Removal of Toxic Cr(VI) Ions from Water Sample a Novel Magnetic Graphene Oxide Nanocomposite

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ABSTRACT

This work describes the synthesis of a novel magnetic graphene oxide composite for removal of Cr(VI) ions. The synthesized nanosorbent were characterized with various techniques such as FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM), elemental analysis and vibrating sample magnetometry (VSM). This material is illustrated to represent a viable sorbent for the removal of Cr(VI) ions. A Box-Behnken design was applied to optimize the parameters affecting the removal of Cr(VI). Three variables including sorption time, amount of the magnetic sorbent and sample pH were optimized in the removal process. Besides, the recovery of the sorbent was studied. Equilibrium isotherms were studied, and three models were applied to analyze the equilibrium adsorption data. The results revealed that the adsorption process obeyed the Langmuir model. Kinetic studies indicated the adsorption process followed a pseudo-second-order model. Maximum sorption capacity of the sorbent for Cr(VI) ions was 250 mg g⁻¹.

Keywords: Magnetic graphene oxide composite, Cr(VI) ions, Adsorption isotherm, Kinetic studies, Removal.
Introduction

Great attention has been attracted to the utilization of nano-structure sorbents especially graphene, graphene oxide [1,2] and magnetic nanoparticles [3-5]. Graphene (G) and graphene oxide (GO) have been widely employed as sorbent owing to their excellent properties such as large specific surface area and sorption capacity, single layered structure and excellent physicochemical properties [1,2,6]. However, there are some limitations when G and GO are employed as the sorbents such as the poor dispersibility in water samples, difficult collection of them from the extraction media, long sample loading time and high back pressure when packed into a cartridge. Thereby, combination of the high surface area, nanoscaled and tubular configurations of G and GO with super paramagnetic characteristic of Fe$_3$O$_4$ are expected to be excellent candidates for high-performance magnetic solid phase extraction (MSPE) [2]. The resultant nanocomposite can be easily dispersed and collected from the extraction media and benefit from the excellent extraction properties of G and GO along with magnetic properties of Fe$_3$O$_4$ NPs [1].

Environmental pollution character of heavy metals and metalloids has attracted great attention owing to their high toxicity. Heavy metals have a high tendency to form complexes with various compounds, particularly biological ligands containing nitrogen, sulfur, and oxygen atoms [7]. The complex formation can resulted to changes in the molecular conformation of proteins, enzymes inhibition and hydrogen bonds breaking. One of these heavy metals is chromium. The toxicity of chromium is related to its oxidation states. Two dominant oxidation states of chromium in the environment are Cr(III) and Cr(VI) [8]. These two species have very different properties. In one hand, Cr(III) is considered as an essential element in organisms [9,10] for the maintenance of glucose, lipid and protein metabolism [11]. The role of insulin hormone, which controls the blood sugar levels, is depends to Cr(III) [12]. Besides, Cr(III) compounds are slightly soluble except in cases where complex formation is occurred [13]. On the other hand, Cr(VI) species such as CrO$_4^{2-}$, HCrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ are highly toxic and hazardous to human and other mammals due to their adverse effect on various organisms such as lung, liver and kidney. These species are categorized as carcinogenic agents even at very low levels [14,15]. Moreover,
Cr(VI) ions are very mobile and soluble in water samples and are not adsorbed into many soils [6,10]. Thereby, removal of very low levels of Cr(VI) is often a major task in environmental science. Hence, development easy, quick, sensitive and environmentally friendly methods for Cr(VI) removal are of particular significance.

Herein, for the first time magnetic graphene oxide coated with poly(2-aminothiazole) nanocomposite, GO@Fe₃O₄@PAT, has been synthesized and utilized as a novel sorbent for the fast removal of Cr(VI) ions from water sample. The nanocomposite was characterized by various methods such as FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM), elemental analysis and vibrating sample magnetometry (VSM). The magnetic properties of the sorbent along with excellent properties of GO and polymer coating make the entire method a rapid and easy approach for the removal of Cr(VI) ions. The presence of polymer layer promotes the selectivity of the new sorbent toward Cr(VI) through ion exchange process. Design of experiments approach was utilized in order to find the best uptake conditions through response surface methodology. Equilibrium isotherms along with kinetic studies were conducted too.

