Silica coated Fe_3O_4 magnetic nanospheres for high removal of organic pollutants from wastewater

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HIGHLIGHTS

- $Fe_3O_4@SiO_2$ nanospheres are synthesized successfully.
- $Fe_3O_4@SiO_2$ nanospheres have high removal ability of CR from solutions.
- $Fe_3O_4@SiO_2$ nanospheres can be easily separated from solution using magnetic separation method.
- $Fe_3O_4@SiO_2$ nanospheres have high reusability and stability.

GRAPHICAL ABSTRACT
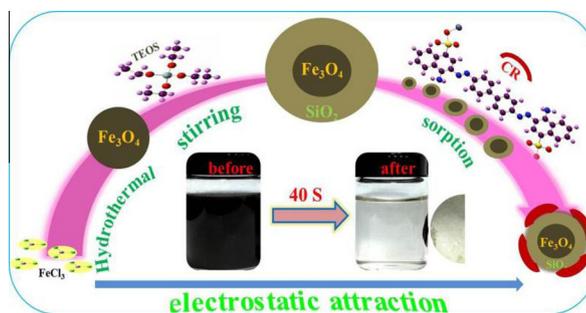
ABSTRACT

Fe_3O_4 nanoparticles were synthesized by hydrothermal technique and then modified with tetraethyl orthosilicate to form $Fe_3O_4@SiO_2$ nanospheres through Stöber method. The characterization results of X-ray diffraction, Fourier transformed infrared spectroscopy, transmission electron microscopy, scanning electron microscopy and magnetic measurements evidenced the successful synthesis of $Fe_3O_4@SiO_2$ nanospheres. The as-prepared $Fe_3O_4@SiO_2$ was applied as adsorbent to remove congo red (CR) from aqueous solutions at different experimental conditions, and the results indicated that CR adsorption on $Fe_3O_4@SiO_2$ was strongly pH-dependent and weakly ionic strength-dependent at relative low pH values, indicating that the adsorption was mainly dominated by electrostatic interactions. The maximum adsorption capacities of CR on $Fe_3O_4@SiO_2$ were calculated to be 54.64 mg/g from Sips model and 50.54 mg/g from Langmuir model at T = 308 K and pH = 5.3. The thermodynamic parameters calculated from temperature-dependent isotherms indicated that the adsorption of CR on $Fe_3O_4@SiO_2$ was an spontaneous and endothermic process. The CR-adsorbed $Fe_3O_4@SiO_2$ nanospheres could be easily separated from aqueous solutions using magnetic separation technique within 40 s. These results suggested that the $Fe_3O_4@SiO_2$ nanospheres might be suitable materials for the efficient separation of dye pollutants from aqueous solutions in possible real applications.

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1. Introduction

With the development of industry, more and more colored wastewater was released from the factories (e.g. food processing

plants, the printing shop and textile mills) into natural environment. The colored wastewater discharged from these industries may cause an eco-toxic hazard and thereby results in the potential danger of bioaccumulation [1–3]. For example, congo red (CR), a kind of synthetic anionic dyes, has been widely applied in dyeing clothes, photosensitizer, coloring paper and hair colorant [4,5]. CR was derived from naphthionic acid and benzidine, and its metabolic products might induce illnesses. The results of investigation show that CR is a mutagen and reproductive effector and it may cause cancer or be harmful to unborn child even at ultra-low concentration [6,7]. In addition, CR is highly stability, solubility and durability in water, so it has attracted more and more attentions because it is hard to be removed from aqueous solutions. Therefore scientists proposed many techniques to remove CR from large volumes of aqueous solutions, such as chemical coagulation [8,9], photo-degradation [10], trickling filters and membrane separation [11,12]. Because of their high cost and strictly conditions, these methods can only be used for small-scale wastewater treatment. In contrary, due to the cost effectiveness, simple operation and high efficiency, sorption technique is regarded as a kind of the most promising method [1,13].

Conventional adsorbents such as clay minerals[14,15], oxides [16,17] and carbon nanomaterials [18,19] have been applied to remove CR from wastewater. Although carbon nanomaterials endowed excellent sorption capacity, the high cost and hardly separation from aqueous solutions limited their application in real wastewater cleanup, which would cause serious health problems when discharged into the environment randomly [20,21]. The magnetic materials endowed the excellent separation property and had been served in many fields, such as medicine, biotechnology and separation [22–26] etc. Numerous reports affirmed that magnetic materials had been widely used in environmental decontamination due to their extremely small size, low-toxicity and easy separation [27–31]. For example, Li et al. [31] reported that Fe$_3$O$_4$@β-cyclodextrin could remove 1-naphthylamine (Q_{max} = 144.74 mg/g) from the organic wastewater efficiently. Zhang et al. [32] reported the high sorption capacities of Fe$_3$O$_4$@NiO for As(V) (117.6 mg/g) and Cr(VI) (184.2 mg/g). Comparing with traditional methods (e.g. filtration and centrifugation), magnetic separation is regarded as a rapid and effective technique for the separation of nanomaterials from aqueous solutions because of its less energy requirement and high separation ability [29]. Fe$_3$O$_4$ nanoparticles, one of the most commonly used magnetic materials, have been widely applied in many fields, such as wastewater treatment [22,23], drug delivery system [24], magnetic resonance imaging [26] and protein separation [25]. However, due to the less functional groups and unstable in acidic solutions, the application of Fe$_3$O$_4$ nanoparticles is greatly limited. Based on the aforementioned problems, the coating of Fe$_3$O$_4$ nanoparticles is imperative to enhance Fe$_3$O$_4$ nanoparticles' absorbance, dispersion and stability [33,34].

