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Preparation and application of stability enhanced magnetic nanoparticles for rapid removal of Cr(VI)

Ya Pang [a,b], Guangming Zeng [a,b,*], Lin Tang [a,b,*], Yi Zhang [a,b], Yuanyuan Liu [a,b], Xiaoxia Lei [a,b], Zhen Li [a,b], Jiachao Zhang [a,b], Zhifeng Liu [a,b], Yiqun Xiong [a,b]

[a] *College of Environmental Science and Engineering, Hunan University, Changsha, 410082 China*
[b] *Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, 410082, China*

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ABSTRACT

A stable magnetic nanoparticle with a shell core structure of γ-Fe_2O_3@Fe_3O_4 was developed. Water soluble Polyethylenimine (PEI) was grafted to the nanoparticle to prepare a positive charged adsorbent, which was characterized by XRD, FTIR and SEM. The adsorbent was able to effectively remove anionic Cr(VI) in the pH range of 2–3 due to the large amount of protonated imine groups on its surface, and could be magnetically separated from liquid quickly. Adsorption equilibrium was reached within 30 min and independent of initial Cr(VI) concentration. The Cr(VI) maximum sorption capacity at a temperature range of 35–15 °C was obtained using the Langmuir adsorption isotherm. The calculated thermodynamic parameters (ΔG, ΔH, and ΔS) indicated that adsorption of Cr(VI) was spontaneous and exothermic in nature. Competition from coexisting ions (K^+, Na^+, Ca^{2+}, Cu^{2+}, Cl^-, and NO_3^-) was found insignificant. The adsorbent had satisfying acid–alkali stability and could be regenerated by 0.02 mol L^{-1} NaOH solution. The results suggested the potential application of the PEI-modified magnetic nanoparticles in selective removal of Cr(VI) from wastewater.

1. Introduction

Hexavalent chromium Cr(VI) is a highly toxic heavy metal, which is able to cause carcinogenesis, mutation to humans and animals, thus has been designated as one of the top-priority toxic pollutants by the U.S. EPA [1]. Metal finishing, electroplating, leather tanning, and chromate production are the main sources of Cr(VI) wastewater [2,3]. In some industry processes, the improper even untreated effluent was discharged randomly, leading to the Cr(VI) pollution. Therefore, developing effective method to removal Cr(VI) from effluent is of great importance to the public health and ecological system. Among the methods for Cr(VI) pollution remediation, such as adsorption, electrochemical precipitation, ion exchange, and membrane filtration, adsorption is one of the most popular and effective options. Various natural materials such as bark, clay, seaweed and biomass, as well as synthetic adsorbent like activated carbon, resin, and mesoporous silica [4,5], have been used to remove heavy metals. Furthermore, regeneration of exhausted adsorbent with economy operation is possible, and in many cases, the treated effluent is suitable for reuse [5].

Recently, using nanosized magnetic material as adsorbent has attracted increasing interest due to their high surface area and unique superparamagnetism. For instance, Fe_3O_4 nanoparticle coated with humic acid was found to be an effective adsorbent for Hg, Pb, Cd, and Cu from wastewater [6]. Chitosan-bound Fe_3O_4 particles with a mean diameter of 13.5 nm were able to rapidly remove Cu [7]. Superparamagnetic Fe_3O_4 nanoparticles with a surface functionalization of dimercaptosuccinic acid were performed to bind Hg, Ag, Pb, Cd, and Ti availably [8]. For the above reported adsorbent, Fe_3O_4 nanoparticle is the magnetic source, however, it is susceptible to air oxidation, resulting in the loss of magnetization. Although coating the Fe_3O_4 with inorganic shell, such as silica [9] and carbon [10], was capable to improve its chemical stability, the magnetic response of adsorbent would decrease after coating. An effective way to solve the contradiction between chemical stability and magnetic response is to calcine Fe_3O_4 nanoparticles to obtain a good crystalline [11].

