Poly(amidoamine) dendrimer modified superparamagnetic nanoparticles as an efficient adsorbent for Cr(VI) removal: Effect of high-generation dendrimer on adsorption performance

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Poly(amidoamine) dendrimer modified superparamagnetic nanoparticles as an efficient adsorbent for Cr(VI) removal:

Effect of high-generation dendrimer on adsorption performance

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Abstract: Heavy metal ions pollution is one of the most dangerous and critical threats to human health and environment. In this work, three different generations of PAMAM dendrimer decorated on magnetic Fe₃O₄ composites (Fe₃O₄@SiO₂-G1, Fe₃O₄@SiO₂-G3, Fe₃O₄@SiO₂-G5) were fabricated and characterized by FTIR, XRD, TEM, and TGA. The obtained composites were used for Cr(VI) removal. Batch adsorption studies showed that the adsorption reached equilibrium within 60 min, and the optimal pH was 3.0. The result of adsorption kinetics was simulated by the pseudo-second-order model. The adsorption equilibrium isotherm was well fitted with the Langmuir adsorption model. Furthermore, thermodynamics calculations revealed that the adsorption process was endothermic and spontaneous. Importantly, adsorption capacity of Cr(VI) obey the sequence of Fe₃O₄@SiO₂-G1 < Fe₃O₄@SiO₂-G5 <

$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$, 3 generation of PAMAM (3G) is the optimal for adsorption capacity of Cr(VI). The maximum theoretical Cr(VI) adsorption capacity (q_m) of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ was 334.45 mg/g, and removal ration remained above 89.5% after five cycles of adsorption–desorption. Thus, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ is predicted to be an efficient adsorbent for the adsorption of Cr(VI) from aqueous solution, and the obtained results can help in the generation optimization during fabrication of dendrimer modified adsorbents.

Key words: Superparamagnetic Fe_3O_4 ; Poly(amidoamine) dendrimer; generation; adsorption; Cr(VI)

1 Introduction

Water contamination arises from heavy metal ions has attracted great attention due to its high toxicity, non-degradability, carcinogenicity, and ecological unbalance [1–3]. Of the heavy metals, chromium is widely used in the fields of electroplating, cement production, paper processing and textile industry [4]. Chromium ion is harmful to the environment and human health because of its biological build-up and tremendous toxicity. Cr(III) and Cr(VI) are the primary Cr ion states in aqueous solution. The latter is more toxic and carcinogenic [5]. Therefore, the development of low cost materials and effective techniques for the removal of Cr(VI) is imperative.

A various number of methods like chemical precipitation, oxidation–

reduction, ion exchange, electrodialysis, membrane filtration and adsorption have been employed to decontaminate Cr(VI) pollution [6–10]. Adsorption has been found out to serve as an efficient and economical technology for dealing with Cr (VI) due to its easy operation, low cost and environmentally friendly. To date, Numerous adsorbents including activated carbon [11], biological adsorbent [12], resins [13] and magnetic nanoparticles [14] have been extensively applied for Cr(VI) removal. Among these adsorbents, Fe_3O_4 nanoparticles is the most attractive adsorbent due to its large specific area, biocompatibility, cheap price, especially simply magnetic separation [15]. However, naked Fe_3O_4 nanoparticles are easy to be oxidized in air and aggregated in solution, that reduces their adsorption ability and selectivity for heavy metal ions. Surface-modified with functional groups is the most efficient method to overcome these disadvantages [16]. The surface of Fe_3O_4 nanoparticles is easy to be functionalized by amine groups [17], oxygen-containing groups (carboxyl, hydroxyl) [18] and sulfur-containing groups (sulfhydryl, sulfonic acid) [19]. The existence of these groups can improve the stability of Fe_3O_4 nanoparticles and prevent aggregation, in addition, functional groups can selectively adsorb specific heavy metal ions through complexation effect, electrostatic attraction or ion exchange, thus improving the adsorption selectivity and capacity. For instance, Alhokbany et al. prepared Schiff base polymer decorated magnetic Fe_3O_4 composite

(MPOP) for removing of Cd(II) and Hg(II) from aqueous solution, the interaction between N atom and metal ion dominated the adsorption of Cd(II) and Hg(II) [20]. Fu et al. fabricated magnetic Fe₃O₄-encapsulated C₃N₃S₃ polymer/reduced graphene oxide composite (rGO-poly(C₃N₃S₃)/Fe₃O₄) for aqueous Pb(II) and Hg(II) removal, adsorption mechanism in that Hg(II) preferentially binds to sulfur functional groups and Pb(II) tends to be adsorbed by nitrogen groups in poly(C₃N₃S₃) matrix [21].