Experimental

Materials and solutions

All reagents including (NH₄)₂Fe(SO₄)₂·6H₂O, FeCl₃, NaClO₄, HCl, HNO₃, NaOH, K₂CrO₄, 2-aminothiazole (2-AT), diphenylcarbazide (DPC), ammonium persulfate (APS), NH₄OH, acetone, ethanol, and methanol which were of analytical grade, were purchased from Merck (Darmstadt, Germany) or Fluka (Seelze, Germany) and were used without further purification. Stock standard solution (1000 mg L⁻¹) of Cr(VI) ions was prepared by dissolving an proper amount of K₂CrO₄ in deionized water. All working solutions were prepared in deionized water. Stock solutions (1000 mg L⁻¹) of potentially interfering ions including Na⁺, Ca(II), Zn(II), Ni(II), Cr(III), Cu(II), Cl⁻, NO₃⁻, SO₄²⁻, MoO₄²⁻, MnO₄⁻ and CH₃COO⁻ were prepared in deionized water. All of these solutions were stored at ambient temperature before use.
Instrumentation

A 2100 UV-Vis spectrophotometer (Shimadzu, Japan) equipped with a tungsten lamp as the radiation source and a 10 mm matched quartz cell was used for measurements of absorbance of Cr(VI) ions. The pH of the solutions were measured at 25 ± 1 ºC with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. A Bruker IFS-66 FT-IR Spectrophotometer was employed for FT-IR spectra recording. A Philips-PW 17C diffractometer with Cu Kα radiation (Philips PW, The Netherlands) was used to obtain high-angle XRD patterns. Scanning electron microscopy (SEM) was conducted by gently distributing the sample powder on the stainless steel stubs, using an SEM (KYKY-3200, Beijing, China) instrument. Magnetic properties of nanocomposites were measured by a vibrating sample magnetometer (VSM) model AGFM/VSM 117 3886 (Kashan, Iran) with a magnetic field strength of 1 Tesla and at room temperature. Elemental contents of nanocomposite were determined.

Synthesis of the nanocomposite

The magnetic graphene oxide@Fe₃O₄ (GO@Fe₃O₄) was prepared according to the literature [1]. For this purpose, 0.5 g GO was suspended in 500 mL deionized water and ultrasonicated for 3 h to obtain a uniform dispersion. Thereafter, 0.85 g (NH₄)₂Fe(SO₄)₂.6H₂O along with 0.422 g FeCl₃ was added to the mixture at 50 ºC under N₂ atmosphere protection. In the next step, in order to dissolve iron salts, the suspension was sonicated for 10 min and then 20 mL 8 mol L⁻¹ NH₄OH aqueous solution was added dropwise under sonication which precipitates the Fe₃O₄ NPs on the GO surfaces. The reaction was continued at 50 ºC for 30 min to ensure the complete growth of Fe₃O₄ NPs crystals [1]. Afterwards, the mixture was cooled to room temperature and GO@Fe₃O₄ was separated from the reaction medium using a strong permanent magnet. Separated GO@Fe₃O₄ was washed three times with deionized water followed by ethanol.
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To synthesis GO@Fe$_3$O$_4$@PAT nanocomposite, 1.0 g of dried GO@Fe$_3$O$_4$ was suspended in 300 mL deionized water and ultrasonicated for 60 min, then 5.0 mmol NaClO$_4$ as a dopant was added and the mixture was stirred for 5 min in order to dissolve NaClO$_4$. Afterwards, 5 mmol 2-aminothiazole was added to the above mixture and stirred at room temperature for 30 min. The mixture was then heated to 50 °C under stirring. In the next step, 5.0 mmol APS which was dissolved in 10 mL deionized water, was added to the reaction mixture drop by drop. The polymerization reaction was continued for 24 h. Ultimately, after 24 h the synthesized magnetic nanocomposite was separated from the reaction medium by the permanent magnet, washed several times by deionized water and methanol, respectively until obtaining a colorless supernatant and then it was dried. A schematic representation for the synthesis procedure of GO@Fe$_3$O$_4$@PAT is illustrated in Figure 1. It is worth to note that PAT was coated on the surface of both GO sheets and Fe$_3$O$_4$ NPs. The synthesized nanocomposite was characterized by FT-IR spectroscopy, SEM, CHNS, and VSM.
Uptake procedure

The uptake was performed in test tubes containing 25 mL 5.0 mg L\(^{-1}\) solution of Cr(VI). The pH of the solutions was adjusted to 2.2 by the dropwise addition of 0.1 mol L\(^{-1}\) HCl solution. Then 11 mg GO@Fe\(_3\)O\(_4\)@PAT was added into the solutions. Afterward, the mixture was stirred for 7.0 min in order to extract Cr(VI) ions from the solution completely. In the next step, the samples were exposed to the strong magnet (15 cm × 12 cm × 5 cm, 1.4 T) in order to separate the sorbent from solution. The sorbed amounts of Cr(VI) ions were determined by UV-Vis spectrophotometer owing to its concentration change in the solution before and after the sorption procedure. Sorption percentage was computed using the following equation:

\[
\text{Sorption}\% = \frac{c_A - c_B}{c_A} \times 100
\]
where \( C_A \) and \( C_B \) represent initial and final concentration (mg L\(^{-1}\)) of Cr(VI) ions in the solution, respectively.

