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

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ABSTRACT

A stable magnetic nanoparticle with a shell core structure of γ-Fe\textsubscript{2}O\textsubscript{3}@Fe\textsubscript{3}O\textsubscript{4} was developed. Water soluble Polyethyleneimine (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\textsuperscript{+}, Na\textsuperscript{+}, Ca\textsuperscript{2+}, Cu\textsuperscript{2+}, Cl\textsuperscript{−}, and NO\textsubscript{3}\textsuperscript{−}) was found insignificant. The adsorbent had satisfying acid–alkali stability and could be regenerated by 0.02 mol L\textsuperscript{−1} NaOH solution. The results suggested the potential application of the PEI-modified magnetic nanoparticles in selective removal of Cr(VI) from wastewater.

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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\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{4} particles with a mean diameter of 13.5 nm were able to rapidly remove Cu [7]. Superparamagnetic Fe\textsubscript{3}O\textsubscript{4} nanoparticles with a surface functionalization of dimercaptosuccinic acid were performed to bind Hg, Ag, Pb, Cd, and Ti available [8]. For the above reported adsorbent, Fe\textsubscript{3}O\textsubscript{4} nanoparticle is the magnetic source, however, it is susceptible to air oxidation, resulting in the loss of magnetization. Although coating the Fe\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{4} nanoparticles to obtain a good crystalline [11].

In this study, prepared Fe\textsubscript{3}O\textsubscript{4} was submitted to calcinations to form γ-Fe\textsubscript{2}O\textsubscript{3}@Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles. Polyethyleneimine (PEI), which not only chelates cationic metal ions such as Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, and Pb\textsuperscript{2+} [4,12], but also binds metal oxygenion 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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as such kinetic, isotherms, thermodynamics, and competitive uptake were evaluated.

2. Materials and methods

2.1. Preparation of adsorbent

The Fe₃O₄ was prepared by the conventional chemical coprecipitation method [9]. Briefly, 0.4 mol of FeCl₃·6H₂O and 0.2 mol of FeCl₂·4H₂O were dissolved in 250 mL ultrapure water, soon the solution was bubbled with N₂ gas for 20 min to remove dissolved O₂. 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 with a 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 K₂Cr₂O₇. 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 Fe₃O₄ nanoparticles. Six typical peaks for Fe₃O₄ (2θ = 30.1°, 35.5°, 43.1°, 53.4°, 57.0°, and 62.6°), marked by their indices (220), (311), (400), (422), (511), and (440)), were observed, which accorded well with the database (JCPDS 01-1111), demonstrating the successful synthesis of Fe₃O₄ nanoparticles with a cubic structure [11]. It was reported that γ-Fe₂O₃ can be produced by heating Fe₃O₄ to 300 °C [13]. The calcined Fe₃O₄ nanoparticles presented a red–brown, which was the characteristic color of the formed γ-Fe₂O₃ [14]. However, the XRD pattern for the calcined magnetic nanoparticle was very similar to that of the Fe₃O₄ (data not shown), implying that only superficial Fe₃O₄ transformed to γ-Fe₂O₃ as confirmed by previous studies [11,14–16]. Thus a shell core structure of γ-Fe₂O₃@ Fe₃O₄ 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 Fe²⁺–O²⁻ stretching vibration, changed to 563 cm⁻¹ after the nanoparticle was calcined (Fig. 2b), implying that the Fe²⁺ was oxidized to Fe³⁺ [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
observed. These changes must be due to the imine groups in PEI [12], suggesting the introduction of PEI on the magnetic nanoparticles.

Fig. 3 presents the photomicrographs of MNPs before and after surface modification. The diameter of the particles after modification (Fig. 3b approximate 100 nm) was larger than that of the pristine magnetic ones (Fig. 3a approximate 40 nm), which was attributed to the graft of PEI. EDS analysis revealed that the content of N in adsorbent was 5.35% (w/w).

3.2. Effect of solution pH

The solution pH significantly influences the surface charge and the protonation degree of adsorbent. The zeta potential of the pristine and PEI-MNPs at different pH are shown in Fig. 4. The zero point of zeta potential (pHzpc) for pristine particle had been found at pH 5.5. In contrast, the pHzpc for the PEI-MNPs was increased to a much higher value of 11.4, which was attributed to the protonation of imine groups on the particle surface. In agreement with earlier study [2], the pHzpc was significantly increased after the modification of PEI to the matrix surface.