Poly(amidoamine) dendrimers (PAMAM) are regarded as a kind of biopolymer, which are widely studied in many fields, such as drug delivery, gene therapy, ultrasensitive sensor, catalyst carrier and adsorption in wastewater treatment, because of their excellent biocompatibility, highly branched three-dimensional structure, lots of reactive terminal groups, and monodispersed molecular weight [22–24]. Tremendous amine groups located within their interior and their surface enable PAMAM to bind with heavy metal ions by complexation effect, ion exchange and electrostatic attraction [25]. Nevertheless, PAMAM dendrimers are easily soluble in aqueous media, which makes their separation/recovery difficult to recycle. So PAMAM dendrimer is usually anchored on support substances such as silica [26], graphene [27], and magnetic substance [28]. Furthermore, adsorption capacity is related to the dendrimer generation of PAMAM. Niu et al. found that the increase of adsorption capacity of Hg(II) and Ag(I)

with dendrimer generation ($2G > 1G > 0.5G$), which is attributed to high content of sulfur group that high generation dendrimer possess [29]. However, as we all known that with the increase of generation, the steric hindrance increases, and serious surface defects of PAMAM appeared, thus the adsorption capacity may be affected. To date, the influence of high-generation dendrimer of PAMAM on adsorption capacity for Cr(VI) has not been studied.

In this work, three different generations of PAMAM dendrimer were immobilized on magnetic Fe_3O_4 composites ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$) to combine the merits of the two components for the efficient removal of Cr(VI), and compared the adsorption capacity of Cr(VI) between the three different adsorbents. The effective factors on the adsorption capability such as adsorbent dosage, adsorption time, temperature, initial concentration and pH of sample solution were examined and optimized. In addition, the adsorption isotherms, adsorption kinetics, thermodynamic and reusability were investigated to evaluate the adsorption properties and adsorption mechanism.

2 Materials and Methods

2.1 Materials

Ferric chloride (FeCl_3), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), sodium hydroxide, 1,2-diaminoethane and methyl acrylate were purchased

from Sinopharm Chemical Reagent Co. Ltd., China. 3-aminopropyltrimethoxysilane (APTMS) was obtained from Shanghai Aladdin Bio-Chem Technology Co. Ltd., China. Potassium dichromate ($K_2Cr_2O_7$) was obtained from Sigma-Aldrich (St. Louis, MO, USA). All the chemicals were of analytical grade. 1,2-diaminoethane and methyl acrylate were distilled before use, and other reagents were used as received without further purification. Deionized water was used throughout the experiment.

2.2 Characterization

The synthetic materials were characterized by Fourier-transform infrared spectra (FTIR), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and Thermogravimetric analysis (TGA). FTIR spectra were obtained on a Perkin-Elmer spectrophotometer in the range from 4000 to 400 cm^{-1} . The crystalline structure of Fe_3O_4 , $Fe_3O_4@SiO_2-G1$, $Fe_3O_4@SiO_2-G3$ and $Fe_3O_4@SiO_2-G5$ were characterized by XRD (PANalytical Empyrean, Netherlands) with Cu Ka radiation ($k = 1.54178 \text{ \AA}$) at a scanning rate of 2° min^{-1} in the 2θ range from 4° to 70° . The particle size and morphology of nanocomposites were observed by TEM (JEM-2010 (HT)). The samples for TEM were prepared as follows: dilute solution of synthetic materials was dripped onto the carbon-coated copper grid and excess water was wicked off by filter paper. After drying naturally, the grid was observed by TEM. TGA measurements

were performed on Diamond TG/DTA 6300 (Perkin–Elmer USA) at a heating rate of $5^{\circ}\text{C min}^{-1}$ under nitrogen.

