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Strong enhancement of methylene blue removal from binary wastewater by *in-situ* ferrite process

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ABSTRACT

Dye wastewater containing heavy metal ions is a common industrial effluent with complex physicochemical properties. The treatment of metal–dye binary wastewater is difficult. In this work, a novel *in-situ* ferrite process (IFP) was applied to treat Methylene Blue (MB)–Cu(II) binary wastewater, and the operational parameters were optimized for MB removal. Results showed that the optimum operating conditions were OH/M of 1.72, Cu^{2+}/Fe^{2+} ratio of 1/2.5, reaction time of 90 min, aeration intensity of 320 mL/min, and reaction temperature of 40°C. Moreover, the presence of Ca^{2+} and Mg^{2+} moderately influenced the MB removal. Physical characterization results indicated that the precipitates yielded in IFP presented high surface area (232.50 m^2/g) and a multi-porous structure. Based on the Langmuir model, the maximum adsorption capacity toward MB was 347.82 mg/g for the precipitates produced in IFP, which outperformed most other adsorbents. Furthermore, IFP rapidly sequestered MB with removal efficiency 5 to 10 times greater than that by general ferrite adsorption, which suggested a strong enhancement of MB removal by IFP. The MB removal process by IFP showed two different high removal stages, each with a corresponding removal mechanism. In the first brief stage (<5 min), the initial high MB removal (~95%) was achieved by predominantly electrostatic interactions. Then the sweep effect and encapsulation were dominant in the second longer stage.

Introduction

Every year, more than 10,000 types of commercial dyes, with production of 7×10^5 tons, are used in various industries, including textiles, paper, plastics, and leather tanning (Natarajan et al., 2017; W. Wang et al., 2017). Approximately 15% of the produced dyes are released as wastewater (Konicki et al., 2017), causing serious threats to public health and the environment (Daneshvar et al., 2017; Srivastava and Sillanpää, 2017). Moreover, hazardous heavy metals commonly coexist with dyes in some effluents (Stawiński et al., 2017; Zhao et al., 2015). The conventional removal techniques, such as ion-exchange and

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adsorption on activated carbons, are time-consuming and arduous, with mediocre efficiency due to the complexity of metal–dye binary wastewater (Stawiński et al., 2017; Visa et al., 2010). Hence, developing an efficient and cost-effective method to treat such refractory wastewater is significant and urgent.

The ferrite process (FP) is an effective method for removing various heavy metal ions from wastewater (Barrado et al., 2002; Erdem and Tumen, 2004; Tu et al., 2012, 2013). In FP, heavy metal ions can be incorporated into a spinel structure through co-precipitation to form ferrites. The principle is presented as shown below:

$$xM^{2+} + (3{-}x)Fe^{2+} + 6OH^{-} + 1/2O_2 \longrightarrow M_xFe_{(3-x)}O_4 + 3H_2O$$

Lou and Huang (2009) indicated that sewage containing metal ions treated by FP could meet effluent standards, and the resulting sludge also satisfied the toxicity characteristic leaching procedure (TCLP). Moreover, the ferrite precipitates generated from FP can be separated easily due to its magnetism (Tu et al., 2013) and can be recycled as catalysts (M.-Q. Cai et al., 2017; Lou and Huang, 2009).

Furthermore, ferrites with magnetic and electrical properties have attracted extensive attention due to their applications in preparation of adsorbents, active catalysts, magnetic recording media, suspension materials in ferromagnetic liquids, refractory materials, magnetic seeds, super-hard materials and high temperature sensors (Cai et al., 2017; Ding et al., 2013; Manna et al., 2017). So far, application of magnetic ferrites to treat environmental pollution has received a great deal of interest (Almasian et al., 2016; Mahmoodi, 2013; Wu et al., 2016). Magnetic ferrites such as copper ferrite ($CuFe_2O_4$), manganese ferrite ($MnFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$) not only possess photocatalytic and catalytic activity (López-Ramón et al., 2017; Ren et al., 2015; Stoia et al., 2017), but also exhibit good adsorption efficiency owing to electrostatic interaction and surface functional group complexation (Wang et al., 2012, 2015; Wu et al., 2016; Yavari et al., 2016; Zhao et al., 2014). In particular, some magnetic ferrites synthesized by sol–gel, co-precipitation or hydrothermal methods were reported to be effective in adsorbing various dyes such as azo–dyes (Chen et al., 2014; Wang et al., 2012; Wu et al., 2004), and heterocyclic dyes (K. Cai et al., 2017; Hashemian et al., 2013; Iram et al., 2010).