In addition, Cr(VI) exists in solution as different ionic forms. The main Cr(VI) species are CrO_4^{2-}, Cr_2O_7^{2-}, and HCrO_4^{-}, depending on the solution pH and total chromate concentration [17,18]. Based on thermodynamic database [18], a predominance diagram for Cr(VI) using pH and total Cr(VI) concentration as variables is presented in Fig. 5. The two vertical lines divide the diagram into three parts, and the area between the two horizontal dashed stands for the Cr(VI) concentration ranging from 50 mg L^{-1} to 500 mg L^{-1}. As shown in it, HCrO_4^{-} and CrO_4^{2-} are the predominant species at the experimental total Cr(VI) concentration. For pH lower than 6.8, HCrO_4^{-} is the dominant component of hexavalent chromium, and above pH 6.8, only CrO_4^{2-} existed.

The effect of pH on adsorption of Cr(VI) is shown in Fig. 6. The removal efficiency was more than 95% in the pH range of 2–3; subsequently, it decreased sharply in the solution pH range of 4–7, ultimately, less than 55% Cr(VI) was removed in the alkali solution. Therefore, pH value between 2 and 3 was an ideal parameter in this work. As the adsorbent was positively charged when the solution pH < 11.4, from the viewpoint of electrostatic

**Fig. 3.** SEM micrographs of (a) MNPs and (b) PEI-MNPs.

**Fig. 4.** Zeta potential of MNPs and PEI-MNPs as a function of pH.

**Fig. 5.** Cr(VI) species in solution as a function of pH and total Cr(VI) concentration.

**Fig. 6.** Effect of pH on removal of Cr(VI) (metal concentration 100 mg L^{-1}, adsorbent dose 0.08 g, contact time 30 min, temperature 25 °C).
interaction, lower pH was favourable to the adsorption of anionic Cr(VI). With the increase of pH, the zeta potential of the adsorbent decreased and the competition from −OH increased, resulting in the weak interaction between Cr(VI) and adsorbent, thus the removal efficiency decreased. Fig. 5 illustrated that the predominant form of Cr(VI) changed to CrO₄²⁻ from HCrO₄⁻ at pH>7. The adsorption free energy of CrO₄²⁻ (−2.1 to −0.3 kcal mol⁻¹) is higher than that of HCrO₄⁻ (−2.5 to −0.6 kcal mol⁻¹) [19]. Consequently, CrO₄²⁻ is less likely adsorbed than HCrO₄⁻ at the same concentration.

3.3. Effect of contact time on adsorption

The effect of contact time on removal of 100, 200, 400 and 500 mg L⁻¹ Cr(VI) is shown in Fig. 7. The adsorption rate was considerably fast, with over 92% of the Cr(VI) removed in the first 10 min. The required equilibrium time for different initial concentrations had no significant difference, indicating a strong interaction between the adsorbent and adsorbate. The rapid adsorption performance of PEI-MNPs might be related to the properties of itself. Since the adsorbent was nanosized, a high surface area was provided for easy contacting between Cr(VI) and active site. In addition, the adsorbent was dispersed in solution evenly due to the water soluble nature of PEI, producing little external diffusion resistance [7,8], ultimately, bringing about fast adsorption equilibrium. However, the equilibrium time for Cr(VI) adsorption by some other adsorbents was much longer. For example, uptake of Cr(VI) by PEI-modified fungal biomass took 3–6 h to reach saturation [2], while 10–50 h was needed for activated carbon [20]. The maximum removal efficiency of Cr(VI) with initial concentration of 100, 200, 400, 500 mg L⁻¹ reached 98.2%, 92.6%, 72.5%, and 64.6%, respectively, suggesting that the Cr(VI) removal efficiency decreased with the increase of initial concentration. This phenomenon was predictable due to the fact that the dosage of adsorbent was fixed, thus the total available active sites were limited, leading to the decrease of removal efficiency corresponding to an increased initial Cr(VI) concentration.

Adsorption kinetic model not only allows estimation of adsorption rate but also provides insights into rate characteristic of possible reaction mechanisms. It was pointed out that pseudo-second-order adsorption model was based on the assumption that the rate-controlling step, involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate, was able to well describe the adsorption kinetics [21]. Therefore, the model was applied in this work with its expression as

\[
\frac{t}{q_t} = \frac{1}{q_e} + \frac{t}{q_e v_0}
\]

where \(q_e\) and \(q_t\) (mg g⁻¹) is the amount of adsorbed heavy metal at equilibrium and at time \(t\), respectively, \(v_0\) (mg g⁻¹ min⁻¹) is the initial sorption rate; \(v_0 = k_2 q_e^2\), in which \(k_2\) (g mg⁻¹ min⁻¹) is the rate constant.

