwise addition and second addition feeding modes were concerned in this research at pH value 12, 150 mg/L magnesium ion. Magnesium ion was added to the solution drop by drop in 45 s. The second addition feeding mode means adding 75 mg/L magnesium ion first then adding another half after 20 s. In the mixing process, inertial forces divide the solution into smaller elements that are distributed and deformed. According to Figure 8, compared with one time addition, the FI value for the others were relatively small. It is quite common to find very high supersaturation at the feed point when magnesium ion is added to water samples one time. This leads to rapid primary nucleation and hence explains why the floc size is bigger in the one time addition feeding mode. It is likely that, during the process of floc breakage and re-growth there is a limiting floc size. All of the flocs under investigation showed a limited capacity for re-growth when they had been previously broken. The changes of zeta potential

![Figure 7](https://iwaponline.com/wst/article-pdf/71/9/1310/468848/wst071091310.pdf)

**Table 2 | Coagulation performance under different feeding modes**

<table>
<thead>
<tr>
<th>Feeding modes</th>
<th>Zeta potential (mV)</th>
<th>K-GN removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One time addition</td>
<td>−0.59</td>
<td>98.3</td>
</tr>
<tr>
<td>Dropwise addition</td>
<td>−4.56</td>
<td>91.6</td>
</tr>
<tr>
<td>Second addition</td>
<td>−3.58</td>
<td>92.6</td>
</tr>
</tbody>
</table>
and K-GN removal with different feeding modes are shown in Table 2. The zeta potential remained negative but reached −0.59 mV when the feeding mode was one time addition. Magnesium hydroxide can act as a charge neutralization species. In general, removal efficiency was related to the zeta potential and final floc size during coagulation. The coagulation behavior indicates that charge neutralization is one of the mechanisms (Zhao et al. 2012).

CONCLUSIONS

Magnesium hydroxide as a coagulant can remove reactive orange effectively. The optimum magnesium coagulant dose tended to decrease with the increase of pH value. Magnesium ion dose was 150 mg/L and 90 mg/L for initial pH values of 12 and 12.5, respectively. FI value showed that an increase in pH will result in shorter floc formation time at the same magnesium dose. Flocs formed at one time addition feeding mode with significant precipitation of magnesium hydroxide were larger than those of other feeding modes. Floc images show that magnesium hydroxide-reactive orange floc size is relatively small and some aggregations can reach 15 μm. The experimental results show that the mechanisms of magnesium hydroxide coagulation are charge neutralization and precipitate enmeshment.

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REFERENCES


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