**Experimental design methodology**

The effect of experimental variables, their interaction along with nonlinear interactions on the extraction performance was investigated using experimental design approach. A rational experimental design allows concurrent variation of all experimental variables, reduces the test time and number of trials which ends in the reduction of the overall required costs. Box-Behnken design (BBD) is perhaps the most widely used experimental design method employed for fitting a second-order response surface. BBD is a spherical, rotatable, or nearly rotatable second-order design and consists of linear, quadratic and interaction terms [17]. The precise optimum value can be achieved with the aid of response surface methodologies illustrating a graphical relationship between variables and responses [18].

In this study the StatGraphics plus 5.1 package was used for the analysis of experimental design data and calculating the predicted responses.

**Results and discussion**

**Characterization studies**

The FT-IR spectrum of GO@Fe\(_3\)O\(_4\)@PAT was recorded using KBr pellet method. The absorption peaks appeared at 576 cm\(^{-1}\) (Fe-O), 3399 cm\(^{-1}\) (N-H), 1031 cm\(^{-1}\) (C-N), 1612 cm\(^{-1}\) (C=N) and 1524 cm\(^{-1}\) (C=C) confirmed the presence of PAT on the surface of GO@Fe\(_3\)O\(_4\) and successful synthesis of the nanocomposite. The CHNS analysis of GO@Fe\(_3\)O\(_4\)@PAT
demonstrated the presence of C, N, H, and S atoms with 25.4, 3.7, 1.6 and 2.4 percent, respectively. These results confirmed the existence of PAT on the surface of GO nanosheets. The XRD pattern of GO@Fe$_3$O$_4$@PAT is shown in Figure 2a. In the pattern, seven characteristic diffraction peaks appeared at $2\theta = 30.03^\circ$, 35.72$^\circ$, 43.07$^\circ$, 53.63$^\circ$, 57.00$^\circ$, 62.64$^\circ$ and 74.97$^\circ$ that are related to (220), (311), (400), (422), (511), (440) and (622) Bragg diffractions of face centered cubic structured Fe$_3$O$_4$ NPs, were observed [16].

The morphology and dimension of GO@Fe$_3$O$_4$@PAT was explored by SEM imaging. The SEM image of nanocomposite (Figure 2b) depicted that Fe$_3$O$_4$ NPs with an average size of 40 nm were coated on the surfaces of GO nanosheets. Moreover, it is revealed that Fe$_3$O$_4$ NPs have grown on the surface of GO and well distributed, so the aggregation problem of MNPs is almost solved by employing GO as a support and spacer [2].

The magnetic properties of GO@Fe$_3$O$_4$, and GO@Fe$_3$O$_4$@PAT were investigated by VSM method and the corresponding plots are illustrated in Figure 2c. As exhibited in Figure 2c, the saturation magnetization of GO@Fe$_3$O$_4$, and GO@Fe$_3$O$_4$@PAT was 56 and 34 emu g$^{-1}$ respectively, which is desirable for magnetic separation with a common magnetic field. For superparamagnetic composite, when the external field is zero the magnetization became zero. The hysteresis plot of all the mentioned composites passed through the zero point of magnetization and illustrated a superparamagnetic property [19].
Figure 2: (a) XRD pattern (b) SEM micrograph and (c) VSM plot of GO@Fe₃O₄@PAT nanosorbent
Optimization of uptake parameters

Box-Behnken design (BBD) was conducted to find the best conditions for uptake of Cr(VI) ions on the magnetic nanosorbent. pH of sample, sorption time and GO@Fe₃O₄@PAT amount were selected and optimized in this step. The concentration of Cr(VI) ions (5.0 mg L⁻¹) was kept constant.

