Magnetic amine-functionalized polyacrylic acid-nanomagnetite for hexavalent chromium removal from polluted water

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A novel magnetic amine-functionalized polyacrylic acid-nanomagnetite (Fe$_3$O$_4$-PAA-NH$_2$) adsorbent prepared using a facile surface-initiated polymerization (SIP) method has delivered a great Cr(VI) removal performance compared to as-received Fe$_3$O$_4$ nanoparticles. The maximum amine group (amine-H$_2$) concentration grafted onto Fe$_3$O$_4$-PAA is determined to be 3.925 mg g$^{-1}$ based on acid–base titrimetric analysis. The optimal pH value for Cr(VI) adsorption is around 2.0 with a Fe$_3$O$_4$-PAA-NH$_2$ dose of 30 mg and contact time of 10 min at room temperature. A multilayer adsorption for the Freundlich isotherm model is well-fitted and fits better than the monolayer adsorption of the Langmuir isotherm model. The kinetics of Cr(VI) removal by the Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent is found to follow pseudo-second-order behavior with a calculated room temperature rate constant of 1.23 g mg$^{-1}$ min$^{-1}$ for a solution with an initial Cr(VI) concentration of 7.0 mg L$^{-1}$ and pH value of 2.5. The competition adsorption tests show that the presence of other metals in polluted water, including Cu(II), Zn(II), Cd(II), K(I), Ca(I), Na(I), and Mg(I), favors the Cr(VI) adsorption by the fabricated Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent due to the affinity of the chemical potential and electronegativity of each metallic element. Moreover, the prepared Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent exhibits a good reusability and retains around 85% of its Cr(VI) adsorption capacity even after 5 cycles.

1. Introduction

Currently, increasing contamination in wastewater systems is a critical problem to solve. In particular, the heavy metals, such as chromium (Cr), cadmium (Cd), mercury (Hg), lead (Pb), and arsenic (As), are highly toxic water pollutants resulting from industries including metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries, pesticides, etc., which can cause severe public health problems to animals and human beings since they can be stored, accumulated and transferred by organisms. Among these heavy metal ions, hexavalent chromium (Cr(VI)) is a common contaminant in polluted water and exhibits extreme toxicity and notorious mobility. The U.S. Environmental Protection Agency (EPA) has set a maximum contaminant level for total Cr in drinking water as 0.1 mg L$^{-1}$. The U.S. Environmental Protection Agency (EPA) has set a maximum contaminant level for total Cr in drinking water as 0.1 mg L$^{-1}$. According to the national primary drinking water regulations, rapid, efficient and economical technologies are required to be used to stringently treat industrial wastewater before discharge in order to meet the limitations. Adsorption is a traditional, favorable and feasible technique to eliminate heavy metal ions for environmental remediation due to its low cost and high efficiency. In addition, adsorption can effectively remove heavy metals present in the wastewater system at lower concentrations compared with other methods, such as chemical precipitation and electrochemical methods.

Recently, nanostructured adsorbents have shown promise for application in water decontamination owing to their high specific surface area and having many more active sites than bulk materials for trapping heavy metal ions. However, the recycling of these nanosized adsorbents after treatment of polluted water still remains a challenge. Generally, the introduction of magnetism into nanoadsorbents can help with the recycling of adsorbents from the wastewater system via direct application of an external magnetic field. These recycled magnetic nanoadsorbents can also be regenerated and reused for economic and practical applications. Therefore, researchers have started to pay attention to the design of magnetic nanoadsorbents for heavy metal remediation. For example, Kim et al. prepared a hierarchical structured MnO$_2$-coated magnetite nanocomposite (Fe$_3$O$_4$/MnO$_2$) using a mild hydrothermal process with a maximum adsorption capacity toward Cd(II) of 53.2 mg g$^{-1}$. Liu et al. fabricated magnetic biopolymer hybrid hydrogels consisting of cellulose and chitosan as coating.
polymers and Fe$_3$O$_4$ as the core nanoparticles from ionic liquid as the solvent, which exhibited high adsorption capacities for different heavy metals (Cu(II), Fe(II), and Pb(II)). Gu et al. reported that magnetic Fe$_3$O$_4$-polyaniline (PANI) nanocomposites showed a unique capability to remove Cr(VI) from polluted water with a wide pH range and could be easily regenerated and reused without decreasing the Cr(VI) removal performance.

Meanwhile, it has been found that the surface functionality of adsorbents could greatly affect the adsorption of heavy metals at the interface. The introduced functional groups, such as carboxylate, hydroxyl, sulfate and amino groups, on the adsorbent surface are responsible for the heavy metal adsorption due to their affinity for heavy metals, forming metal complexes or chelates. Zhang et al. reported that thiol-functionalized multiwalled carbon nanotube/magnetite nanocomposites (CNT/Fe$_3$O$_4$) showed maximum adsorption capacities for Hg(II) and Pb(II) of 65.52 and 65.40 mg g$^{-1}$, respectively. Xin et al. noted that amine-functionalized mesoporous Fe$_3$O$_4$ nanoparticles obtained using a hydrothermal method possessed maximum adsorption capacities for Pb(II), Cd(II), and Cu(II) of 369.0 to 523.6 mg g$^{-1}$. Qiu et al. prepared ethyl cellulose (EC) composites modified with 20.0 wt% polyethylenimine (PEI) (PEI/ECs), which showed effective Cr(VI) removal from solutions with a wide pH range.

Based on the aforementioned advantages, this work combines magnetism with surface functionality to design a novel magnetic amine-functionalized polyacrylic acid (PAA)-nanomagnetite (Fe$_3$O$_4$-PAA-NH$_2$) nanoadsorbent, which shows efficient Cr(VI) removal from polluted water. The PAA is introduced on the surface of Fe$_3$O$_4$ using a facile surface-initiated polymerization (SIP) method in order to link the nanomagnetite with the amine groups. The presence of PAA on the surface of Fe$_3$O$_4$ can also protect Fe$_3$O$_4$ from acid etching. The effects of initial Cr(VI) concentration, solution pH values and adsorbent doses on the Cr(VI) removal have been systematically investigated. The room temperature adsorption kinetics are explored by studying the Cr(VI) concentration change with different contact times. The effect of the presence of other heavy metals, including Cu(II), Zn(II), and Cd(II), on the adsorption of Cr(VI) and the stability of the nanoadsorbent is studied as well. The synthesized Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent can satisfy the limitation of the US EPA requirement.

