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Synthesis and characterization of superparamagnetic activated carbon adsorbents based on cyanobacteria

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HIGHLIGHTS

- Fe_3O_4/activated carbon composite is an efficient adsorbent.
- It is the first time to modify cyanobacteria to magnetic adsorbent.
- The adsorbent could easily be recovered by magnetic separation technique.
- The adsorption mechanism was proposed.

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ABSTRACT

Fe_3O_4/activated carbon (Fe_3O_4/AC) composites were synthesized from cyanobacteria for the first time through a simple immersion and calcination process. The composite was prepared by using cyanobacteria, and this preparation provided environmental benefits. The as-synthesized Fe_3O_4/AC composite was then characterized and then used to remove methylene blue (MB) from aqueous solution under various experimental conditions. Results demonstrated that MB is physically adsorbed onto Fe_3O_4/AC composites but chemically adsorbed on monolayer and heterogeneous surfaces. The maximum adsorption capacity (q_m) determined from the Langmuir isotherm is 207.90 mg g^{-1}. This high adsorption capacity may be attributed to small particles, increased surface area, and functional groups on the surface of the composite. The adsorption mechanism was also discussed. These results indicated that Fe_3O_4/AC composite is a promising and competitive absorbent with abundant source, easy separation process, and environmentally friendly characteristics for wastewater treatment.

1. Introduction

Activated carbons (ACs) are materials mainly composed of carbon and characterized by well-developed internal surface area and porosity [1,2]. With these features, along with the presence of functional groups on their surfaces, ACs are adsorbents commonly used to remove pollutants from wastewater [3]. However, the widespread use of ACs in adsorption is restricted because commercial carbons are costly and ACs are difficult to separate from solutions [4].

ACs exhibiting advantageous characteristics, such as renewable sources, inexpensive precursors, and effective adsorbability, have been produced [5,6]. For instance, biomass from wastes, such as pine fruit shell [7], garlic peel [8], walnut shell [9], sunflower oil cake [10], and oil palm shell [11], has been utilized to prepare ACs. The reuse of these natural resources not only produces an applicable and low-cost adsorbent to purify contaminated environments but also helps minimize chemical load [12]. Various methods have also been proposed to provide magnetic properties for adsorbents, which can be separated from treated water through a simple magnetic process [13,14].

With the rapid social-economic development, excessive anthropogenic nutrients have been discharged into lakes [15]. As a result, lakes characterized by high nutrient concentrations and proper temperatures support rapid algal growth, leading to harmful algal blooms; algal blooms in turn cause serious environmental problems and economic losses. For instance, cyanobacteria can cause oxygen depletion, fish gill clogging, and toxicant and foul odor production [16]. Therefore, cyanobacteria should be

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comprehensively treated to prevent and reduce the associated risks. However, current situations remain severe because of various difficulties in treatments. Similar to other biomass materials, cyanobacteria contain a large amount of carbon and many functional groups, which can chelate various metal ions, including iron ion. If cyanobacteria can be utilized to produce magnetic AC, products can provide double environmental benefits; for instance, magnetic ACs from cyanobacteria can be used to remove pollutants from wastewater; cyanobacteria can also be employed efficiently to reduce contamination to a remarkable extent.

In this study, Fe_3O_4/activated carbon (Fe_3O_4/AC) composites were synthesized using cyanobacteria and ferric ammonium oxalate. This process is considered as one-pot synthesis; in this process, activation and washing were not conducted after carbonization was completed. The Fe_3O_4 nanoparticles successfully generated as precursors were carbided during the process. The specific characteristics and adsorption properties of the composite were subsequently investigated. Different isotherm and adsorption kinetic models were fitted to the experimental data. Fourier-transform infrared spectroscopy was performed to evaluate the adsorbent before and after adsorption occurred; the adsorption mechanism was also proposed. To the best of our knowledge, this study is the first to develop a Fe_3O_4/AC composite from cyanobacteria. Our study provided a promising adsorbent for wastewater treatment because the proposed cyanobacterium-based Fe_3O_4/AC composite does not require any pretreatment; furthermore, this composite exhibits competitive adsorption capacity and easy separation characteristics.