The number of experiments (N) in BBD is defined by the following expression:

\[ N = 2K (K - 1) + C_o \]

where \( K \) is the variables number and \( C_o \) is the center points number [20]. In this work, \( K \) and \( C_o \) were set at 3 and 5 respectively, and which means that 17 trials should be performed. The levels of each factor in BBD are listed in Table 1. The Pareto chart of main effects along with interaction effects was obtained based on the analysis of variance (ANOVA) results (Figure 3a).

Based on the Pareto chart, the sample pH has the most significant negative effect on the sorption efficiency of Cr(VI). The sorption of Cr(VI) decreases as the pH value increases. Cr(VI) will be present in oxyanionic forms such as \( \text{CrO}_4^{2-} \), \( \text{HCrO}_4^- \), \( \text{Cr}_2\text{O}_7^{2-} \) and \( \text{H}_2\text{CrO}_4 \) depending on solution pH and the concentration. The major species of Cr(VI) in the pH range of 2-4 is \( \text{HCrO}_4^- \) which can be sorbed to the GO@Fe₃O₄@PAT surface through ion exchange process with doped \( \text{ClO}_4^- \) ions [21]. The decrease of the sorption capacity below pH 2.2 is mainly due to the conversion of \( \text{HCrO}_4^- \) to \( \text{H}_2\text{CrO}_4 \). At higher pH values the sorption efficiency was decreased owing to the reduction in the protonation degree of PAT chains [21]. Moreover, sorption time depicted a positive significant effect while GO@Fe₃O₄@PAT amount exhibited a non-significant positive effect on the sorption efficiency. Figure 3b illustrates the response surface and two-dimensional contour plots for the analysis simultaneous effects of the pH and sorption time.

Based on the overall results of the optimization study, the best conditions were selected as: pH,
2.2; sorption time, 7.0 min; GO@Fe₃O₄@PAT amount, 11 mg. The obtained results revealed a fast sorption kinetic (7.0 min) and the need of small amount of sorbent (11 mg) owing to the high surface area and short diffusion route of nano-sized sorbents [22].

**Table 1:** Experimental parameters and their levels in the Box Behnken design for uptake of Cr(VI) ions.

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Central</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: pH</td>
<td>1.0</td>
<td>2.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Sorption step</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B: Sorption time (min)</td>
<td>2.0</td>
<td>6.0</td>
<td>10.0</td>
</tr>
<tr>
<td>C: GO@Fe₃O₄@PAT amount (mg)</td>
<td>5.0</td>
<td>10.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

![Standardized Pareto Chart for Removal%](image)

**Figure 3:** (a) Pareto chart of the main effects in the BBD (sorption step). AA, BB and CC are the quadratic effects of sample pH, the sorption time and GO@Fe₃O₄@PAT amount, respectively. (b) Response surface and two-dimensional contour plot obtained by plotting pH vs. sorption time in the BBD.
Recovery test

The effect of NaOH, KCl, NaClO₄, Na₂CO₃ and mixture of them on the recovery of Cr(VI) ions were investigated. Other parameters including pH, sorption time, GO@Fe₃O₄@PAT, eluent volume and elution time were fixed at 2.2, 7.0 min, 11 mg, 3.0 mL and 10 min, respectively. Results showed that mixture of NaOH and NaClO₄ can recover Cr(VI) ions more effectively. In the next step the effect of eluent concentration and its volume along with elution time were investigated and optimized. The best recovery performance was obtained by using 4.5 mL 0.9 mol L⁻¹ NaClO₄ in 0.75 mol L⁻¹ NaOH solution.

Adsorption isotherms and sorption capacity

To investigate the sorption capacity of Cr(VI) on the sorbent, adsorption isotherm models were studied. The obtained equilibrium data were fitted to Langmuir, Freundlich and Temkin as three popular models. The linearized form of the Freundlich, Langmuir and Temkin adsorption isotherms, which were employed to evaluate the relationship between Cr(VI) concentration adsorbed by GO@Fe₃O₄@PAT and its equilibrium concentration in aqueous solution, are depicted in equation 3, 4 and 5, respectively.

Eq. 3

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]

Where \( C_e \) is the equilibrium concentration of Cr(VI) ions, \( q_e \) is the Cr(VI) adsorbed amount (mg g⁻¹), and \( 1/n \) and \( K_F \) are experimental constants corresponding to the parameters influencing the adsorption process [23].
From the linearized form of Langmuir isotherm adsorption capacities and the Langmuir constants can be calculated using the following equation:

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{k_L q_{\text{max}} C_e}
\]

Where \( q_e \) is adsorbed amount of Cr(VI) ions per gram of the sorbent; \( C_e \) is the equilibrium concentration of Cr(VI) in aqueous solution; \( q_{\text{max}} \) is the maximum specific sorption capacity corresponding to the site saturation; \( K_L \) is the adsorption and adsorption rate ratio [23].