### 2. Experimental

#### 2.1. Materials

Acrylic acid (99.0%) was provided by Shanghai RichJoint Chemical Reagents Co., Ltd. Triethylene tetramine (TETA), potassium dichromate ($K_2$Cr$_2$O$_7$), nitric acid (HNO$_3$, 65–68 wt%), potassium nitrate (KNO$_3$, 99.0%, density: 2.109 g cm$^{-3}$ (16 °C)), magnesium nitrate (hexahydrate) (Mg(NO$_3$)$_2$·6H$_2$O, 99.0%, density: 1.464 g cm$^{-3}$), sodium nitrate (NaNO$_3$, 99.0%, density, 2257 g cm$^{-3}$), calcium nitrate (tetrahydrate) (Ca(NO$_3$)$_2$·4H$_2$O, 99.0%, density: 1.896 g cm$^{-3}$), zinc nitrate (hexahydrate) (Zn(NO$_3$)$_2$·6H$_2$O, 99.0%, density: 2.063 g cm$^{-3}$), and cupric nitrate (tribhydrate) (Cu(NO$_3$)$_2$·3H$_2$O, 99.0–102.0%, density, 2.32 g cm$^{-3}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Cadmium (99.98%) was obtained from Aladdin. Ammonium persulfate (APS, (NH$_4$)$_2$S$_2$O$_8$, 98.0%) was from Chinasun Specialty Products Co. Ltd. Fe$_3$O$_4$ nanoparticles with an average size of 12 nm were obtained from Nanjing Emperor Nano Material Co., Ltd. All the chemicals were used as-received without any further treatment.

#### 2.2. Preparation of PAA-modified Fe$_3$O$_4$ nanoparticles

The PAA-modified Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$-PAA) were prepared using a SIP method. First, the Fe$_3$O$_4$ nanoparticles (2.0 g) and oxidant APS (1.0 g) were mixed in a 250 mL beaker with 100 mL deionized water for 20 minutes with sonication. Then, the dispersed solution was transferred into a 250 mL three-neck flask and heated to 70 °C in an oil bath. After that, the acrylic acid was dropped into the above solution under mechanical stirring (300 rpm) and heated at reflux for an additional 4 hours in the oil bath at 70 °C for polymerization of the acrylic acid to form PAA. Finally, the product (Fe$_3$O$_4$-PAA) was vacuum filtered and washed with deionized water to remove the remaining oxidant and any oligomers before amine-functionalization.

#### 2.3. Fabrication of Fe$_3$O$_4$-PAA-NH$_2$ nanoparticles

The obtained Fe$_3$O$_4$-PAA nanoparticles were transferred into a 250 mL three-neck flask and mechanically stirred in the oil bath under reflux at 70 °C. TETA, with a weight ratio of 2 : 1 to the added acrylic acid, was dropped into the above solution for a further reaction time of 3 hours. The obtained powder was vacuum filtered and washed several times with deionized water and ethanol. The final amine-functionalized Fe$_3$O$_4$-PAA-NH$_2$ nanocomposite was dried at 60 °C in an oven overnight. The preparation procedure of Fe$_3$O$_4$-PAA-NH$_2$ is shown in Scheme 1.

#### 2.4. Determination of amine group content in the Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent

The amine group content in Fe$_3$O$_4$-PAA-NH$_2$ was determined using acid–base titrimetric analysis. Around 0.1 g of Fe$_3$O$_4$-PAA-NH$_2$ was weighed precisely and put into a 250 mL glass conical
flask containing 50 mL deionized water and mixed with a bromocresol green–methyl red indicator. A standard hydrochloric acid (HCl) solution was used to titrate the above solution until the color of the above solution turned from green to colorless or red. The amine content \(C_{\text{amine}} \text{mg g}^{-1}\) was evaluated from eqn (1):

\[
C_{\text{amine}} = \frac{C_{\text{HCl}} V_{\text{HCl}} M_{\text{NH}_2}}{m_{\text{amine}}}
\]

where \(C_{\text{HCl}}\) (mol L\(^{-1}\)) is the concentration of the standard HCl solution, \(V_{\text{HCl}}\) (L) is the volume of the consumed standard HCl solution, \(M_{\text{NH}_2}\) (g mol\(^{-1}\)) is the molecular weight of the amine group, and \(m_{\text{amine}}\) (g) is the weight of the used Fe\(_2\)O\(_4\)-PAA-NH\(_2\).

The concentration of the standard HCl solution was obtained using following procedure. 0.0052 g of anhydrous sodium carbonate (Na\(_2\)CO\(_3\)) was dissolved in 50 mL of deionized water in a 250 mL glass conical flask with bromocresol green–methyl red as a mixed indicator. The standard HCl solution was employed to titrate the Na\(_2\)CO\(_3\) solution. As the color of the solution changed from green to red, the solution was boiled for 2 min and cooled down to room temperature. Then, the solution was further titrated with the standard HCl solution until the solution became colorless or red. Thus, the concentration of the standard HCl solution was calculated using eqn (2):

\[
C_{\text{HCl}} = \frac{2 \times m_{\text{Na_2CO_3}}}{M_{\text{Na_2CO_3}} V_{\text{HCl}}}
\]

where \(m_{\text{Na_2CO_3}}\) (g) is the weight of the anhydrous Na\(_2\)CO\(_3\), \(M_{\text{Na_2CO_3}}\) (g mol\(^{-1}\)) is the molecular weight of the anhydrous Na\(_2\)CO\(_3\), and \(V_{\text{HCl}}\) (L) is the volume of the consumed standard HCl solution.

### 2.5. Characterization of Fe\(_2\)O\(_4\)-PAA-NH\(_2\) nanoadsorbent

The chemical structure of the as-prepared nanoadsorbent was analyzed using Fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet NEXUS, Thermo Scientific) in the range of 500 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). The morphologies of the synthesized nanocomposites were observed using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800 system). The samples were prepared by adhering the powders onto an aluminum plate. Elemental mapping was carried out with an electron-probe micro-analyser (JXA-8100, JEOL). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed from ambient temperature to 700 °C in air at a heating rate of 5 °C min\(^{-1}\) using a SDT thermal-microbalance apparatus. X-ray photoelectron spectroscopy (XPS) was carried out with a Kratos AXIS Ultra DLD spectrometer using Al K\(_x\) (\(h\nu = 1486.6\) eV) radiation as the excitation source under an anode voltage of 12 kV and an emission current of 10 mA. The C1s peaks were deconvoluted into the components consisting of a Gaussian line shape Lorentzian function (Gaussian = 80%, Lorentzian = 20%) on Shirley background. The Brunauer–Emmett–Teller (BET) method was used to measure the specific surface area of the as-prepared nanoadsorbent. BET adsorption and desorption isotherms were obtained using a surface area analyzer (TriStar 3000, Micromeritics Instrument Corp.). The samples (around 0.1 g) were weighed and placed inside the sample holder cell. The refrigerant used was liquid nitrogen placed in a vacuum Dewar at about 77 K and the carrier gas was nitrogen. The magnetic properties of the as-received Fe\(_2\)O\(_4\) nanoparticles, Fe\(_3\)O\(_4\)-PAA, and Fe\(_3\)O\(_4\)-PAA-NH\(_2\) were measured on a magnetic property measurement system (Lakeshore 735 VSM Controller 7300 Series Magnetometer).

