



A simplified method for synthesis of Fe₃O₄@PAA nanoparticles and its application for the removal of basic dyes

Yin-Yin Xu^a, Min Zhou^a, Hui-Juan Geng^a, Jun-Jie Hao^a, Qian-Qian Ou^a, Sheng-Da Qi^{a,b}, Hong-Li Chen^{a,b,*}, Xing-Guo Chen^{a,b}

^a Department of Chemistry, Lanzhou University, Lanzhou 730000, PR China

^b State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, PR China

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ABSTRACT

A simplified method for synthesis of polyacrylic acid-bound iron oxide magnetic nanoparticles (Fe₃O₄@PAA NPs) was reported. The as-prepared nanoparticles were characterized by TEM, FT-IR, VSM and XRD. Characterization results indicated that PAA was successfully introduced onto the surface of Fe₃O₄ and did not cause any changes in magnetic property. The Fe₃O₄@PAA NPs were used to adsorb rhodamine 6G (R6G) as a model basic dye pollutant from aqueous solution. Kinetics data and adsorption isotherms were better fitted by pseudo-second-order kinetic model and Langmuir isotherm, respectively. The adsorption equilibrium could be reached at about 20 min, showing that the as-prepared adsorbent exhibited extremely rapid adsorption rate. The aqueous solution of the Yellow River was chosen as the test sample, and the results showed that the magnetic adsorbent was efficient for the removal of the basic dye in the real sample.

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1. Introduction

Dyes are widely used in many industries and their discharge into water causes environmental pollution which attracts many attentions all over the world. Therefore, removal of dyes from the effluents is an essential task for environmental protection [1]. In recent years, various biological and physical/chemical methods such as coagulation, oxidation, membrane filtration, biochemical degradation, and adsorption [2–6] have been used to treat dye wastewater. Among these methods, adsorption is one of the most popular techniques because of its high efficiency, inexpensive, simple of design and ease of operation [7].

Although different adsorbents have been proposed for the removal of dyes from aqueous solution [8–12], magnetic adsorbent has gained more attentions owing to its suitable for bulk solution, easy control and fast separation [13]. To date, in order to impart surface reactivity of the magnetic nanoparticles, numerous types of natural or synthetic polymers, novel molecules, and inorganic materials have been coated on the surface of the magnetic materials [10,14]. The polymers are able to modulate the carrier surface properties for the desired applications because of their presence of a variety of functional groups. There are several reports about

using poly(acrylic acid)-conjugated Fe₃O₄ magnetic nanoparticles (Fe₃O₄@PAA NPs) as adsorbents to adsorb basic dyes and basic proteins [14,15]. However, the synthetic process of Fe₃O₄@PAA NPs which has strict requirements to the acidity of the solution and the reactive temperature [14] is time-consuming due to trivial synthetic steps [15].

On the basis of previous studies, we developed an easy and convenient method to synthesize Fe₃O₄@PAA nanoparticles based on the amine-functionalized magnetite nanoparticles which was synthesized by a facile one-pot method without templates [16]. The Fe₃O₄@PAA NPs were characterized by TEM, FT-IR, VSM and XRD. The adsorption isotherm and adsorption kinetic of this magnetic adsorbent were examined using rhodamine 6G (R6G) as the model contaminant. The effects of buffer pH, contact time, R6G initial concentration and ionic strength on the adsorption efficiency of R6G were also investigated.

2. Experimental

2.1. Materials

Ferric chloride (FeCl₃·6H₂O), anhydrous sodium acetate and ethanol (C₂H₅OH) were purchased from Tianjin Chemical Reagents Factory (Tianjin, China). Ethylene glycol and triethylamine were commercially available from Guang-Fu Fine Chemical Industry Research Institute (Tianjin, China). 1,6-Hexanediamine and polyacrylic acid (PAA) were obtained from Shanghai Chemical

* Corresponding author at: Department of Chemistry, Lanzhou University, Lanzhou 730000, PR China. Tel.: +86 931 8912763; fax: +86 931 8912582.

E-mail address: hlchen@lzu.edu.cn (H.-L. Chen).

Reagent Company (Shanghai, China). N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC·HCl) was purchased from A Meryer Chemical Technology Shanghai Company (Shanghai, China). Rhodamine 6G (R6G) was commercially available from Dongsheng Chemical Reagent Company (Tianjin, China). Stock standard solution of R6G with the concentration of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ was prepared by dissolving an appropriate amount of R6G in 50 mL distilled water, and diluted to desired concentration with distilled water before use. 732 cation exchange resins (0.3–1.2 mesh) which were obtained from SINOPHARM group (China) were adapted to remove the matrix of aqueous sample. Before use, the resins were soaked with 4% (v/v) HCl, 4% (w/v) NaOH and 2 mol L^{-1} HCl for 5 h, 5 h and 2 days, respectively, and then were washed to neutral by distilled water after every soaking.

All chemicals were of analytical grade and used as received without any pretreatment. Distilled water was used to prepare the solution throughout the experiments.

2.2. Instrumentation

The morphologies and particle sizes of as-prepared samples were characterized by a Hitachi-600 Transmission electron microscope (TEM, Japan). X-ray diffraction (XRD) patterns were performed on a D/max-2400 X-ray powder diffractometer (Rigaku, Japan) with Cu K α radiation ($\lambda = 0.154056 \text{ \AA}$). The magnetic property of the samples was investigated using a vibrating sample magnetometer (VSM) with an applied field between -11 kOe and 11 kOe at room temperature (Lake Shore Cryotronics Inc., Westerville, OH, USA). Fourier-transform infrared spectra were collected on a Nicolet Nexus 670 Fourier transform infrared spectrometer (FT-IR, America) using KBr pellets. The concentration of R6G was quantified by a TU-1901 UV-vis absorption spectrophotometry (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) at $\lambda_{\text{max}} = 526.00 \text{ nm}$.