The linearized form of Temkin isotherm is depicted in Eq. 5:

\[
q_e = B \ln A + B \ln C_e
\]

Where \( B = RT/b \) and \( b \) is the Temkin constant which is related to sorption heat (J mol\(^{-1}\)). In this equation \( A, R \) and \( T \) are the Temkin isotherm constant (L g\(^{-1}\)), the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and absolute temperature (K), respectively [24-32].

To study the mentioned adsorption isotherms, in several batch experiments, 11 mg portions of GO@Fe\(_3\)O\(_4\)@PAT were equilibrated with various concentrations of Cr(VI) ion within the range of 5 to 300 mg L\(^{-1}\) at pH 2.2 and stirred for 90 min. The obtained correlation coefficients (\( R^2_{\text{Temkin}} = 0.805 \), \( R^2_{\text{Freundlich}} = 0.978 \), \( R^2_{\text{Langmuir}} = 0.996 \)) revealed that Cr(VI) adsorption equilibrium data were fitted well to the Langmuir isotherm rather than Temkin and Freundlich isotherms. Based on the obtained results and linearized form of the Langmuir model, the maximum specific adsorption capacity (\( q_{\text{max}} \)) and the Langmuir constant (\( K_L \)) were 250 mg g\(^{-1}\) and 0.154 L mg\(^{-1}\), respectively.

\( \text{Sorption kinetic} \)
For investigating the kinetic mechanism of Cr(VI) sorption onto GO@Fe₃O₄@PAT sorbent, two popular kinetic equations named Lagergren pseudo first order and pseudo second order models were employed. The obtained regression equations for pseudo-first order and pseudo-second order kinetic model along with the related correlation coefficients were $y = -0.006x + 1.567$ ($r^2 = 0.926$) and $y = 0.009x + 0.048$ ($R^2 = 0.999$), respectively. As the results exhibited and based on the obtained $r^2$ values, pseudo-second order kinetic model has a higher $r^2$ value for all kinetic data. The pseudo-second order kinetic equation was developed for the sorption process and there are 3 consecutive steps which occurring during the sorption of Cr(VI) ions by GO@Fe₃O₄@PAT sorbent: (1) migration of Cr(VI) ions from solution to the surface of GO@Fe₃O₄@PAT; (2) migration of Cr(VI) ions into the pores of GO@Fe₃O₄@PAT sorbent; and (3) sorption of Cr(VI) ions on the interior surface of GO@Fe₃O₄@PAT sorbent [25,26]. The rate of the sorption is mainly controlled by the first two steps. The rate constant of adsorption ($k_{ads}$) was calculated to be $0.0017 \text{ g mg}^{-1} \text{ min}^{-1}$ which indicates that it is a second order kinetic.

**Conclusion**

In this work, a novel magnetic graphene oxide composite coated by poly(2-aminothiazole) was synthesized and employed as a viable sorbent for removal of Cr(VI) ions. The developed removal method was simple, fast and reliable. The modification of magnetic graphene oxide with the polymer coating led to its chemical stability in hard acidic medium and enhanced its selectivity towards Cr(VI) ions. This new sorbent exhibited the advantages of high sorption capacities (250 mg g⁻¹), and fast extraction dynamic (7.0 min) compared to previously reported methods (Table 2). Owing to high surface area of the nanocomposite, satisfactory results can be obtained using fewer amounts of the sorbent (11 mg).
Table2: Comparison of the sorption capacity of the new nanosorbent with those of the other reported sorbents.

<table>
<thead>
<tr>
<th>Method</th>
<th>Instrument</th>
<th>SC&lt;sup&gt;a&lt;/sup&gt; (mg g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO@Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;@polyaminothiazole</td>
<td>ETAAS</td>
<td>250</td>
<td>This work</td>
</tr>
<tr>
<td>Ionic liquid-functionalized silica</td>
<td>HPLC-UV</td>
<td>-</td>
<td>[27]</td>
</tr>
<tr>
<td>Amberlite XAD-1180</td>
<td>FAAS</td>
<td>-</td>
<td>[28]</td>
</tr>
<tr>
<td>Multiwalled carbon nanotubes</td>
<td>FAAS</td>
<td>9.5</td>
<td>[29]</td>
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<tr>
<td>Flow injection analysis</td>
<td>ETAAS</td>
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<td>[30]</td>
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References


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