### 2.6. Cr(\(\text{vi}\)) removal tests

All the Cr(\(\text{vi}\)) removal tests were conducted in a 50 mL glass conical flask at room temperature. The concentration of heavy metals was determined using atomic absorption spectroscopy (AAS, Agilent 3510, USA). The reported values were the average of three measurements of each sample with a standard deviation of ±5%.

#### 2.6.1 Effect of pH value

The effect of pH value on the Cr(\(\text{vi}\)) removal by the synthesized Fe\(_2\)O\(_4\)-PAA-NH\(_2\) was investigated by selecting solutions with pH values of 1.0, 2.0, 3.0, 5.0, 7.0, 9.0, 10.0 and 11.0. The initial pH value of the Cr(VI) solutions was adjusted using NaOH (1.0 mol L\(^{-1}\)) and HCl (1 mol L\(^{-1}\)) with a pH meter (model: PHS-25C). The Fe\(_3\)O\(_4\)-PAA-NH\(_2\) (30.0 mg) was ultrasonically dispersed (model: KQ-800KDE) for 10 min in 20.0 mL solutions with an initial Cr(\(\text{vi}\)) concentration of 5.4 mg L\(^{-1}\). Then, the solution was taken out and centrifuged (model: TDL-80-2B) for Cr(\(\text{vi}\)) concentration determination. Meanwhile, the Fe\(_3\)O\(_4\)-PAA-NH\(_2\) could also be separated from the solutions by using a permanent magnet to give similar results.

#### 2.6.2 Effect of initial Cr(\(\text{vi}\)) concentration

The effect of initial Cr(\(\text{vi}\)) concentration on the Cr(\(\text{vi}\)) removal was investigated by using Fe\(_3\)O\(_4\)-PAA-NH\(_2\) (30.0 mg) to treat Cr(\(\text{vi}\)) solutions (20.0 mL) with initial Cr(\(\text{vi}\)) concentration varying from 1.3 to 7.5 mg L\(^{-1}\) for 10 min.

#### 2.6.3 Effect of Fe\(_2\)O\(_4\)-PAA-NH\(_2\) dose

The effect of the dose of synthesized Fe\(_2\)O\(_4\)-PAA-NH\(_2\) on the Cr(\(\text{vi}\)) removal was studied by using Fe\(_3\)O\(_4\)-PAA-NH\(_2\) with loadings from 0.25 to 4.0 g L\(^{-1}\) to treat 20.0 mL Cr(\(\text{vi}\)) solutions with an initial Cr(\(\text{vi}\)) concentration of 7.5 mg L\(^{-1}\) and an initial pH of 3.0 for 10 min. For comparison, as-received Fe\(_3\)O\(_4\) nanoparticles, Fe\(_3\)O\(_4\)-PAA, and Fe\(_3\)O\(_4\)-PAA-NH\(_2\) (10.0 mg) were used to treat a neutral solution of 20.0 mL Cr(\(\text{vi}\)) with an initial Cr(\(\text{vi}\)) concentration of 1.0 mg L\(^{-1}\) for 5 min.

#### 2.6.4 Isotherm study

For the isotherm study, the synthesized Fe\(_3\)O\(_4\)-PAA-NH\(_2\) (20.0 mg) nanoparticles were used to treat different initial Cr(\(\text{vi}\)) concentrations varying from 0.5 to 4.5 mg L\(^{-1}\) with a contact time of 15 min at room temperature.

#### 2.6.5 Kinetics study

For the kinetics study, the synthesized Fe\(_3\)O\(_4\)-PAA-NH\(_2\) (30.0 mg) was used to treat a 20.0 mL solution with an initial Cr(\(\text{vi}\)) concentration of 7.0 mg L\(^{-1}\) and pH of 3.0 for different contact times.

#### 2.6.6 Effect of multiple metals on the adsorption of Cr(\(\text{vi}\)) by Fe\(_3\)O\(_4\)-PAA-NH\(_2\)

To investigate the effect of other heavy metals, including Cu(\(\text{ii}\)), Zn(\(\text{ii}\)), and Cd(\(\text{ii}\)), and other metal ions, such as K(\(\text{i}\)), Na(\(\text{i}\)), Ca(\(\text{ii}\)), Mg(\(\text{ii}\)) (which are normally present in real water systems), in the solution on the adsorption of Cr(\(\text{vi}\))
by Fe3O4-PAA-NH2, Fe3O4-PAA-NH2 (30.0 mg) was added into the mixed-metal solution with an initial heavy metal concentration of 5.0 mg L\(^{-1}\) and pH of 3.0 for 10 min treatment.

### 2.6.7 Regeneration of Fe3O4-PAA-NH2

The Fe3O4-PAA-NH2 (30.0 mg) was used to treat a 20.0 mL solution with an initial Cr(VI) concentration of 5.0 mg L\(^{-1}\) for 15 min. After adsorption, the used Fe3O4-PAA-NH2 nanoparticles were separated from the solution using a permanent magnet. The separated Fe3O4-PAA-NH2 nanoparticles were placed into a conical flask containing 20 mL of deionized water and sonicated for 15 min for desorption, and then separated from the solution using a permanent magnet. Finally, the regenerated Fe3O4-PAA-NH2 nanoparticles were dried at 60 °C for 3 h for reuse.

The Cr(VI) removal percentage (R%) is obtained using eqn (3):

\[
R\% = \frac{C_0 - C_e}{C_0} \times 100\% \tag{3}
\]

where \(C_0\) (mg L\(^{-1}\)) is the initial Cr(VI) concentration, and \(C_e\) (mg L\(^{-1}\)) is the final Cr(VI) concentration in the solution after treatment. The Cr(VI) removal capacity (\(q\), mg g\(^{-1}\)) is quantified by eqn (4):

\[
q = \frac{(C_0 - C_e)V}{m} \tag{4}
\]

where \(V\) (L) represents the volume of the Cr(VI) solution, and \(m\) (g) stands for the mass of the used Fe3O4-PAA-NH2 nanoadsorbent.