Plotting \(t/q_t\) against \(t\) gives a straight line to reflect the goodness-of-fit (Fig. 8). It indicated that the experimental data could be described by the pseudo-second-order model with correlation coefficients \(r^2 > 0.99\) for all concentrations. The corresponding rate constant \(k_2\) was 0.1140, 0.0425, 0.0127, and 0.0110 g mg⁻¹ min⁻¹, respectively, for 100, 200, 400 and 500 mg L⁻¹ Cr(VI) adsorption. The rate constant decreased with the increase of initial Cr(VI) concentration, which was consistent with the previous research [22].

3.4. Adsorption isotherms and thermodynamic evaluation

The adsorption isotherms at 35 ºC, 25 ºC, and 15 ºC were evaluated respectively, by changing the initial concentration of Cr(VI) from 50 to 500 mg L⁻¹. The calculated parameters based on Langmuir adsorption model were listed in Table 1. The Langmuir adsorption model, which assumes that all the binding sites are equal and the adsorbent surface is homogeneous, is expressed as

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]

where \(q_e\) (mg g⁻¹) is the amount of Cr(VI) adsorbed at equilibrium; \(q_m\) (mg g⁻¹) is the maximum adsorption capacity; \(C_e\) (mg L⁻¹) is the equilibrium solute concentration, and \(K_L\) is the equilibrium constant (L mg⁻¹) related to adsorption energy.

Besides Langmuir model, Freundlich sorption model was also applied to analyze the experimental data. It is commonly presented as

\[
q_e = K_F C_e^{1/n}
\]

where \(K_F\) and \(n\) are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively [21].

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Langmuir and Freundlich model parameters for Cr(VI) adsorption at different temperatures.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir model</strong></td>
<td><strong>Freundlich model</strong></td>
</tr>
<tr>
<td>(q_m) (mg g⁻¹)</td>
<td>(K_L) (L mg⁻¹)</td>
</tr>
<tr>
<td>35 ºC</td>
<td>74.07</td>
</tr>
<tr>
<td>25 ºC</td>
<td>78.13</td>
</tr>
<tr>
<td>15 ºC</td>
<td>83.33</td>
</tr>
</tbody>
</table>

Fig. 7. Effect of contact time on removal of different initial concentrations Cr(VI) (adsorbent dose 0.08 g, pH value 2.2, temperature 25 ºC).

Fig. 8. Linear fit of experimental data using pseudo-second-order kinetic model.
Table 2
Values of thermodynamic parameters for Cr(VI) removal using PEI-MNPs.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\ln K_L$</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>1.2697</td>
<td>-3.251</td>
<td>-22.04</td>
<td>-60.46</td>
</tr>
<tr>
<td>298</td>
<td>1.7526</td>
<td>-4.342</td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>1.8718</td>
<td>-4.481</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Langmuir model provided the best results for these sorts of lines based on the correlation coefficients ($r^2 > 0.98$). The maximum adsorption capacities ($q_m$) for Cr(VI) by PEI-MNPs at 35–15 °C were 74.07–83.33 mg g$^{-1}$, which was much higher than that of unmodified MNPs ($q_m = 12.66$ mg g$^{-1}$ at 25 °C). The high capacity indicated its potential application in Cr(VI) removal from wastewater. The correlation coefficients of the Freundlich model under all temperatures were more than 0.92. The best-fit Freundlich parameter $n$ was in the range of 2–10, suggesting a favourable adsorption process [23].

The adsorption isotherms were carried out under different temperatures, thus thermodynamic evaluation was able to be done based on it. The thermodynamic parameters of the adsorption process such as change in standard free energy ($\Delta G$), enthalpy ($\Delta H$), and entropy ($\Delta S$) can be obtained using the following equations [24]

$$\Delta G = -RT \ln K_L$$

(4)

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

(5)

where $K_L$ is the Langmuir constant (L mol$^{-1}$), $R$ is the ideal gas constant (8.31 mol$^{-1}$ K$^{-1}$), and $T$ is the absolute temperature. $\Delta H$ and $\Delta S$ could be obtained from the slope and intercept of van't Hoff plots of $\ln K_L$ versus $1/T$. The values of the thermodynamic parameters are presented in Table 2.

The negative values of $\Delta G$ and $\Delta H$ meant that the adsorption was a spontaneous exothermic process; and consequently a lower temperature was favourable to the reaction, which might explain the increase of $q_m$ with the decrease of temperature. The negative $\Delta H$ was noteworthy, since Li et al. [22] and Bayramoglu [25] had reported the positive $\Delta H$ in investigation of Cr(VI) adsorption. The phenomenon might be attributed to the electrostatic interaction between Cr(VI) and the PEI-MNPs, which is an exothermic process, resulting in the observed negative $\Delta H$. The negative entropy changes ($\Delta S = -60.46$ J mol$^{-1}$ K$^{-1}$) indicated that the order degree increased during the adsorption process.

