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In situ nano-silicate functionalized graphene oxide composites to improve MB removal

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ABSTRACT

In this paper, a novel composite material for methylene blue (MB) removal was successfully synthesized from dolomite and graphene oxide. The graphene oxide/calcium magnesium silicate composite (GO/Si-Ca-Mg) was prepared through *in-situ* functionalizing silicates on the surface of GO. Briefly, metal ions (Ca^{2+} or Mg^{2+}) were anchored by oxygen-containing functional groups on the GO and acted as growth centers of silicates. Properties of the material were characterized by XRD, FT-IR, SEM-EDS and TEM, and spectral results implied that silicates were successfully *in-situ* functionalized on the GO. During the preparation process, experimental factors were studied to investigate the optimum conditions. The adsorption capacity for MB could reach 230 mg/g. Thermodynamic and kinetic studies were also carried out to investigate the adsorption characteristics of the composite. This work came up with a feasible method to synthesize GO/silicate composite, which pleasantly avoided the severe aggregation of silicates in synthesis process.

1. Introduction

Organic dye pollution has been a prominent worldwide problem in recent decades [1]. It is estimated that 10–15% of the total dyes, widely employed in many related industries like textile, pulp, paper, printing, food, plastic and tanneries, are discharged into wastewater per year [2]. As is known to all, these dyes have a great toxicity to fauna and flora because they are usually easily water-soluble and carcinogenic [3]. Hence, effective measures should be taken to get rid of these harmful dyes from wastewater. At present, a large number of techniques including physical, chemical, and biological technologies have been proposed for dye removal [4–7]. Adsorption is undoubtedly an economic and practical one among those separation methods [8]. Up to now, various adsorbents including bottom ash [9], activated carbon [10], clay [11], fly ash [12], coir pith [13] and sawdust [14] have been verified to show an appreciable adsorption capacity for MB by scholars and researchers.

Graphene oxide (GO), a new member of the carbon-based material family, is famous for two-dimensional structure which makes it one of the most intensively investigated materials [15]. It is recognized that the basal planes of GO are mostly decorated by oxygen-containing functional groups like hydroxy (–OH), carboxyl (–COOH) and epoxy (C–O–C) [16]. The existence of these oxygenic groups certainly will make a significant contribution to functionalization of GO [17,18]. However, there exist some serious defects, *e.g.* difficult to be separated from aqueous solution due to its high hydrophilicity, easy to form irreversible aggregation because of its large surface energy and inevitable to induce environmental problems owing to its potential toxicity when GO is employed in practice [19].

In addition to some excellent carbon material adsorbents [20,21], zeolite-like materials with abundant pore channels are certainly considered as effective adsorbents. A lot of papers have investigated the adsorption performance on these materials so far, such as Acid Orange 8 (AO8) [22], phosphate ions [23], Cu^{2+} [24], Cd^{2+} [25] and Methylene Green (MG) [26]. It is a quite smart choice to anchor silicate materials onto GO in order to strengthen the adsorption capacity of silicate materials and solve the separation problem of GO from aqueous solution. Dolomite, widespread in nature, contains plentiful calcium and magnesium ions. Some papers indicate that both calcium silicate and magnesium silicate show some affinity to MB [27,28]. Therefore, the dolomite theoretically can be utilized to synthesize a sort of silicate material which is applied for MB removal. But serious aggregation which has restrictions to adsorption ability will happen during the gen-

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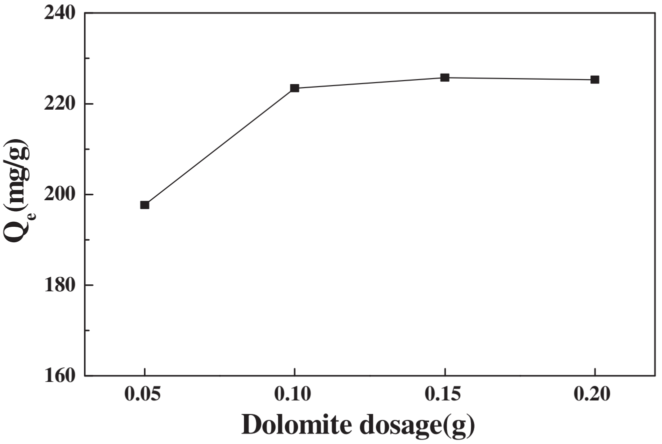

Fig. 1. Effect of dolomite dosage on MB removal (adsorbent dose = 0.01 g/30 mL; dye concentration = 250 mg/L; adsorption temperature = 298.15 K).

eration of these silicates owing to the nanometer surface effect [29,30].

So it is profound to couple calcium magnesium silicate with GO during the generation of silicates. The purpose of this work is to prepare a novel graphene oxide/calcium magnesium silicate composite by *in-situ* synthesis and then to enhance the MB removal through improving the dispersibility of inorganic silicates.

