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Removal of reactive dyes from wastewater assisted with kaolin clay by magnesium hydroxide coagulation process

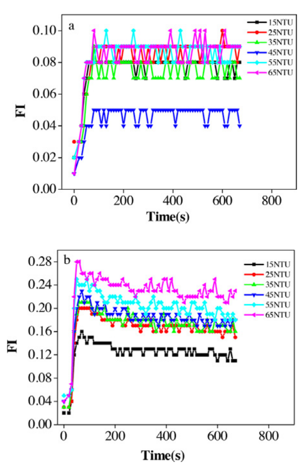
Haiyan Li [a,*], Shiyu Liu [b], Jianhai Zhao [b], Na Feng [b]

[a] *Beijing Engineering Research Center of Sustainable Urban Sewage System Construction and Risk Control, Beijing University of Civil Engineering and Architecture, Beijing 100044, China*
[b] *Tianjin Key Laboratory of Aquatic Science and Technology, School of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin 300384, China*

HIGHLIGHTS

- Magnesium hydroxide was used as coagulant.
- Relationship between FI and reactive dyes removal were discussed.
- Kaolin clay can promote reactive dyes removal.
- Floc properties were analyzed under different conditions.
- Charge neutralization and precipitate enmeshment were the main mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

Application of magnesium hydroxide as a coagulant for treating reactive dyes wastewater assisted with kaolin was studied. The coagulation performance and floc properties were investigated under different dosages and initial turbidity. The relationship between Flocculation Index (FI) and reactive dyes removal was then discussed with controlled experiments using intelligent Particle Dispersion Analyzer (iPDA). Kaolin clay had significantly influence on floc formation and reactive dyes removal. The suitable magnesium ion dose of 144 mg/L was obtained under initial turbidity of 45 NTU and pH value of 12. The results showed that final turbidity decreased with increasing coagulant dose. Reactive dyes removal efficiency tended to increase with the increase of initial turbidity of kaolin. The experiments showed that the higher FI value of the system, the higher reactive dyes removal efficiency was obtained. Floc image showed that average floc size of reactive red (X-3B) is smaller than that of reactive yellow (X-R). Based on the changes of zeta potential and floc properties, charge neutralization and precipitate enmeshment were proposed to the main coagulation mechanisms.

1. Introduction

Reactive dyes effluents release certain chemical hazards and produce amount of environmental problems [1,2]. Most of reac-

* Corresponding author.
E-mail address: lihaiyan@bucea.edu.cn (H. Li).

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tive dyes in wastewater are usually difficult to biodegrade with high pH, high COD and strong color [3]. Thus, the various methods are studied in literatures for the removal of dyes from wastewater, including biological processes, combined chemical and biochemical processes, chemical oxidation, adsorption, coagulation and membrane treatments [4,5]. Among these methods, coagulation is a well-established process in water treatment to remove suspended particles by combining small particles into larger aggregates. Coagulants based on hydrolyzing metal salts such as aluminum and iron are widely used. The metal salts hydrolyze rapidly to form various cationic species, which are adsorbed by negatively charged particles and cause charge reduction [6].

Coagulation of dye-containing wastewater has been used for many years as main treatment or pretreatment due to its low capital cost [7]. 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 [8,9]. The most attractive feature of this process is that the magnesium can be removed from the precipitated sludge and recycled through the process. This recoverability may significantly reduce the chemical costs and sludge disposal problems associated with the use of many conventional coagulants [10]. Furthermore, the effectiveness of magnesium hydroxide for color removal of water-soluble anionic dyes under alkaline conditions is mainly due to charge neutralization, enmeshment of colloidal particles by $Mg(OH)_2$ precipitate and adsorptive coagulating mechanism [5,8,10]. Coagulation can also be described as the formation of larger particles, or flocs, from the small particles in the wastewater [11]. Floc size, structure and settling characteristics are the main parameters influencing particle removal efficiency [12,13]. Small particles formed into larger aggregates by coagulation are not uniform in size, and vary over a wide range [14]. Surface characteristics of flocs and their zeta potential are important in influencing flocs aggregation and setting properties [15,16]. Additionally, kaolin will affect floc formation and growth rate in magnesium hydroxide coagulation process [17,18].