2. Materials and methods

2.1. Materials

Fresh cyanobacteria were collected from Lake Tai, P. R. China. Ferric ammonium oxalate and methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All of the aqueous solutions were prepared using analytical-grade reagents and then applied without further purification.

2.2. Preparation of the Fe_3O_4/AC composites

Fresh cyanobacteria were washed with distilled water and dried in an oven at 60 °C overnight. The dried cyanobacteria were then allowed to pass through a 1 mm mesh sieve to produce powdered cyanobacteria.

The Fe_3O_4/AC composites were synthesized through a one-pot method; in this process, activation and washing were not required after carbonization was completed. In brief, 1 g of dried cyanobacterium powder was added to 30 mL of 10 mg mL^{-1} ferric ammonium oxalate solution and immersed for 24 h. The mixture was then dried for 12 h at 60 °C; afterward, the sample was carbonized under N_2 atmosphere at 800 °C for 2 h at a rate of 3 °C/min. The Fe_3O_4/AC composites were obtained after the sample was cooled.

2.3. Characterization of Fe_3O_4/AC composites

The morphological characteristics of the pure cyanobacterium powder and the as-synthesized Fe_3O_4/AC composite were obtained using a scanning electron microscope (SEM, HITACHI S-4800, Japan). Particle size distribution was determined using a particle size distribution analyzer (Mastersizer 2000, Malvern Instruments, UK). Phase structure property was determined using an X-ray diffractometer (XRD, Bruker D8 Advance, Germany). Thermal characteristics were evaluated using a thermogravimetric analyzer (TGA, PerkinElmer, USA). Magnetic property was characterized through vibrating sample magnetometry (VSM, Lakeshore-7304, US) at room temperature. Fourier transform infrared spectroscopy (FTIR, Tensor27, Germany) was employed to verify the functional groups present in pure cyanobacteria, Fe_3O_4/AC composite, and Fe_3O_4/AC composite with adsorbed methylene blue (MB); results were recorded between 4000 and 500 cm^{-1}.

2.4. Adsorption experiments

A certain amount of composite was mixed with MB solution, and the mixture was shaken at 150 rpm in a thermostatic shaker at 25 °C. The Fe_3O_4/AC composites with the adsorbed MB were separated by using a magnet, and the MB concentration was determined using a UV–Vis spectrophotometer (Hitachi Co., Japan) at a wavelength of 664 nm. The results were obtained thrice, and data were expressed as mean. The amount of MB adsorbed at each time interval and at equilibrium was calculated using the following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 ($mg \cdot L^{-1}$) is the initial concentration of MB solution; C_t and C_e ($mg \cdot L^{-1}$) are the concentrations at time t and at equilibrium, respectively; V (L) is the volume of the solution; and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characterization of Fe_3O_4/AC composites

The general morphological characteristics of the dried cyanobacterium powder and the Fe_3O_4/AC composites are shown in Fig. 1. The surface morphological characteristics of the dried cyanobacterium powder and the Fe_3O_4/AC composites are completely different. In Fig. 1(a), the microstructure of the dried cyanobacterium powder is spherical and the average diameter is approximately 4 μm. Furthermore, the surface of the cyanobacteria is very smooth and no pore is found. In Fig. 1(b), the shape is changed and the size is decreased to approximately 300 nm. The composite exhibits a unique reticular structure, and many pores are generated; these pores possibly provide a comparatively large surface area. The Fe_3O_4 nanoparticles are homogeneously attached to the surface of AC, which was produced from cyanobacteria. Based on these changes, our conclusion is that immersion and calcination have manifested great impacts on the increase in specific surface area and the development of pores [17].

The particle size distribution of the pure cyanobacterium powder and the Fe_3O_4/AC composites is shown in Fig. 2(a). The particle size distribution of the pure cyanobacterium powder exhibits a volume mean diameter of 4.9 μm; by contrast, the Fe_3O_4/AC composite yields a volume mean diameter of 325 nm. However, the Fe_3O_4/AC composite shows poor uniformity compared with the pure cyanobacterium powder; this difference may be due to the instability and difficulty in controlling the preparation process. These results are consistent with the SEM result. A small particle size of the composite corresponds to a large specific surface area; thus, the number of adsorption sites is increased and the adsorption capacity is enhanced.

Chemical modification may cause changes in the crystalline structures of biomaterials. Thus, XRD analysis was conducted to