Recently, it has been demonstrated that *in-situ* formed materials, such as Mn-(hydr) oxides (*in-situ* MnO_x) (Lu et al., 2014; Zhang et al., 2008), present a smaller particle size and higher adsorption capacity than aged materials. Thus, it can be an interesting option to conduct an *in-situ* FP in metal-dye binary wastewater, in which co-precipitation will occur between non-ferrous metals and Fe, as well as dye adsorption by the *in-situ* formed ferrites. However, to our knowledge, no previous report exists on metal–dye binary wastewater treatment using *in-situ* FP.

In this study, an *in-situ* FP (IFP) was developed to treat Cu (II)–Methylene Blue (MB) binary wastewater. The influence of operational parameters and solution conditions in IFP formation on MB uptake was studied for practical applications. Then, the MB removal performance was also evaluated through isothermal analysis. In addition, the MB removal mechanism by IFP was elucidated after detailed characterization using various techniques.

1. Materials and methods

1.1. Materials

All the chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) in analytically pure grade and were used without further purification. Stock solutions were prepared by dissolving appropriate amounts of metal salts or dye powder in deionized water.

1.2. Batch experiment

The experiment was performed in a series of 30 × 300 mm glass test tubes, in which the solution was mixed with aeration by an air pump. A rubber stopper with a condensing tube and an aerator pipe was used to plug each glass test tube. The reaction temperature was controlled by a thermostatic water bath. After transferring 80 mL of simulated dye wastewater containing Cu^{2+} to the tube, a desired amount of solid $FeSO_4 \cdot 7H_2O$ was added. The solution was mixed well by aeration, and then various quantities of NaOH (5 mol/L) were added dropwise, upon which a fine precipitate formed immediately. The precipitate was maintained in suspension by continuous aeration. Blank experiments without the addition of NaOH were conducted to ensure that the decrease in concentration was not actually due to evaporation. Samples were withdrawn intermittently and filtered by a 0.45 μm membrane. The residual dye concentrations in the solution were determined using a UV–visible spectrophotometer (MAPADA UV-6100, Shanghai, China) at 662 nm for MB. The metal concentrations were analyzed by inductively coupled plasma optical atomic emission spectrometry (ICP-OES) ICPE-9800 (Shimadzu, Japan). All the tests were conducted in duplicate. The calculation of adsorption capacity (mg/g) is shown in Eq. (1), and the removal efficiency was calculated using Eq. (2):

$$qt = (C_0 - C_t) \times \frac{V}{m} \quad (1)$$

$$W = \frac{C_0 - C_t}{C_0} \quad (2)$$

where C_0 (mg/L) is the residual concentration of blank sample (mg/L) and C_t (mg/L) is the residual concentration of analyte; V (L) is the initial solution volume; m (g) is the total initial Cu^{2+} and Fe^{2+} dosage.

The effects of OH/M, Cu^{2+}/Fe^{2+} ratio, reaction temperature, aeration intensity, adsorption isotherms, and water hardness on MB removal were investigated. The influence of OH/M was investigated by changing the molar ratio of hydroxyl ions to the combined heavy metal (Cu^{2+} and Fe^{2+}) concentration. When testing the effect of different experimental conditions, only one condition was varied at a time while all other factors remained constant. Unless otherwise specified, the initial MB concentration and Cu^{2+} concentration of the simulated dye wastewater were 50 mg/L and 0.02 mol/L, respectively.

1.3. Characterization methods

After the formation of IFP, the precipitates were collected, washed with distilled water, and then freeze-dried in vacuum prior to analysis unless otherwise specified. Scanning electron

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