3.5. Effect of common ions

Various ions exist in wastewater. The presence of other solutes may reduce the adsorption of any given adsorbate to some extent. In addition, the uptake of the other ions influences the recovery of Cr(VI) directly. Thus, K$, Na^+$, Ca$^{2+}$, and Cu$^{2+}$, as well as the anions of Cl$^-$ and NO$_3^-$, which are the commonly coexisting ions with Cr(VI), were chosen for study. Fig. 9 revealed that the effect of the studied common ions on the adsorption of Cr(VI) was considerably insignificant, even if the ions concentration increased to double, implying that they did not compete for the active sites with Cr(VI) [26]. It is noteworthy that some PEI modified adsorbents adsorbed Cu$^{2+}$ effectively [4,12], much different with this work. The distinct performances were mainly due to the different adsorption mechanisms, which was electrostatic interaction and chelating adsorption respectively, under different solution pH. Therefore, selective adsorption of Cr(VI) can be achieved by the prepared adsorbent.

Furthermore, actual wastewater (from an electronics factory) with Cr(VI) concentration of 37.98 mg L$^{-1}$ was reduced to 0.375 mg L$^{-1}$ after adding 2.67 g L$^{-1}$ adsorbent for 30 min treating, indicating the feasibility of removing Cr(VI) from multi-component effluent using the PEI-MNPs.

3.6. Stability and regeneration

The PEI-MNPs were exposed to different concentrations of HCl or NaOH for 3 h. The leached Fe content and the adsorption capacity of the treated adsorbent were determined, respectively. No significant Fe leaching was observed in acid or alkali solution with concentration range of 0.2–1 mol L$^{-1}$ (Table 3). The magnetization of these adsorbents was strong enough for magnetic separation. In contrast, the naked Fe$_3$O$_4$ was dissolved completely in 1 mol L$^{-1}$ HCl. Furthermore, the adsorbent could be preserved for five months at room temperature without deterioration. The excellent stability could be due to the formed γ-Fe$_2$O$_3$ on the surface of nanoparticles, which has similar magnetic properties to Fe$_3$O$_4$ but better chemical stability to protect inner Fe$_3$O$_4$ [15,16].

A slight increase in removal efficiency for acid incubated adsorbent (Table 3) was probably due to the surface protonation of the adsorbent caused by HCl treatment. Since the suppressed Cr(VI) adsorption was found at high pH (confirmed in Section 3.2), alkali wash was a feasible approach to regenerate the Cr(VI) loaded adsorbent. Therefore, 0.02 mol L$^{-1}$ NaOH solution was adopted for regeneration, and the regenerated adsorbent was used for six consecutive cycles. The removal efficiency of Cr(VI) did not change significantly during the repeated adsorption–desorption operations (decreased only 5% in the sixth cycle), suggesting that the regeneration method was quite effective.

Table 3
Leached Fe rate and Cr(VI) removal efficiency of adsorbent after treated by different concentrations HCl and NaOH solution.

<table>
<thead>
<tr>
<th></th>
<th>HCl (mol L$^{-1}$)</th>
<th>NaOH (mol L$^{-1}$)</th>
<th>Untreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>0.2</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Leaching rate (%)</td>
<td>2.74</td>
<td>4.68</td>
<td>21.6</td>
</tr>
<tr>
<td>Removal rate (%)</td>
<td>88.4</td>
<td>91.0</td>
<td>92.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>88.6</td>
</tr>
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</tbody>
</table>
4. Conclusions

In this work, MNPs with enhanced stability were prepared by calcining Fe3O4 to form a protecting shell of γ-Fe2O3. PEI was grafted to the nanoparticle to develop a positive surface charge for effective removal of anionic Cr(VI) mainly by electrostatic interaction. The removal efficiency was highly pH dependent and the optimal adsorption occurred at pH of 2–3. Adsorption of Cr(VI) was very fast, only 30 min was needed to reach equilibrium. The saturated capacity of 74.07–83.33 mg g⁻¹ was obtained in the temperature range of 35–15 °C. Thermodynamic evaluation revealed that the adsorption process was spontaneous and exothermic. The competitive studies showed the effect of common coexisting ions was negligible on Cr(VI) adsorption. The regeneration studies revealed that the adsorbent can be used for six consecutive adsorption–desorption cycles without significant loss of adsorption capacity.

Acknowledgments

This study was financially supported by the Program for Changjiang Scholars and Innovative Research Team in University (IRT0719), the National Natural Science Foundation of China (50978088, 51039001, 50608029), the Hunan Key Scientific Research Project (2009FJ1010), the Hunan Provincial Natural Science Foundation of China (10JJ7005), the Hunan Provincial Innovation Foundation For Postgraduate (CX2009B080, CX2010B157) and the Fundamental Research Funds for the Central Universities, Hunan University.

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