### 3. Results and discussion

#### 3.1. Structural characterization of amine-functionalized Fe3O4 nanoadsorbent

Fig. 1 illustrates the SEM microstructures of the as-received Fe3O4 nanoparticles, Fe3O4-PAA, and Fe3O4-PAA-NH2. The as-received Fe3O4 nanoparticles are ball-like in morphology with an average diameter of 13.3 nm, determined using the Nano measure software (Fig. 1(a)), which is consistent with the information obtained from the supplier. However, Fe3O4-PAA exhibits a different morphology from the as-received Fe3O4 nanoparticles. The Fe3O4-PAA is observed to be stuck together due to the polymerized PAA on the surface of the Fe3O4 nanoparticles (Fig. 1(b)). After amino-functionalization, the Fe3O4-PAA-NH2 becomes particulate again with an average diameter of 20.1 nm obtained from the Nano measure software (Fig. 1(c) and (d)). The increased nanoparticle diameter of Fe3O4-PAA-NH2 arises from the formed PAA and amino-functionalization process.

Elemental mapping of microstructures by SEM with energy dispersive X-ray spectroscopy (EDS) is widely applied in science, engineering, and technology fields. An element map is an image to display the 2-dimensional elements distributions in a material. In this work, the elemental mapping is conducted on the synthesized Fe3O4-PAA-NH2 to further clarify the specific components of Fe3O4-PAA-NH2. Fig. 2 shows the zero loss image (a), elemental maps of (b) O, (c) C, (d) Fe, (e) N and (f) the summation of the O, C, Fe, N elements. The different colors are used to represent the different elements in order to identify their compositions in the synthesized Fe3O4-PAA-NH2. The presence of N element confirms the successful preparation of amino-functionalized Fe3O4-PAA.

Fig. 3(A) shows the FT-IR spectra of the as-received Fe3O4 nanoparticles, Fe3O4-PAA, and Fe3O4-PAA-NH2. The absorption peak at around 533 cm\(^{-1}\) in the as-received Fe3O4 nanoparticles, Fig. 3(A)-a, is attributed to the vibration of the Fe-O band, which shifts to 567 and 581 cm\(^{-1}\) for Fe3O4-PAA (Fig. 3(A)-b) and Fe3O4-PAA-NH2 (Fig. 3(A)-c), respectively. In the Fe3O4-PAA, Fig. 3(A)-b, the strong absorption peaks at 1552 and 1710 cm\(^{-1}\) correspond to the C-O and C=O stretching vibrations of the carboxylic groups, respectively. The peak at around 2909 cm\(^{-1}\) is related to the C-H stretching vibration of the PAA polymer backbone. The peak at 3354 cm\(^{-1}\) is assigned to the O-H stretching vibration in the carboxylic groups of PAA. For the Fe3O4-PAA-NH2, Fig. 3(A)-c, the peaks at around 3419 and 1320 cm\(^{-1}\) are due to the stretching and bending vibrations of N-H, respectively. The peak at 2924 cm\(^{-1}\) is related to the C-H stretching vibration. The band at 1563 cm\(^{-1}\) (C-N stretching vibration) together with the small band at 1642 cm\(^{-1}\) (C=O stretching vibration) are the characteristic absorption peaks for the formation of –CONH– groups, which confirms the linkage of TETA onto the PAA polymer backbone.

Fig. 3(B) depicts the pore size distribution of the as-received Fe3O4 nanoparticles, Fe3O4-PAA, and Fe3O4-PAA-NH2. It is observed that the pore diameter of these three samples is widely distributed within the range of 1.5–40 nm. For the as-received Fe3O4 nanoparticles, the highest pore volume of 0.05297 cm\(^3\) g\(^{-1}\) corresponds to the pore diameter of 15.1 nm. However, for Fe3O4-PAA, the highest pore volume of 0.03254 cm\(^3\) g\(^{-1}\) appears at pore diameters of 15.5 and 5.3 nm, and for Fe3O4-PAA-NH2, the highest pore volume of 0.03653 cm\(^3\) g\(^{-1}\) corresponds to the pore diameter of 8.7 nm. These results show that the pore volume of the Fe3O4 nanoparticles is reduced after polymerization of PAA and amino functionalization on the surface of the Fe3O4 nanoparticles. The BET specific area of the as-received Fe3O4 nanoparticles, Fe3O4-PAA, and Fe3O4-PAA-NH2, and (c) Fe3O4-PAA-NH2, and (d) enlarged picture of Fe3O4-PAA-NH2 nanoadsorbent.
Fig. 2  SEM elemental mapping photographs of (a) Fe₃O₄-PAA-NH₂ nanoparticles, (b) O map, (c) C map, (d) Fe map, (e) N map, and (f) C + O + Fe + N map.

Fig. 3  (A) FT-IR spectra of (a) as-received Fe₃O₄ nanoparticles, (b) Fe₃O₄-PAA, (c) Fe₃O₄-PAA-NH₂; (B) pore size distribution of as-received Fe₃O₄ nanoparticles, Fe₃O₄-PAA, and Fe₃O₄-PAA-NH₂; (C) TGA curves, (D) DSC curves of as-received Fe₃O₄ nanoparticles, Fe₃O₄-PAA, and Fe₃O₄-PAA-NH₂; (E) high resolution C1s XPS spectra of (E) Fe₃O₄-PAA, and (F) Fe₃O₄-PAA-NH₂.
Fe₃O₄ nanoparticles is measured to be 81.4216 m² g⁻¹, which is reduced to 61.6277 and 69.9001 m² g⁻¹ for Fe₃O₄-PAA and Fe₃O₄-PAA-NH₂, respectively.