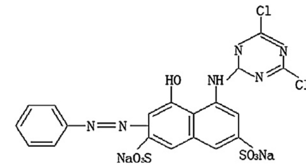
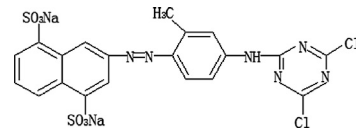
Although there are some studies on coagulation performance and the characteristics of floc using magnesium hydroxide as coagulant, there are limited studies on floc properties of reactive dyes system assisted with kaolin. The main objectives of this laboratory study were to evaluate the floc characteristics, especially to understand the effects of kaolin on floc formation in magnesium hydroxide treating reactive dyes processes. The effects of coagulant dose and turbidity on the process of coagulation are investigated. Furthermore, Flocculation Index (FI) is used to assess the influences of turbidity onto the process of coagulation. 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

Kaolin clay (Tianjin Chemical Reagent Co. Tianjin, China) was used as a model suspension. 100 g of kaolin was dispersed in 1 L of deionized water, stirring at 500 rpm for 10 min and then the suspension was stand overnight in a measuring cylinder. Supernatant liquor as the stock suspension was used to prepare a variety of turbidity water sample. The average particle size of kaolin suspension is 170.1 nm in this experiment. The simulated reactive dyes wastewater samples were prepared by adding 0.1 g of the reactive dyestuffs into 1 L of deionized water. The reactive dyestuffs are reactive red (X-3B) and reactive yellow (X-R) (Naqi Textile Dyeing Mill, Jiangsu, China). The name, type, molecular structure and the wavelength of maximum absorbance of the two dyes selected for this study are shown in Table 1. 0.1 M NaOH solution was added to each water sample to control the solution pH value to 12. $MgCl_2{\cdot}6H_2O$ was used to prepare coagulant and 0.1 M stock Mg^{2+} solutions were prepared with deionized water. Two reagents (Tianjin Chemical Reagent Co.) used were of analytical grade. Precipitation process of magnesium hydroxide from simulated water sample with an alkaline was carried in this experiment. The reaction formula is given as follows [19]:

Table 1
characteristics of reactive dye.

Name	Molecular structure	λ_{max}(nm)
Reactive red (X-3B)		538
Reactive yellow(X-R)		383

$$Mg^{2+} + OH^- \rightleftharpoons Mg(OH)^+ (1)$$

$$Mg(OH)^+ + H^+ \rightleftharpoons Mg^{2+} + H_2O (2)$$

$$Mg(OH)^+ + OH^- \rightleftharpoons Mg(OH)_2 (3)$$

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 $20 \pm 1\,^{\circ}C$. The solutions were stirred rapidly at 200 rpm for 40 s when initial adding magnesium ion, followed by slow stirring as 40 rpm for 10 min and finally sedimentation for 30 min before color removal and turbidity were measured. Different magnesium ion dose were added to the water sample with initial turbidity 0–65 NTU. Throughout coagulation periods, an on-line intelligent Particle Dispersion Analyzer (iPDA) was used to monitor the condition of suspensions and determined FI of the process of coagulation. The suspension sampled by the iPDA using standard tube of 3 mm internal diameter was then pumped back into the jar with a flowing rate of 20 mL/min. In this method the Flocculation Index (FI) was measured to reflect the floc size. Flocculation Index (FI) can be used to reflect the changes in the state of aggregation of a suspension in coagulation-flocculation process. The average transmitted light intensity (dc value) through the flowing sample and the root mean square (rms) value of the fluctuating component were measured. The ratio between the rms and the average transmitted light intensity (10 rms/dc) provides a sensitive measure of particle aggregation and the value is often termed the flocculation index (FI). A higher FI value suggested a bigger size of flocs. The instrument is much better suited to the early detection of the floc formation [20].

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). The Zeta potential was measured by zetasizer Nano ZS (Malvern, UK) and the concentration of magnesium ion was analyzed by