Applied Surface Science 433 (2018) 790–797

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Carbon dots decorated magnetic $ZnFe_2O_4$ nanoparticles with enhanced adsorption capacity for the removal of dye from aqueous solution

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ARTICLE INFO

Article history:
Received 20 July 2017
Received in revised form 9 October 2017
Accepted 14 October 2017
Available online 18 October 2017

Keywords:
CDs
$ZnFe_2O_4$
Magnetic composite
Methyl orange
Adsorption

ABSTRACT

Widely used synthetic dyes have been caused serious environmental pollution. Therefore, it is imperative to acquire highly efficient adsorbent to remove them. Here, we report the carbon dots/$ZnFe_2O_4$ (CDs/ZFO) composites were prepared through a facile hydrothermal route for absorption removal of dye from aqueous solution. The characterizations reveal the CDs were uniformly deposited on the surfaces of ZFO nanoparticles in the composite. The CDs/ZFO composites as adsorbents exhibit enhanced adsorption behavior for methyl orange (MO) in comparison of pristine ZFO, in which the 5% CDs/ZFO (with the CDs mass content of 5 wt%) shows the highest absorption activity. Experimental studies on adsorption isotherms of MO over the 5% CDs/ZFO composite indicate that experimental data were found to follow Langmuir model with a monolayer adsorption capacity of 181.2 mg g^{-1}. The corresponding adsorption kinetics was fitted well with the pseudo-second-order kinetic model. Moreover, thermodynamics parameters including ΔG°, ΔH° and ΔS° were tested, demonstrating that the adsorption of MO over CDs/ZFO composite was spontaneous and exothermic in nature. The remarkably increased adsorption performance of CDs/ZFO composites can be attributed to abundant oxygen-containing groups on the surface of CDs.

1. Introduction

Synthetic dyes are widely used in the manufacture of textile, paper, plastic, leather, and are the most common organic pollutants in industrial waste water, which pose a serious threat to the ecosystem due to their high toxicity and possible accumulation in the environment [1,2]. Hence, the removal of dyes from wastewaters is still highly desirable. Some treatment techniques, such as chemical oxidation [3], membrane filtration [4] and photocatalytic degradation [5] and adsorption [6,7], have been developed for removing dyes from aqueous solutions. Among these techniques, adsorption has been found to be an efficient and economic process for the efficient removal of various organic contaminants from water. Owing to its high surface area and porous structure, activated carbon is often used as an adsorbent to remove certain classes of chemical pollutants in treating wastewater [8,9]. However, filtration, a method of conventional separation of activated carbon, may cause blockage of filters or the loss of carbon, which is also a time-consuming process. Therefore, activated carbon is generally discarded after sewage treatment, which can easily lead to the secondary pollution [10,11]. Crucially, it is essential to pursue more 'ideal' alternatives to activated carbon possessing high adsorption capacity, relatively inexpensive production and easy recyclability.

In recent years, magnetic separation technology has received extensive attention in solving environmental problems. Ferrites of the type MFe_2O_4 (M is a divalent metal cation) are magnetic materials with the cubic spinel structure, which have been widely used in treatment of water [12–14]. Among ferrites, $ZnFe_2O_4$ is an interesting magnetic material with moderate saturation magnetization, excellent chemical stability and mechanical hardness, which exhibited the excellent adsorptive properties with the highly effective

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https://doi.org/10.1016/j.apsusc.2017.10.099
0169-4332/

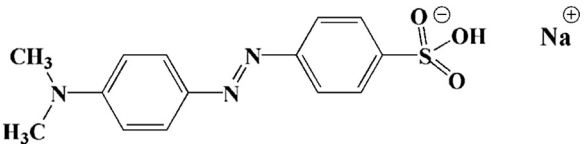

Fig. 1. Molecular structure for MO dye.

recovery of the magnetic separation technique [14–17]. Nevertheless, its adsorption capacity is still far from enough, and further enhancement of its adsorption properties is required.

Carbon dots (CDs) with abundant hydroxyl and carboxyl groups on the surface, as the latest member in nano carbon family, have found wide applications such as fluorescent probes, photovoltaic devices, bioimaging, thanks to its excellent optical properties, low toxicity, chemical stability and water dispersity [18–20]. Previous reports have demonstrated that the functional groups (—OH, —COOH, etc.) are helpful for improving the adsorption performance of reactants [21,22]. Therefore, we attempted to combine CDs with magnetic $ZnFe_2O_4$ nanoparticles to construct a high adsorption capacity composite for efficient removal organic pollutants from aqueous solution.