2.3 Preparation procedure

The synthetic route of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--G3}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--G5}$ is presented in Scheme 1. Briefly, APTMS coated Fe_3O_4 was synthesized according to the reported method [30]. About 3.0 g of APTMS coated Fe_3O_4 and 5.0 mL of methyl acrylate were dispersed in 80 mL methanol under N_2 . The suspension was reacted at room temperature for 72 h. The resulting particles were washed with methanol and then reacted with 10.0 mL 1,2–diaminoethane in 100 mL methanol at room temperature for another 72 h. After that, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--G1}$ was obtained after separation and the subsequent washed with ethanol. The Michael addition of Fe_3O_4 with methyl acrylate and amidation with 1,2–diaminoethane was repeated until the desired 3 generation of PAMAM dendrimer modified Fe_3O_4 ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--G3}$) and 5 generation of PAMAM dendrimer modified Fe_3O_4 ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--G5}$) were obtained.

2.4 Batch adsorption experiments

$\text{K}_2\text{Cr}_2\text{O}_7$ was dissolved with deionized water as a stock Cr (VI) solution (1000 mg/L). The Cr (VI) solution with different initial concentrations was prepared by dilution of the stock Cr (VI) standard solution with deionized water. The effects of five parameters on the adsorption of Cr(VI) by $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--G3}$ and

Fe₃O₄@SiO₂-G5 were studied. The range of the tested parameters was as follows: initial pH (3–10), adsorbent dosage (4–16 mg), adsorption time (10–150 min), temperature (293–308 K), and initial Cr(VI) concentration (10–120 mg/L). For a typical example, when measuring the effect of the adsorption time, 10 mg of adsorbent was added into a 150 ml stoppered conical flask containing 50 ml of 50 mg/L Cr(VI) solution, with an initial pH of 3.0, and shaking with 150 rpm at 303 K. After designated time periods (10, 15, 20, 30, 40, 60, 90, 120, 150 min), the Cr(VI) solution samples were collected by a 5 mL syringe and filtered immediately through a 0.45 µm microfiltration membrane. The concentration of Cr(VI) was determined by atomic absorption spectrophotometry (AAS, AA240FS-GTA120, USA). The pH was regulated by HCl (0.1 M) and NaOH (0.1 M). All experiments were carried out triplicate in order to effectively reduce the experimental error.

The difference between the initial concentration and the adsorption equilibrium concentration is allowed to evaluate the amount of metal ion adsorbed. The equilibrium adsorption capacity (q_e , mg/g) of the adsorbent towards Cr(VI) is calculated by Equation (1)

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

3 Results and discussion

3.1 Characterization of the adsorbents

FTIR spectra of Fe₃O₄, Fe₃O₄@SiO₂-G1, Fe₃O₄@SiO₂-G3 and

$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$ are presented in Fig. 1a. Both in the FTIR spectra of Fe_3O_4 and PAMAM dendrimer functionalized Fe_3O_4 composites, we all observed the absorption peak at 598 cm^{-1} due to the vibration of Fe–O. Compared with unmodified Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$ possessed absorption bands at 2925 cm^{-1} and 2853 cm^{-1} due to the vibration of the CH_2 group, absorption bands at 1632 cm^{-1} , 1518 cm^{-1} and 1429 cm^{-1} due to the vibration of –CO–NH– group, and at 1147 cm^{-1} belongs to Si–O–Si [31], which indicates the successful decoration of Fe_3O_4 with PAMAM.

The XRD patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$ are shown in Fig. 1b. The XRD of Fe_3O_4 shows the typical (220), (311), (400), (422), (511), and (440) crystal planes at 30.12° , 35.43° , 43.09° , 53.49° , 57.18° and 62.63° , respectively [19]. After decoration of Fe_3O_4 with different generations of PAMAM dendrimer, the characteristic peaks of the above crystal planes still exist and do not change the position and intensity, suggesting the crystal structure of Fe_3O_4 is not destroyed during the functionalization.