Silica is a kind of fundamental mineral in nature and has been widely applied as pharmaceutical binders, chromatographic agents, stabilizers and photographic emulsions [35–38]. Furthermore, silica possesses a lot of advantages such as uniform size and shape, resistance of acid and alkali, thermal stability and low cytotoxicity [39,40]. On the other hand, abundant hydroxyl groups on its surface enhanced the adsorption capacity. Thereby silica is often selected as modifying agent to stabilize and to enhance the properties of other materials. For example, Mirji [41] reported that the Si(1 0 0)@SiO$_2$ could efficiently remove octadecyltrichlorosilane from aqueous solutions. Mihaylov et al. [42] reported that Ni@SiO$_2$ could selectively remove CO from the air mixture.

In this paper, Fe$_3$O$_4$@SiO$_2$ core-shell nanospheres were synthesized by a simple and environmental-friendly hydrothermal and Stöber method, and characterized by powder X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), zeta-potential and magnetic curve. The prepared Fe$_3$O$_4$@SiO$_2$ nanospheres were applied as adsorbents to remove CR from aqueous solutions. The effects of ionic strength, pH, contact time and temperature on the adsorption of CR were also investigated to study the adsorption mechanism and to evaluate the potential applications in real possible environmental pollution cleanup.

2. Materials and method

2.1. Materials

Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), sodium acetate (NaAc), sodium citrate (Na$_3$Cit), and ammonia (NH$_3$·H$_2$O) were purchased from Tianjin Bodi Chemical Co. Ltd. (China). Ethylene glycol, tetraethyl orthosilicate (TEOS), polyethylene glycol (PEG) and CR were supplied from National Medicines Corporation Ltd. (China). All chemicals were reagent grade and used without further purification.

2.2. Preparation of Fe$_3$O$_4$@SiO$_2$

The Fe$_3$O$_4$ nanoparticles were synthesized by a traditional hydrothermal method [43]. Generally, NaAc (5.4 g), PEG (1.0 g) and Na$_3$Cit (0.72 g) were added into the mixture solutions of FeCl$_3$·6H$_2$O (0.9 g) dissolved in ethylene glycol (60 mL). After stirred for 30 min, the suspensions were sealed in a Teflon-lined stainless-steel autoclave. The mixtures were kept at 200 °C for 8 h, and then cooled to room temperature naturally. Finally, the black precipitates were washed with distilled water and ethanol five times, and dried in vacuum at 70 °C overnight prior to further use.

Fe$_3$O$_4$@SiO$_2$ nanospheres were prepared through a modified Stöber method [44]. 0.2 g Fe$_3$O$_4$ nanoparticles were dispersed into 250 mL solution containing ethanol and distilled water (V/V = 4:1) and 3 mL NH$_3$·H$_2$O under ultrasonication. Then 2 mL TEOS was dropped slowly into the mixture with the reaction stirred, and further stirred for 6 h. Thus prepared material was achieved by centrifugation and washed with Milli-Q water and ethanol for several times, and dried in vacuum at 70 °C for 7 h. The detailed synthesis process of Fe$_3$O$_4$@SiO$_2$ was shown in Fig. 1.

2.3. Characterization

Magnetic curves were obtained by using a MPMS-XL SQUID magnetometer at room temperature. The micro-structures and morphology of Fe$_3$O$_4$@SiO$_2$ were characterized using TEM (JEOL-2010 microscope) and SEM (JEOL JSM-6330F). The FT-IR spectra of naked Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$ before and after CR adsorption were recorded on a Nicolet Magana-IR 750 spectrometer in the range of 4000–450 cm^{-1}, in KBr pellet at room temperature. XRD patterns of Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ were recorded in reflection mode (Cu Kα radiation, λ = 1.5418 Å) using a Scintag XDS-2000 diffractometer. The zeta-potential value of Fe$_3$O$_4$@SiO$_2$ was measured by ZETASIZER 3000 HSA system.

2.4. Batch adsorption experiments

Adsorption experiments were carried out in 10 mL polyethylene test tubes. 0.3 g Fe$_3$O$_4$@SiO$_2$ was dispersed in 100 mL Milli-Q water and 30 mg CR was dispersed in 500 mL Milli-Q water to prepare CR solution. The stock Fe$_3$O$_4$@SiO$_2$ suspension, CR solution, and NaCl solution were added into the polyethylene test tubes to achieve the desired concentrations of different components. The pH values were adjusted by adding negligible volumes of 0.1 or 0.01 mol/L