Fig. 3(C)&(D) show the TGA and DSC curves, respectively, of the as-received Fe₃O₄ nanoparticles, Fe₃O₄-PAA, and Fe₃O₄-PAA-NH₂ in air. In the TGA curve of the as-received Fe₃O₄ nanoparticles, the slight weight loss before 150 °C is attributed to the loss of moisture and there is no weight change after a further increase in temperature. This is consistent with the DSC curve of the as-received Fe₃O₄ nanoparticles, in which no endothermic peak is observed during the whole procedure (Fig. 3(D)). However, for Fe₃O₄-PAA, there is a significant weight loss observed around the temperature range of 250–300 °C, which corresponds to the thermal degradation of the PAA polymer chains. In the DSC curve (Fig. 3(D)) the thermal degradation of the PAA polymer chain appears as a sharp endothermic peak (the temperature is around 260 °C). Normally, the Fe₃O₄ nanoparticles will be oxidized to form hematite (α-Fe₂O₃) at high temperature.²⁹ The weight residue of Fe₃O₄-PAA in the TGA curve is determined to be 89.8% (weight percentage of α-Fe₂O₃) at 700 °C, which corresponds to 86.8 wt% of Fe₃O₄ nanoparticles. This means that the Fe₃O₄-PAA contains 13.2 wt% of PAA polymer. Meanwhile, the TGA profile of Fe₃O₄-PAA-NH₂ is distinct from that of Fe₃O₄-PAA, in which two weight loss regions are observed. The weight loss from 100 to 200 °C is due to the elimination of the functionalized TETA small molecules on the PAA polymer backbone. The major weight loss around the temperature range of 250–300 °C is assigned to the thermal degradation of the PAA polymer backbone, which is similar to that of Fe₃O₄-PAA. Both the decomposition of the TETA small molecules and PAA polymer contributes to the broad endothermic peak in the DSC curve of Fe₃O₄-PAA-NH₂ (Fig. 3(D)).

Fig. 3(E)&(F) show the deconvolution of the high-resolution C1s XPS spectra of Fe₃O₄-PAA and Fe₃O₄-PAA-NH₂, respectively. The C1s peak from Fe₃O₄-PAA is deconvoluted into three major components with peaks at 284.9, 285.6 and 289.0 eV, which are attributed to the –CH₂=, –CH, and –C=O of the PAA polymer backbone, respectively, as shown in Fig. 3(E).²⁸ However, the C1s spectrum of Fe₃O₄-PAA-NH₂ is distinct from that of Fe₃O₄-PAA, in which four curves is properly fitted (Fig. 3(F)). The first peak, located at 285.0 eV, is attributed to the aliphatic carbon of –CH₂=–. The higher binding energy of 286.1 arises from the C–C of PAA and TETA. The binding energy peak located at 289.1 eV is due to the carboxylate carbon (–COO⁻). Most importantly, the characteristic peak of amide (–CONH–) appears at 287.0 eV.²⁹ These results indicate the successful fabrication of amino-functionalized Fe₃O₄-PAA nanocomposites. The amine content is determined to be 3.925 mg g⁻¹ from the acid–base titrimetric analysis.

Fig. 4 shows the magnetization curves of the as-received Fe₃O₄ nanoparticles and Fe₃O₄-PAA-NH₂ at room temperature. Both samples show no hysteresis loop in their magnetization curve. This means that the coercivity ($H_c$) is zero Oe, which indicates a superparamagnetic behavior.³⁰ The magnetization of neither sample reaches saturation in the measured magnetic field range. Therefore, the saturation magnetization ($M_s$) is determined from the extrapolated $M_s$ obtained from the intercept of $M$ ~ $H$ at high magnetic field.²¹ The $M_s$ of the as-received Fe₃O₄ NPs is 54.47 emu g⁻¹, which is smaller than that of the bulk Fe₃O₄ (92 emu g⁻¹).²² The obtained $M_s$ value of Fe₃O₄-PAA-NH₂ is 47.71 emu g⁻¹. This value is sufficient for the immediate recycling of Fe₃O₄-PAA-NH₂ from a solution using a permanent magnet, as shown in the inset of Fig. 4. This is an essential factor in the separation and reuse of magnetic Fe₃O₄-PAA-NH₂ for the purification of water.²³ The weight percentage of Fe₃O₄ in the synthesized Fe₃O₄-PAA-NH₂, estimated from the $M_s$ value, is found to be around 87.0%, which is consistent with the TGA result (86.8%).

### 3.2. Evaluation of Cr(Ⅵ) removal by Fe₃O₄-PAA-NH₂ nanoadsorbent

Fig. 5(a) shows the Cr(Ⅵ) removal percentage and removal capacity from the solutions with different initial Cr(Ⅵ) concentrations at pH of 3.0 after treatment with Fe₃O₄-PAA-NH₂ for 10 min. The synthesized Fe₃O₄-PAA-NH₂ with a weight of 30.0 mg is observed to be able to treat a 20.0 mL solution with an initial Cr(Ⅵ) concentration of 1.3 mg L⁻¹ for 100% Cr(Ⅵ) removal, which achieves the limitation of the US EPA requirement. After further increasing the initial Cr(Ⅵ) concentration, the Cr(Ⅵ) removal percentage of Fe₃O₄-PAA-NH₂ decreases to 54.3% for a solution with an initial Cr(Ⅵ) concentration of 7.5 mg L⁻¹. In contrast, the Cr(Ⅵ) removal capacity increases from 0.88 to 3.31 mg g⁻¹ for solutions with an initial Cr(Ⅵ) concentration changing from 1.3 to 6.5 mg L⁻¹, and then decreases to 2.70 mg g⁻¹ for solutions with an initial Cr(Ⅵ) concentration of 7.5 mg L⁻¹. Normally, the active sites of the amine-functionalized nanoadsorbent result from the chelation between the heavy metals and the amine functional groups.³⁴ As the gradual saturation of these active sites occurs at high Cr(Ⅵ) concentrations, the Fe₃O₄-PAA-NH₂ cannot accommodate the excess Cr(Ⅵ), leading to the decreased Cr(Ⅵ) removal percentage and removal capacity as the initial Cr(Ⅵ) concentration increases to 7.5 mg L⁻¹. A similar result is also observed with carboxyl
group-functionalized multi-walled carbon nanotubes (MWNTs).  

Fig. 5(b) shows the Cr(\text{VI}) removal percentage and removal capacity with different Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} doses in a 20.0 mL Cr(\text{VI}) solution with an initial Cr(\text{VI}) concentration of 7.5 mg L\textsuperscript{-1} and pH of 3.0 after 10 min contact time at room temperature. Both the Cr(\text{VI}) removal percentage and removal capacity are observed to increase with increasing Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} dose due to the increased active sites and amine groups for trapping Cr(\text{VI}). The Cr(\text{VI}) removal percentage increases from 21.8% for a Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} dose of 0.25 g L\textsuperscript{-1} to 90.2% for a Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} dose of 4 g L\textsuperscript{-1}. Meanwhile, the Cr(\text{VI}) removal capacity increases from 0.36 mg g\textsuperscript{-1} for a Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} dose of 0.25 g L\textsuperscript{-1} to 24.0 mg g\textsuperscript{-1} for a Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} dose of 4 g L\textsuperscript{-1}.