In this study, prepared Fe_3O_4 was submitted to calcinations to form γ-Fe_2O_3@Fe_3O_4 magnetic nanoparticles. Polyethylenimine (PEI), which not only chelates cationic metal ions such as Cu^{2+}, Zn^{2+}, and Pb^{2+} [4,12], but also binds metal oxyanion through electrostatic interaction [2], was chosen to modify the particles. The adsorbent was positive charged over a wide pH range, and Cr(VI) exists in wastewater as negative charged anion, bringing about strong electrostatic interaction between adsorbent and adsorbate. The prepared PEI-modified magnetic adsorbent was characterized

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[*] Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, China. Tel.: +86 731 88822754; fax: +86 731 88823701.
E-mail addresses: zgming@hnu.cn (G. Zeng), tanglin@hnu.cn (L. Tang).

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by SEM, XRD, and FTIR. The sorption performances, such as kinetics, isotherms, thermodynamics, and competitive uptake were evaluated.

2. Materials and methods

2.1. Preparation of adsorbent

The Fe_3O_4 was prepared by the conventional chemical coprecipitation method [9]. Briefly, 0.4 mol of $FeCl_3{\cdot}6H_2O$ and 0.2 mol of $FeCl_2{\cdot}4H_2O$ were dissolved in 250 mL ultrapure water, soon the solution was bubbled with N_2 gas for 20 min to remove dissolved O_2. Then, 50 mL of 4 mol L^{-1} ammonia solutions were added under vigorous mechanical stirring to adjust the pH to about 10. The reaction was maintained at 65 °C for 30 min. The resulting black nanoparticles were separated by an external magnetic field followed by repeated washing with ultrapure water to neutrality. Finally, they were vacuum-desiccated at 55 °C. The dry nanoparticles were calcined at 300 °C for 1 h to gain red–brown magnetic nanoparticles (MNPs). Next, the MNPs were activated at 80 °C using 1.5 mol L^{-1} lauric acid solutions with pH 10. After washing with ethanol and water, the particles were added into 5% PEI in 50% methanol to covalently bind with PEI at 80 °C for 1 h. The developed adsorbent (abbreviated as PEI-MNPs) was thoroughly rinsed and then dried and ground for subsequent use.

2.2. Characterization of magnetic nanoparticles

The XRD patterns were performed on a Rigaku D/max-II B X-ray diffractometer with Cu Kα radiation ($\lambda = 0.1541$ nm) in the 2θ range of 10–80°. FTIR spectra were collected on a WQF-410 FTIR spectrometer, by accumulating 32 scans at a spectra resolution of 4 cm^{-1}, with the ration of sample to KBr of 1:100. Scanning electron microscope (SEM) images were obtained on a JEOL JSM-6700 equipped with energy dispersive spectroscopy (EDS). To prepare the samples, the nanoparticles were first added into water and sonicated for 15 min for dispersion. Then, 10 μL suspensions were dropped on conductive adhesive and dried. To measure the zeta potentials of the naked and PEI-bound MNPs, sample of 0.01 g was dispersed in 100 mL of 1 mmol/L NaCl solution to sonicate for 15 min. After placing for 24 h, the supernatant was used for zeta potential measurement using Malvern ZEN3600 Zetasizer Nano.

2.3. Batch adsorption experiments

Batch experiments were conducted in glass conical flasks by shaking at 150 rpm in a water bath shaker. Each treatment contained 0.08 g adsorbents and 20 mL of chromium solutions prepared with $K_2Cr_2O_7$. After finishing adsorption, the adsorbent was magnetically separated and the supernatant was collected for Cr(VI) measurement. The concentration of Cr(VI) was determined using UV–vis spectrophotometer (UV-754N shanghai, China) at 540 nm. All experiments were performed in duplicate with the averaged values reported here.

2.4. Stability and regeneration studies

Stability of the PEI-MNPs was examined by dispersing 0.08 g adsorbent in 20 mL different concentration of HCl or NaOH solution. After shaking for 3 h at 25 °C, the leached iron concentration was determined by AAS (Hitachi Z-8100, Japan). The treated adsorbent was washed to neutrality for reuse to infer its stability.

