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Core–shell magnetic manganese dioxide nanocomposites modified with citric acid for enhanced adsorption of basic dyes

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ABSTRACT

Chemically surface modified core–shell magnetic manganese dioxide nanocomposites were prepared by redox reaction of $KMnO_4$ to MnO_2 on the surface of hydrophilic carbon coated magnetite (Fe_3O_4/C) microspheres in alkaline media, coupling with the modification by citric acid (CA). Properties of the synthesized adsorbent were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and vibration sample magnetometer (VSM) analysis and Brunauer–Emmett–Teller (BET) technique. Characterization results showed that prepared material had well-defined core–shell structure composed of inner magnetite core with superparamagnetic property and outer shell of nano-manganese dioxides modified with citric acid. The adsorption kinetics and isotherm were studied to examine the adsorption efficiency of citric acid modified magnetic manganese dioxide ($Fe_3O_4/C/MnO_2$-CA) nanocomposites towards methylene blue (MB) as basic dye. The kinetic data were found to fit pseudo-second-order model as compared to pseudo-first-order model. Langmuir isotherm model fitted the experimental data better than the Freundlich isotherm model. The adsorption mechanism study suggested that the hydrogen bonding, electrostatic and electron acceptor-donor interactions were responsible for the adsorption of MB on $Fe_3O_4/C/MnO_2$-CA nanocomposites.

Introduction

Various industries, such as paper, leather and textile industry, etc., use many synthetic dyes. The discharge of effluent containing synthetic dyes from these industries generates serious water pollution. Thus, the development of effective and economic approaches for removal of dye pollutants from aqueous solutions is very important in order to solve human health and environmental problems. In the past years, adsorption has been used as one of the most popular method in removing the pollutants from contaminated water, because it is considered to be an effective, efficient and economic method [1]. Recently, manganese oxides, due to their chemical and physical properties, have received significant attention as adsorbents for decontamination of wastewater and many efforts have been devoted to extend their application [2–6,10–12].

In general, the surface charge of manganese oxides is negative, and it can be used as adsorbents to remove cationic dyes or heavy metal ions from wastewater. Pristine manganese oxides with various nanostructures [2,3] and manganese oxide composites combined with other materials [4–6] were prepared and successfully used for adsorption removal of basic dyes from aqueous solution. However, the methods to improve the adsorption capacity of manganese oxides and separate them easily from aquatic environments are still a challenge with respect to expending their application. The surface chemical modification of manganese oxides may be one method for adsorption enhancement of basic dyes in water treatment. It has been known that the surface chemical property of adsorbents affects their adsorption performance. For example, oxygen-containing groups were introduced onto the surface of carbon or carbon aerogels by oxidative treatment and chemically surface modified materials exhibited the enhanced adsorption performance for basic dyes than their pristine materials [7–9]. However, to our knowledge, no attention has been to improve the adsorbent performance of manganese oxides by the surface chemical modification. Meanwhile, there were some efforts to improve separation efficiency of manganese oxides by using the unique advantage of magnetic materials [10–12]. Research results have demonstrated that manganese oxides combined with magnetic materials can be rapidly and easily isolated from the bulk solution under an external magnetic field after they adsorb the desired components. Therefore, manganese oxides functionalized with oxygen-containing groups and magnetic material may exhibit

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enhanced properties in adsorption removal of basic dyes from aqueous solution.

In this paper, $Fe_3O_4/C/MnO_2$-CA nanocomposites were prepared for the first time. The prepared magnetic nanocomposites were used for adsorption/removal of MB from aqueous solution. The effects of pH, ionic strength, adsorption time and initial MB concentration on adsorption capacity of $Fe_3O_4/C/MnO_2$-CA microspheres were investigated. The reusability of $Fe_3O_4/C/MnO_2$-CA microspheres and adsorption mechanism were also explored.

2. Experimental

2.1. Materials

MB was purchased from Guangdong Xilong Chemical Company. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shenyang, China). All chemicals were of analytical grade and used as received without further purification. Water used was distilled and purified by a Milli-Q system.

2.2. Preparation of Fe_3O_4 and Fe_3O_4/C microspheres

The preparation of Fe_3O_4 and Fe_3O_4/C microspheres was based on the previously reported methods [13] with minor modification. Briefly, $FeCl_3 \cdot 6H_2O$ (1.35 g) was completely dissolved in ethylene glycol (40 ml), followed by the addition of sodium acetate anhydrous (3.6 g). The mixture was stirred vigorously for 2 h. Then, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 200 °C for 6 h. The obtained products were cooled naturally, washed with water and ethanol, and dried at 60 °C for future use. As-prepared Fe_3O_4 microspheres (0.2 g) were treated by 0.1 M HNO_3 followed by ultrasonicated for 10 min, and washed with deionized water. Then, Fe_3O_4 microspheres were dispersed in 30 ml glucose aqueous solution (0.5 M) under vigorous stirring for 30 min. The suspension was transferred into a Teflon-lined stainless-steel autoclave and heated at 180 °C for 6 h, then cooled to room temperature. The obtained products (Fe_3O_4/C microspheres) were separated by a magnet, washed several times with water and ethanol, and dried at 60 °C.