2. Experiment

2.1. Materials and methods

2.1.1. Materials

The dolomite used in this investigation is purchased from Xingtang County, Hebei Provice of China. Other relative agents are introduced as follows: graphite powder (AR), H_2SO_4 (AR), HCl (AR), H_2O_2 (30%), $KMnO_4$ (AR), $NaNO_3$ (AR), NaOH (AR), $NH_3 \cdot H_2O$ (AR), CH_3CH_2OH (AR), tetraethyl orthosilicate (TEOS, AR), methylene blue (85%, Kermel), and deionized water.

2.1.2. Preparation of GO

Graphene oxide was prepared by the modified Hummers method [31]. Briefly, 1 g of graphite powder and 0.5 g of $NaNO_3$ were mixed in 33 mL of concentrated sulfuric acid for 0.5 h. Then, the mixture was placed in an ice bath and 3 g of $KMnO_4$ was slowly and carefully added within 1 h. Then, the temperature of mixture was raised to 308.15 K. After reacting for 0.5 h, 80 mL of deionized water was slowly introduced into the mixture and the temperature was rapidly increased to 358.15 K. Following reaction for 0.5 h, 60 mL of deionized water was added into the mixture and stopped the reaction. Finally, 5 mL of 30% H_2O_2 solution was added. The mixture was filtered and washed with 10% (v/v) HCl solution and deionized water several times to eliminate any residuals. The product was obtained by freeze-drying. It was notable that vigorously stirring was always required through the preparation process.

2.1.3. Preparation of inorganic silicates

2.0 g of dolomite powder (major compositions: CaO (29.5%), MgO (21.5%), SiO (1.2%), XRD pattern in Fig. 1) was dissolved into 20 mL of 10% (v/v) HCl, and the filtrate was obtained by filtering the precipitation. Then, 10 mL of TEOS was added into the filtrate with the help of stirring (stirring rate = 300 rpm). pH was adjusted to 9 by ammonia. Finally, the mixture was continuously stirred at room temperature for 2 h. Stewing and aging for 12 h, solid phase could be eventually collected through filtering, washing with ethyl alcohol and deionized water several times and drying under 373.15 K for 10 h.

2.1.4. Synthesis of composites

0.06 g of GO was dispersed into 50 mL of ethyl alcohol with the help of ultrasound and a given quality of dolomite was dissolved into 10 mL of 10% (v/v) HCl solution. Next, a part of the filtrate was added under constant stirring. After 10 min, 0.2 mL of TEOS and the rest of filtrate were added into the mixture. The pH was adjusted to 9 by ammonia. After reaction, products were obtained by centrifugation, washing with ethyl alcohol and deionized water several times and freeze-drying. In order to investigate the effects of preparation conditions like dolomite dosage, reaction time and reaction temperature, the variation ranges of these factors were listed as below: dolomite dosage (0.05 g, 0.10 g, 0.15 g, 0.20 g), reaction time (0.5 h, 1.5 h, 3.5 h, 5.5 h) and reaction temperature (293.15 K, 298.15 K, 303.15 K, 308.15 K).

2.2. Preparation of dye solution

Stock solution of MB was prepared with deionized water. The concentrations of experiment solution were obtained by diluting the stock solution.

2.3. Adsorption experiment

Adsorption experiment was conducted by agitating experiment solution under 200 rpm in a stable temperature horizontal shaking bath (SHA-C). Portions of experiment solution were collected at predetermined time intervals. Concentration of solution was measured by spectroscopy (UV-2100 SPECTROPHOTO-METER). Adsorption capacity Q_t (mg/g) was calculated from the following equation:

$$Q_t = \frac{(C_o - C_t) \cdot V}{m} \tag{1}$$

where C_o and C_t (mg/L) are concentrations of MB at initial time and at a predetermined time interval, respectively. V (L) is the volume of experiment solution and m (g) is the mass of adsorbent.

2.4. Characterization

The phases of samples were determined by X-ray diffraction (D8 Discover, Bruker, Germany). The Fourier transform infrared spectra (Nicolet 6700, Thermo Electron Scientific Instruments) were performed over the range of 4000–400/cm to investigate chemical bonds. Field emission scanning electron microscopy (Mira3, Tescan, Czech Republic) and transmission electron microscopy (1004961S, JEM-2100F) were employed to observe the surface topography and inner structure.

3. Results and discussion

3.1. Determination of composite preparation conditions

3.1.1. Effect of dosage of dolomite

Fig. 1 shows that the adsorption capacity initially increases with dolomite dosage, but it rarely changes when the dosage of dolomite surpasses 0.15 g. This result indicates that 0.15 g of dolomite is the optimum dosage for MB removal. Other preparation conditions are set as reaction for 1.5 h and room temperature.

3.1.2. Effect of reaction time

The effect of reaction time on MB removal was shown in Fig. 2. It indicates that the composite gets the largest adsorption capacity when reaction time is 1.5 h. Other preparation conditions are set as 0.15 g of dolomite and room temperature.

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