2.3. Preparation of Fe₃O₄@PAA magnetic nanoparticles

2.3.1. Preparation of Fe₃O₄@NH₂ NPs

Amine-functionalized magnetite nanoparticles (Fe₃O₄@NH₂ NPs) were synthesized via a versatile solvothermal reaction reported by Li et al. [16] with a slight modification. Typically, 3.0 g of FeCl₃·6H₂O, 10.8 g of 1,6-hexanediamine and 12.0 g of anhydrous sodium acetate were added to 90 mL of ethylene glycol to get a transparent solution via vigorous mechanical stirring at normal temperature. This mixture was then transferred to a Teflon-line autoclave (100 mL) and treated at 200 °C for 6 h. The obtained products were isolated with a magnet, washed with distilled water and ethanol several times, and then dried in a vacuum oven at 60 °C for 2 h for further processing.

2.3.2. Preparation of Fe₃O₄@PAA NPs

Fe₃O₄@PAA magnetic nanoparticles were synthesized according to the method previously reported with a slight modification [15]. The above Fe₃O₄@NH₂ NPs (250 mg), EDC·HCl (25 mg) and triethylamine (35 μL) were suspended in the ethanol solution (16.65 mL) by ultrasonication for 30 min. Then 4.15 mL PAA (30%) diluted with 20.85 mL ethanol was added dropwise to the mixture for 30 min. The reaction was allowed to proceed at 40 °C for 2 h under continuous mechanical stirring. The product was then cooled to room temperature and washed with ethanol to remove all organic impurities. Finally, the product was dried in vacuum oven at 60 °C for 2 h.

2.4. Sample solution

The aqueous solution from the Yellow River was chosen as the test sample, and the standard addition method was applied to adsorb the dye R6G cation by the carboxylic magnetic nanoparticles. In order to eliminate the matrix interference, two different procedures were adapted: one was only to filter the sample through 0.45 μm membrane filter; the other was to flow the sample through a short glass tube filled with pretreated 732 cation exchange resins. Afterwards, the prepared sample solution was mixed with 5 mg Fe₃O₄@PAA NPs, and then separated by external magnetic field.

2.5. General procedure

Adsorption of R6G was carried out in a batch process by varying pH value of the solution, contact time, R6G initial concentration and ionic strength. The Fe₃O₄@PAA NPs (5 mg, dry weight) was mixed with 10 mL R6G solution of known concentration by ultrasonication for 3 min, and then shaken for 0–90 min with oscillators (Changzhou, China) at a particular temperature. In all cases, adsorption equilibrium was reached within 20 min. If necessary, the pH was adjusted by adding a few drops of 1.0 mol L^{-1} HCl or 1.0 mol L^{-1} NaOH before shaking. Various amount of NaCl was added into the R6G solution to study the effect of ionic strength at the given temperature and contact time. The solid and liquid phases were separated using a magnet and the concentration of R6G remaining in the solution was measured by UV-vis spectrophotometry.

The adsorbed amount of R6G q_t (mg g^{-1}) and removal percentage R are calculated using the following Eqs. (1) and (2):

$$q_t = \frac{(c_0 - c_t)V}{W} \quad (1)$$

$$R = \frac{c_0 - c_t}{c_0} \times 100\% \quad (2)$$

where c_0 (mg L^{-1}) is the initial R6G concentration, c_t (mg L^{-1}) is R6G concentration in supernatant at time t (min) obtained by the calibration curve, V (L) is the volume of the sample solution and W (g) is the weight of dry adsorbent.

3. Results and discussion

3.1. Characterization of the magnetic nanoparticles

The particle size and shape of magnetic nanoparticles which were determined by TEM are shown in Fig. 1. As can be seen in Fig. 1a, the amine-functionalized magnetite nanoparticles have good dispersibility and the average size is about 50 nm. Compared with those reported magnetite microspheres synthesized by solvothermal reaction [17,18], the as-synthesized Fe₃O₄@NH₂ NPs in this work have large specific surface area and are more suitable for absorption application. Fig. 1b shows that the final products exhibit slight aggregation as a result of surface modification by the attachment of PAA. Besides, the mean diameter of Fe₃O₄@PAA NPs has no obvious change compared with that of Fe₃O₄@NH₂ NPs. This could be attributed to the fact that the reaction might occur only on the particle surface and only several PAA molecules were bound to the magnetic particle. But it needs further studies to demonstrate the suspect, so FT-IR is used to confirm the functional groups.

Fig. 2 shows the FT-IR spectra of Fe₃O₄@NH₂ NPs and Fe₃O₄@PAA NPs. The peaks at around 2852–2932 cm^{-1} are ascribed to the N–H stretching vibration of 1,6-hexanediamine and asymmetric or symmetric stretching vibrations of $-\text{CH}_2-$ groups of the alkyl chains of 1,6-hexanediamine in Fig. 2a [17,19]. The above results confirm that the $-\text{NH}_2$ group is successfully grafted onto the surface of the magnetic nanoparticles. From Fig. 2b, the strong FT-IR band

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