In this work, a simple one-pot hydrothermal method was employed to develop a new kind of magnetic adsorbent, CDs/$ZnFe_2O_4$ composite (CDs/ZFO). Methyl orange (MO) was analyzed as the adsorption model to investigate the adsorption performance of as-prepared products. The CDs/ZFO composites adsorbents exhibit superior adsorption behavior in comparison of pristine ZFO, in which the 5% CDs/ZFO (with the CDs mass content of 5 wt%) shows the highest absorption activity. Experimental studies on adsorption isotherms and kinetics of MO over the CDs/ZFO composite indicated that experimental data were found to follow Langmuir model with a monolayer adsorption capacity of 181.2 mg g^{-1}, and adsorption kinetics fitted well with the pseudo-second-order kinetic model. Moreover, thermodynamics parameters including ΔG°, ΔH° and ΔS° were tested, demonstrating that the adsorption of MO over CDs/ZFO composite was spontaneous and exothermic in nature.

2. Experimental section

2.1. Materials

All chemicals were of analytical grade and without purification. Graphite rods (99.99%) were purchased from Alfa Aesar Co. Ltd., USA. $Fe(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, NaOH and methyl orange (MO) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. The chemical structure of MO is shown in Fig. 1.

2.2. Synthesis of CDs

The CDs powders were prepared by an electrochemical method [23]. Generally, the two graphite rods were inserted into ultrapure water in parallel using as an anode and cathode, and a static potential of 30 V was applied to the two electrodes for 120 h. Then, the CDs solution was formed. After filtration for three times, the prepared CDs solution was treated in a freeze-drying way to obtain the CDs solid powders.

2.3. Synthesis of $ZnFe_2O_4$ and CDs/$ZnFe_2O_4$ nanocomposites

Briefly, 35 mL of $Zn(NO_3)_2$ solution (0.2 M), 35 mL of $Fe(NO_3)_3$ solution (0.4 M) and 1.0 g CTAB were mixed and stirred for 30 min. Then, the homogeneous solution was adjusted to pH 10 using NaOH solution (0.1 M) and transferred into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. Afterwards, the autoclave was heated at 130 °C for 24 h in an electric oven. When the autoclave was cooled down to room temperature, the brick red suspension of $ZnFe_2O_4$ was collected and washed with ethanol and deionized water for several times to remove impurities, and finally dried at 75 °C for 6 h in a vacuum oven. For preparation of CDs/$ZnFe_2O_4$ nanocomposites, the CDs solid powders with different weight ratios (1 wt.%, 3 wt.%, 5 wt.% and 10 wt.%) were added to the fabricated process of $ZnFe_2O_4$, which were abbreviated as 1% CDs/ZFO, 3% CDs/ZFO, 5% CDs/ZFO and 10% CDs/ZFO samples.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded using an X'Pert-ProMPD (Holand) D/max-γA X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm). Transform Infrared (FT-IR) spectrum was characterized by a Nicolet 360 spectrometer. Raman spectra were recorded on an HR 800 Raman spectroscope (JY, France). Transmission electron microscope (TEM), high-resolution TEM (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed with a FEI-Tecnai F20 microscope operating at 200 kV, respectively. X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Al Kα X-ray source. The Brunauer-Emmett-Teller (BET) specific surface areas and pore structures were characterized by a Micromeritics ASAP-2050 porosimeter. The equilibrium concentrations of dyes were determined at 460 nm for MO using a UV–vis spectrophotometer (Lambda 750).

2.5. Adsorption experiments

Adsorption experiments were carried out in break (250 mL), where solution of MO (200 mL) with dye concentration of 20 mg L^{-1} and 0.03 g of adsorbent was placed. The break with solution was placed in a constant temperature bath and agitated by magnetic stirrer. To investigate the influence of temperature, five different temperatures with 20, 30, 40, 50, and 60 °C were set in adsorption experiments.

Prior to mixing with the adsorbent, a few drops of 0.1 M HCl or 0.1 M NaOH were added for adjusting the pH of the dye solution.

When the adsorption equilibrium period reached, 3 mL aqueous sample was extracted from the solution and separated from the adsorbent magnetically. And concentration of MO was analyzed by UV–vis spectroscopy at a wavelength of 460 nm. The amount of MO adsorbed at equilibrium q_e (mg g^{-1}) was calculated by following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 (mg L^{-1}) is the initial dye concentration, C_e (mg L^{-1}) the dye concentration at equilibrium, V (L) the volume of the solution, and m (g) is the mass of the adsorbent.

The procedures of kinetic experiments were identical with those of equilibrium tests. At given time intervals, 3 mL aqueous samples extracted from the solution and separated from the adsorbent magnetically. And concentrations of MO were analyzed by UV–vis spectroscopy at a wavelength of 460 nm. The amount of MO adsorbed at time t q_t (mg g^{-1}) was calculated by following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_t (mg L^{-1}) the dye concentration at any time t.