Fig. 5(c) shows the Cr(\text{VI}) removal percentage for the solutions with an initial Cr(\text{VI}) concentration of 5.4 mg L\textsuperscript{-1} and different pH values after treatment with the Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} nanoadsorbent for 10 min at room temperature. The Cr(\text{VI}) removal percentage by Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} is observed to be strongly dependent on the pH value of the solution. The Cr(\text{VI}) removal percentage increases from 61.1% for pH = 1.0 solution to 77.4% for pH = 2.0 solution and sharply decreases with increasing solution pH. The Cr(\text{VI}) removal percentages for pH = 3.0, 5.0, and 7.0 are 72.0, 41.6 and 27.3%, respectively. As solution pH increases to 9.0, 10.0, and 11.0, the Cr(\text{VI}) removal percentages are only around 5.9, 4.0, and 6.8%, respectively.

These results demonstrate that the amine-functionalized Fe\textsubscript{3}O\textsubscript{4} nanoadsorbent is not sufficient for the Cr(\text{VI}) removal if the pH of the solution is higher than 5, especially for the basic solution. Normally, the pH-dependent heavy metal removal performance is associated with both the metal chemistry in the solution and the type of adsorbent. As one of the heavy metals, the existence of Cr(\text{VI}) in solution is complicated and there are several species of Cr(\text{VI}) present in solutions with the different pH values. Generally, H\textsubscript{2}CrO\textsubscript{4} is a strong acid, which can be ionized in aqueous solution as shown in eqn (5) and (6).

H\textsubscript{2}CrO\textsubscript{4} \rightleftharpoons H\textsuperscript{+} + HCrO\textsubscript{4}\textsuperscript{-} , \textit{K}_7 = 10^{-0.75} \tag{5}

HCrO\textsubscript{4}^{-} \rightleftharpoons H\textsuperscript{+} + CrO\textsubscript{4}^{2-} , \textit{K}_8 = 10^{-6.45} \tag{6}

In the pH < 2 solution, both H\textsubscript{2}CrO\textsubscript{4} and HCrO\textsubscript{4}^{-} are present in the solution; in the pH range from 2 to 4, HCrO\textsubscript{4}^{-} is the predominant form in the solution; when the pH of the solution is higher than 4, CrO\textsubscript{4}^{2-} starts to appear and its content increases with increasing solution pH. When the pH of the solution is above 9, HCrO\textsubscript{4}^{-} disappears, leaving only CrO\textsubscript{4}^{2-} in the solution. The Cr(\text{VI}) removal performance of the amine-functionalized nanoadsorbent is strongly related to the existence of these different forms of Cr(\text{VI}). The obtained results from Fig. 5(c) indicate that the amine group prefers to chelate with HCrO\textsubscript{4}^{-} ions in the solution rather than to chelate with H\textsubscript{2}CrO\textsubscript{4} and CrO\textsubscript{4}^{2-}. Therefore, Fe\textsubscript{3}O\textsubscript{4}-PAA-NH\textsubscript{2} delivers a good
Cr(VI) removal performance within the pH range of 2–3 and a poor performance at pH > 5. The proposed Cr(VI) removal mechanism is illustrated in Scheme 2. These results are consistent with the mechanism reported by Mohan et al. They confirmed that the Cr(VI) adsorption on aminated polyacrylonitrile fibers was affected by both the electrostatic attraction and surface complexation at low solution pH values (around pH of 3.0). Mayer-Gall et al. also reported that the amino groups are easily protonated to form the ammonium salts in the acidic solution, which could adsorb the negatively charged chromate ion.

Fig. 5(d) illustrates the Cr(VI) removal percentage in a solution with an initial Cr(VI) concentration of 1.0 mg L⁻¹ after treatment with the as-received Fe₃O₄ nanoparticles, Fe₃O₄-PAA, and Fe₃O₄-PAA-NH₂ (10.0 mg) for 5 min for comparison. The as-received Fe₃O₄ nanoparticles only exhibit Cr(VI) removal from the aqueous solution with a low removal percentage of 14.9%, which is lower than that of a previous report (around 22%). Fe₃O₄-PAA also shows a poor Cr(VI) removal percentage of 15.7%. In contrast, the synthesized Fe₃O₄-PAA-NH₂ exhibits a Cr(VI) removal percentage of 55.8%, which is almost 4 times higher than the as-received Fe₃O₄ nanoparticles and the prepared Fe₃O₄-PAA. As previously mentioned, the BET results show that the average specific surface areas for the as-received Fe₃O₄ nanoparticles, Fe₃O₄-PAA, and Fe₃O₄-PAA-NH₂ are 81.4216, 61.6277, and 69.9001 m² g⁻¹, respectively. Even though the specific surface area decreases for the Fe₃O₄ nanoparticles after amino functionalization, the Cr(VI) removal percentage is increased. These results demonstrate that the amine group plays an important role in the Cr(VI) removal from the polluted water system. This further confirms the significance of the functional groups on the adsorbent for water treatment. A 1 mol L⁻¹ HCl solution is used to measure the stability of the as-received Fe₃O₄ nanoparticles and synthesized Fe₃O₄-PAA-NH₂ in acidic solution. The obtained results are shown in the inset of Fig. 5(d). After immersion in the acidic solution for 1 h, the as-received Fe₃O₄ nanoparticles are observed to be dissolved in the acid solution with the formation of a light yellow-green color. However, the Fe₃O₄-PAA-NH₂ is still at the bottom of the solution and the color of the solution is still clear without any changes. These results confirm that the amine-functionalized Fe₃O₄-PAA nanoadsorbent is more stable in acid solution than the as-received Fe₃O₄ nanoparticles.

From an economic and practical point of view, the regeneration and reusability was investigated in this work. After treating a Cr(VI) solution, the Fe₃O₄-PAA-NH₂ was placed into deionized water and sonicated for 15 min for desorption at room temperature. The regenerated Fe₃O₄-PAA-NH₂ was used to treat an initial Cr(VI) concentration of 5.0 mg L⁻¹ (20 mL) for 15 min. The adsorption–desorption process was conducted for 5 cycles and the obtained adsorption capacity is depicted in Fig. 6. It is observed that the adsorption capacity of Fe₃O₄-PAA-NH₂ still remains around 85% after 5 cycles, exhibiting relatively good reusability and stability. This indicates that the synthesized Fe₃O₄-PAA-NH₂ can be used as a reversible efficient nanoadsorbent for practical wastewater treatment.