Desorption studies were conducted by incubation of 0.08 g Cr-loaded adsorbent in 15 mL of 0.02 mol L^{-1} NaOH solution for 1 h. To evaluate the regeneration, the eluted adsorbent was exploited to remove Cr(VI) again. Prior to the next adsorption–desorption cycle, the magnetic adsorbent was washed thoroughly with ultrapure water to neutrality and reconditioned for adsorption.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 1 shows the XRD pattern of the Fe_3O_4 nanoparticles. Six typical peaks for Fe_3O_4 ($2\theta = 30.1°$, 35.5°, 43.1°, 53.4°, 57.0°, and 62.6°), marked by their indices ((2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0)), were observed, which accorded well with the database (JCPDS 01-1111), demonstrating the successful synthesis of Fe_3O_4 nanoparticles with a cubic structure [11]. It was reported that γ-Fe_2O_3 can be produced by heating Fe_3O_4 to 300 °C [13]. The calcined Fe_3O_4 nanoparticles presented a red–brown, which was the characteristic color of the formed γ-Fe_2O_3 [14]. However, the XRD pattern for the calcined magnetic nanoparticle was very similar to that of the Fe_3O_4 (data not shown), implying that only superficial Fe_3O_4 transformed to γ-Fe_2O_3 as confirmed by previous studies [11,14–16]. Thus a shell core structure of γ-Fe_2O_3@ Fe_3O_4 was formed and applied to crosslink with PEI. FTIR spectroscopic analysis further proved the structure (Fig. 2a–c). The peaks at 580 cm^{-1} (Fig. 2a), belonging to Fe^{2+}–O^{2-} stretching vibration, changed to 563 cm^{-1} after the nanoparticle was calcined (Fig. 2b), implying that the Fe^{2+} was oxidized to Fe^{3+} [15]. In concomitance with the modification of PEI onto magnetic nanoparticles, new peaks at 1003, 1471, and 2941 cm^{-1} (Fig. 2c), representing the C–N stretching, C–H bending, and CH– stretching vibration, respectively, were

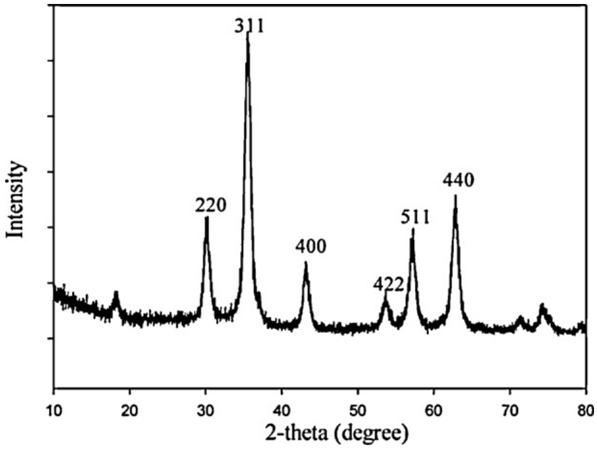
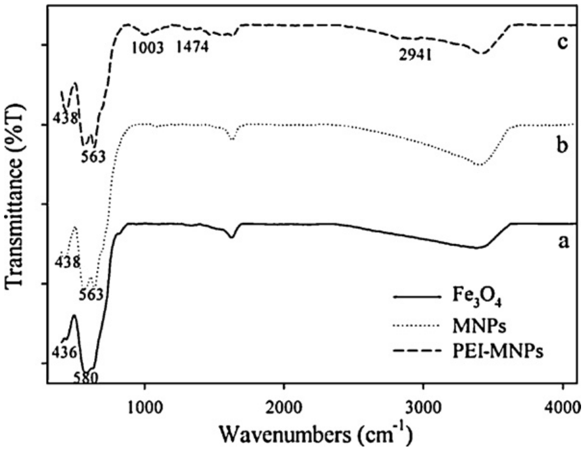


Fig. 1. XRD pattern of prepared Fe_3O_4 nanoparticles.



b]

Fig. 2. FTIR spectra: (a) Fe_3O_4 nanoparticles; (b) MNPs; (c) PEI-MNPs.