2.3. Preparation of $Fe_3O_4/C/MnO_2$-CA nanocomposites

$Fe_3O_4/C/MnO_2$-CA microspheres were prepared based on the redox reaction of $KMnO_4$ to MnO_2 in alkaline media [14] on the surface of hydrophilic carbon coated magnetite (Fe_3O_4/C) microspheres, coupling with modification by citric acid. Briefly, 0.2 g of Fe_3O_4/C microspheres, 0.2 M $KMnO_4$ and 0.1 M citric acid were added into 30 ml of the alkaline solution (0.4 M NaOH). After stirring for 30 min, the mixture was heated to reflux for 1 h. Then the suspension was cooled to room temperature. The obtained products were separated magnetically, washed with water several times. In the final step of rinsing, 2 M HCl solution was added, and the products were collected and again washed using water five times, then dried at 60 °C. For comparison, core–shell magnetic manganese dioxide microspheres were prepared using the same process but in the absence of citric acid, which were denoted as $Fe_3O_4/C/MnO_2$ microspheres.

2.4. Characterization of magnetic microspheres

The specific surface area and porous texture of the as-synthesized products were measured by nitrogen adsorption by using a surface area and porosimetry system (ASAP 2020 HD 88, USA).

Particle sizes and morphology of magnetic microspheres were characterized by TEM (Tecnai G220, Fei, USA) and SEM (Ultra Plus, Carl Zeiss AG, Germany), respectively. The analysis of chemical composition of $Fe_3O_4/C/MnO_2$-CA microspheres was performed by using EDS attached to SEM. XRD was conducted on a X'pert Pro diffractometer (PANalytical, Holland) with Cu Kα radiation (λ=0.15406 nm) from 20° to 70°. Fourier transform infrared spectra in KBr were obtained by using Vertex70 FT-IR (Bruker, Germany). The magnetization curves were recorded on VSM at room temperature (Lakeshore, Serial, No.1740H, REV-127, USA). The zeta potentials were tested by Zen1690 Zetasizer (Malvern Instruments, UK) at room temperature. Samples were prepared by suspending the magnetic microspheres in 10^{-3} M $NaNO_3$ solution at different pH (1–10) adjusted with 0.1 M NaOH or HNO_3.

2.5. Adsorption of MB by $Fe_3O_4/C/MnO_2$-CA nanocomposites

10 mg $Fe_3O_4/C/MnO_2$-CA microspheres was added in 20 ml MB aqueous solution (pH 7.0) and the mixed suspension was shaken with an oscillator (150 rpm) for a certain time to reach equilibrium at 25 °C. At suitable time intervals, $Fe_3O_4/C/MnO_2$-CA microspheres were isolated from the solution using a magnet. Changing the contact time and initial MB concentration, adsorption kinetics and isotherm models were studied. The pH of solution was adjusted in the range of 1.0–10.0 with 0.1 mol/l HCl or 0.1 mol/l NaOH solutions and various amounts of NaCl were added into the MB solution to study ionic strength on the adsorption capacity. The concentration of MB in solution was measured at 663 nm by using a TU-1900 UV–vis adsorption spectrophotometry (Beijing Purkinjie General Instrument Co., Ltd., Beijing, China). The adsorption percentage of MB in the solution was calculated according to Eq. (1):

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

where C_0 (mg/l) is the initial MB concentration, C_t (mg/l) is MB concentration in supernatant at time t (min). The amount of MB adsorbed per gram of $Fe_3O_4/C/MnO_2$-CA microspheres (q_t, mg/g) was calculated using Eq. (2):

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

V (l) is the volume of MB solution used, and W (g) is the weight of $Fe_3O_4/C/MnO_2$-CA microspheres used, respectively. All the experiments were carried out in triplicate and the average values were reported. The standard deviation was calculated and mostly less than 5% of the reported value. The negative controls (with no adsorbent) were simultaneously carried out to ensure that MB was adsorbed by $Fe_3O_4/C/MnO_2$-CA microspheres and not by the container.

3. Results and discussion

3.1. Characterization of $Fe_3O_4/C/MnO_2$-CA microspheres

Brunauer–Emmett–Teller (BET) surface areas and porosity of the $Fe_3O_4/C/MnO_2$ and $Fe_3O_4/C/MnO_2$-CA microspheres were calculated from nitrogen adsorption isotherms (Fig. 1(a) and (b)). The specific surface area (84.51 m^2/g) of $Fe_3O_4/C/MnO_2$-CA microspheres was slightly smaller than that (87.07 m^2/g) of $Fe_3O_4/C/MnO_2$ microspheres, which could be due to reason that some pores became clogged by CA molecules after chemical surface modification [15]. The pore volume and average pore size of $Fe_3O_4/C/MnO_2$ and $Fe_3O_4/C/MnO_2$-CA microspheres were 0.177 cm^3/g, 0.152 cm^3/g, 5.2 nm and 4.7 nm, respectively.

XRD patterns of prepared magnetic microspheres are shown in Fig. 1(c). There was no apparent difference between XRD patterns of Fe_3O_4/C and $Fe_3O_4/C/MnO_2$-CA microspheres. All observed

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