3.3. Cr(VI) adsorption isotherm of Fe₃O₄-PAA-NH₂ nanoadsorbent

The adsorption isotherm can describe the adsorption equilibrium of adsorbate at the surface of an adsorbent. The adsorption equilibrium models can provide some insights into the adsorption mechanism, the surface properties and the affinity of the adsorbent. Two commonly used isotherm models, namely the Langmuir and Freundlich isotherm models, can explain solid–liquid adsorption systems. The Langmuir model is often used to describe monomolecular layer adsorption, which assumes uniform distribution of adsorbent energy on the surface and no migration of adsorbate in the plane of surface. The Langmuir model is expressed as eqn (7):

\[
q_e = \frac{a b C_e}{1 + b C_e}
\]

where \( C_e \) is the equilibrium concentration (mg L⁻¹ of Cr(VI)), \( q_e \) is the amount of adsorbed Cr(VI) at equilibrium (mg g⁻¹), and \( a \) (mg g⁻¹) and \( b \) (L mg⁻¹) are Langmuir isotherm parameters. The Freundlich model is an empirical equation, which focuses on the adsorption on an energetically heterogeneous surface.

![Scheme 2 Proposed adsorption of Cr(VI) species on Fe₃O₄-PAA-NH₂ in the pH 2–4 solution.](image)

![Fig. 6 Cr(VI) adsorption capacity of the regenerated Fe₃O₄-PAA-NH₂ in a 20 mL solution with an initial Cr(VI) concentration of 5.0 mg L⁻¹ and a contact time of 15 min.](chart)
The expression of the Freundlich model is given as eqn (8), which provides the relationship between the adsorbed concentration and the solute concentration:

$$q_e = k_f C_e^n$$  (8)

where $k_f$ is the Freundlich equilibrium constant, indicating the extent of adsorption, and $n$ is the power term of the Freundlich isotherm and the heterogeneity factor, illustrating the intensity of the adsorption.\(^{43}\)

In order to study the adsorption equilibrium of Cr(VI) at the surface of the nanoadsorbent, the synthesized Fe$_3$O$_4$-PAA-NH$_2$ (20.0 mg) was used to treat different initial Cr(VI) concentrations varying from 0.5 to 4.5 mg L$^{-1}$ with a contact time of 15 min at room temperature. Both Langmuir and Freundlich isotherm models are used to fit the Cr(VI) adsorption equilibrium process of Fe$_3$O$_4$-PAA-NH$_2$. The obtained results are shown in Fig. 7 and the fitting parameters are listed in Table 1. According to the correlation coefficient values, the Freundlich isotherm model ($R^2 = 0.976$) is observed to be well-fitted for the Cr(VI) adsorption by Fe$_3$O$_4$-PAA-NH$_2$, demonstrating a multilayer adsorption mechanism. However, the correlation coefficient values for these two models only show a little difference for the Cr(VI) removal adsorption ($R^2 = 0.960$ for the Langmuir model). The maximum Cr(VI) adsorption capacity by Fe$_3$O$_4$-PAA-NH$_2$ obtained from parameter $a$ of the Langmuir model is 9.791 mg g$^{-1}$, which is higher than those of activated carbon (around 1.1-9.5 mg g$^{-1}$)\(^{38}\) and chitosan flakes (around 5.246-7.943 mg g$^{-1}$)\(^{44}\) and lower than those of magnetic carbon nanocomposites prepared from Fe(NO$_3$)$_3$/cellulose (15.3 mg g$^{-1}$)\(^{45}\), chitosan-coated gauze containing amino groups (12.4 mg g$^{-1}$)\(^{46}\) and chitosan/poly(vinyl alcohol) containing cerium(III) (52.8 mg g$^{-1}$)\(^{47}\).

### 3.4. Cr(VI) removal kinetics of Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent

The adsorption kinetics are one of the important parameters to describe the Cr(VI) uptake rate and control of the residue time of the adsorbent at the solid-solution interface, from which the efficiency of the Cr(VI) adsorption by the nanoadsorbent can be determined.\(^{48}\) Therefore, the Cr(VI) removal kinetics are investigated to understand the adsorption behavior of Cr(VI) by the prepared Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent. The amount of adsorbed Cr(VI) ($q_t$, mg g$^{-1}$) at time $t$ is calculated using eqn (9):

$$q_t = \frac{(C_0 - C_t)V}{m}$$  (9)

where $C_0$ is the initial Cr(VI) concentration (mg L$^{-1}$) and $C_t$ represents the Cr(VI) concentration in mg L$^{-1}$ at time $t$ (min). The calculated $q_t$ in solution with pH = 2.5 after treatment with Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent for different contact times (3, 5, 7, 12, and 18 min) is depicted in Fig. 8. It is observed that the $q_t$ increases until contact time reaches to 12 min and then become flat after the contact time increases further to 18 min. This indicates that the adsorption of Cr(VI) by the Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent gradually becomes saturated as time increases to 18 min.\(^{49}\) An appropriate kinetic model is required to quantify the changes in adsorbed Cr(VI) with time. Hence, the pseudo-second-order adsorption kinetic model is introduced to describe the Cr(VI) adsorption behavior by the Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent, which is expressed by eqn (10):\(^{50}\)

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  (10)

where $k_2$ is the pseudo-second-order adsorption rate constant (mg g$^{-1}$ min$^{-1}$), and $q_e$ stands for the adsorption capacity at equilibrium time (mg g$^{-1}$). If the pseudo-second-order adsorption kinetic model is suitable for this system, the plot of $t/q_t \sim t$ is supposed to give a linear line, and the $q_e$ and $k_2$ can be calculated from the slope coefficient (1/$q_e$) and intercept (1/$k_2q_e^2$) of the plot. The obtained corresponding kinetic plot is also shown in Fig. 8. A good linear fit of the $t/q_t \sim t$ plot is observed with a fitting correlation coefficient $R^2$ of 0.9996. This means that the Cr(VI) adsorption kinetics of the Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent obey pseudo-second-order adsorption behavior. The obtained equilibrium adsorption capacity of $q_e$ is 4.27 mg g$^{-1}$ at the initial Cr(VI) concentration of 7.0 mg L$^{-1}$, which is consistent with the calculated $q_e$ at 18 min of 4.22 mg g$^{-1}$ (Fig. 8). The adsorption rate constant $k_2$ is calculated to be 1.23 g mg$^{-1}$ min$^{-1}$, which is higher than that of chitosan/naoclloyd nanocomposites (8.763 x 10$^{-4}$ g mg$^{-1}$ min$^{-1}$).\(^{31}\) The initial adsorption rate $h$ (mg g$^{-1}$ min$^{-1}$) at time $t$ approaching zero is defined as eqn (11):\(^{52}\)

$$h = k_2q_e^2$$  (11)

The calculated results show that the prepared Fe$_3$O$_4$-PAA-NH$_2$ nanoadsorbent exhibits an initial adsorption rate of 22.51 mg g$^{-1}$ min$^{-1}$, which is much higher than those of magnetic graphene material (0.28 mg g$^{-1}$ min$^{-1}$)\(^{30}\) and magnetic polypropylene nanocomposites (0.229 mg g$^{-1}$ min$^{-1}$).\(^{8}\)

### 3.5. Effect of multiple metals on the adsorption of Cr(VI)

Normally, many different kinds of toxic heavy metals coexist in polluted water systems\(^{33}\) and the investigation of the effect of...
these multiple metal ions on the adsorption of Cr(vi) is most important since the other heavy metal ions may possess the active sites of the adsorbent and compete with each other for the adsorption sites. Meanwhile, the presence of other metals, such as K, Ca, Na, and Mg, may also influence the adsorption process. In this work, the competition adsorption of multiple heavy metals, including Zn(II), Cd(II), and Cu(II), in the solution with equal initial heavy metal concentration is explored and the effect of the presence of K, Ca, Na and Mg is also investigated.

The obtained results are shown in Fig. 9. For the solution with Cr(vi), the Cr(vi) removal percentage is around 72%. However, for the bi-metal solutions consisting of Cr(vi) with Zn(II), Cr(vi) with Cd(II), and Cr(vi) with Cu(II), the Cr(vi) removal percentages are 84.1, 85.2 and 82.6%, respectively. For the tri-metal solutions composed of Cr(vi) with Cu(II)&Zn(II), Cr(vi) with Cu(II)&Cd(II), and Cr(vi) with Cd(II)&Zn(II), the Cr(vi) removal percentages are 82.4, 80.1, and 85.6%, respectively. For the tetra-metal solution of Cr(vi), Cu(II), Zn(II), and Cd(II), the Cr(vi) removal percentage is found to be 84.2%. These results indicate that after introduction of multiple heavy metal ions, such as Cu(II), Zn(II), and Cd(II), into the solution, the Cr(vi) removal performance is increased. The presence of Cu(II), Zn(II), and Cd(II) favors the Cr(vi) adsorption by the fabricated Fe₃O₄-PAA-NH₂. The heavy metal Cd(II) is suggested to have greater effect on the Cr(vi) removal performance than the heavy metals Zn(II) and Cu(II). Similar results are also reported by Ghorbel-Abid et al. They found that Cd(II) could significantly increase the adsorption capacity for Cr(vi) arising from the affinity of the chemical properties of each element (such as chemical potential, electronegativity, etc.). For the solution consisting of Cr(vi), K(I), Ca(II), Na(I), and Mg(II), the Cr(vi) removal percentage is 60.7%. However, the Cr(vi) removal percentage is increased to 93.9% for the solution containing eight metal ions.

### 4. Conclusions

In this study, the ability of a magnetic amine-functionalized Fe₃O₄-PAA-NH₂ nanoadsorbent synthesized using the SIP method to remove Cr(vi) from polluted water is evaluated. Even though the average specific surface area of Fe₃O₄-PAA-NH₂ is lower than that of as-received Fe₃O₄ nanoparticles, as shown by the BET results, the Cr(vi) removal percentage of Fe₃O₄-PAA-NH₂ is almost 4 times higher than that of the as-received Fe₃O₄ nanoparticles due to the presence of amine groups on the surface of Fe₃O₄-PAA-NH₂. 30 mg of the Fe₃O₄-PAA-NH₂ nanoadsorbent is able to completely remove Cr(vi) from a 20.0 mL solution with initial Cr(vi) concentration of 1.32 mg L⁻¹ after 10 min contact time, which can satisfy the limitation of the US EPA requirement. The Fe₃O₄-PAA-NH₂ dose of 4 g L⁻¹ could remove 90.2% of Cr(vi) from a 20.0 mL 7.5 mg L⁻¹ Cr(vi) solution with pH of 3.0. The Cr(vi) removal percentage of the Fe₃O₄-PAA-NH₂ nanoadsorbent is observed to highly depend on the pH value of the solution and the optimal pH value for Cr(vi) removal is found in the solution with pH of 2.0. The Cr(vi) adsorption isotherm is fitted to the Freundlich isotherm model. The Cr(vi) removal kinetics of the Fe₃O₄-PAA-NH₂ nanoadsorbent obeys pseudo-second-order behavior and the calculated room temperature rate constant is 1.23 g mg⁻¹ min⁻¹ for the solution.

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**Table 1** Langmuir and Freundlich adsorption isotherm parameters

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**Fig. 8** Cr(vi) removal rate qₜ vs. t for 30.0 mg Fe₃O₄-PAA-NH₂ after treatment with 20.0 mL Cr(vi) solution (7.0 mg L⁻¹) under different contact times at room temperature (square line), and corresponding kinetic plot (triangle line).

**Fig. 9** Cr(vi) removal percentage in the multi-metal solutions including Cr(vi), Cu(II), Zn(II), Cd(II), K(I), Ca(II), Na(I), and Mg(II) with an equal initial concentration of 5.0 mg L⁻¹ and pH of 3.0 after treatment for 10 min with 30 mg Fe₃O₄-PAA-NH₂.
with an initial Cr(vi) concentration of 7.0 mg L$^{-1}$ and pH value of 2.5. The presence of other metals, including Cu(II), Zn(II), Cd(II), K(I), Na(I), and Mg(II), in polluted water is beneficial for the Cr(vi) adsorption by the Fe$_{3}$O$_{4}$-PAA-NH$_{2}$ nanoadsorbent. Meanwhile, the prepared Fe$_{3}$O$_{4}$-PAA-NH$_{2}$ nanoadsorbent can prevent acid etching of the Fe$_{3}$O$_{4}$ nanoparticles and be easily recycled from water using a permanent magnet for reuse. The prepared Fe$_{3}$O$_{4}$-PAA-NH$_{2}$ nanoadsorbent still retains around 85% of Cr(vi) adsorption performance even after 5 cycles.

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