The grafted dendrimer content of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$ can be calculated from TGA. As shown in Fig. 1c, the first stage weight loss for water evaporation is observed in the range of $50\text{--}115^\circ\text{C}$, about 1.99%, 2.55% and 1.96% water loss for $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$, respectively. Then, the slight

weight loss from 115 to 230 °C can be observed due to the decomposition of silica. After that, a sharp decrease of the weight loss between 230 and 700 °C due to the decomposition of PAMAM dendrimer. The final mass losses are 4.9%, 12.1% and 24.3% for $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$, respectively, which imply that the modified organic matter percentage increases with generation of PAMAM dendrimer increases.

Particle size and morphology of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$, were determined by TEM. As shown in Fig. 2a, Fe_3O_4 are dispersed as homogeneously distributed individual NPs with well-defined spherical shapes that are around 6–8 nm in diameter. Fig. 2b shows the morphology of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$. Because PAMAM dendrimer do not significantly attenuate electron beams under TEM, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ are largely present as isolated clusters with a spherical shape, further indicating the successful encapsulation of Fe_3O_4 by PAMAM dendrimer.

3.2 Effect of solution pH for Cr (VI) removal

The solution pH has considerable effect on metal ion adsorption as it influences not only on the existing forms of heavy metal ion, but also the surface charge of an adsorbent. To investigate the optimal pH value for Cr(VI) removal, a series of experiments with different initial pH (3–10) was carried out. As presented in Fig. 3, With the solution pH increases from 3 to 10, the adsorption for Cr(VI) is gradually decreased for the three

adsorbents. This is attributed to the different forms of chromium in the aqueous solution at different pH value. When $\text{pH} > 6$, CrO_4^{2-} is the primary form, while $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- are predominant at $\text{pH} 2-6$ [32]. The maximum Cr(VI) adsorption capacity is obtained at $\text{pH} 3$, which is partly attributed to the strong electrostatic interactions between anions ($\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^-) and protonated imidazole N^+ in the three adsorbents (Fig. 4). When the solution pH is greater than 3, due to the deprotonation of N and an increase in the number of bivalent anions (CrO_4^{2-}), both enhance the electrostatic repulsion of the adsorbents and chromium ions, which decline the adsorption capacity for Cr(VI).

Furthermore, the adsorption capacity decreases by the sequence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3} > \text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5} > \text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, the adsorption capacity of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$ are stronger than that of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, which is attributed to lower content of amine groups that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$ possess. But interestingly we found that the adsorption capacity of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$ is relatively poor than that of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$, this may be due to excessively high generation not only causes the large sterically hindered, which hinders the contact of Cr(VI) with the amine groups located within the interior of PAMAM, but also causes serious surface defects of PAMAM, that decreasing amine groups on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$. The above result indicates that the affinity of the composites increase with dendrimer generation increases

only in low generation range, but excessively high generation of PAMAM is unfavourable for the adsorption. Above all, the optimal pH is 3.0, so pH 3.0 was selected for subsequent experiments. In addition, the removal of Cr(VI) is affected by generation of PAMAM dendrimer, 3 generation of PAMAM (3G) is the optimal for adsorption capacity of Cr(VI).

3.3 Effect of adsorbent dosage for Cr(VI) removal

The adsorption capacity of Cr(VI) varies with the adsorbent dosage. Fig. 5 shows the effect of the mass of adsorbent on the adsorption of Cr(VI). It is observed that the adsorption capacity decreases with the increase in the adsorbent dose, the adsorption capacity of Cr(VI) by $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ decreased from 438.75 to 155.16 mg/g with the dosage increased from 4 to 16 mg, this effect can be explained by the active sites of adsorbent were not be completely occupied by Cr(VI) at high dosages of adsorbent. To consider operation consumption, while also ensuring a high adsorption capacity, the optimal amount was 10.0 mg, and q_e was 239.75 mg/g.

3.4 Effect of temperature for Cr(VI) removal and thermodynamic study

The effect of temperature of Cr(VI) adsorption on adsorbent was investigated in the temperature range 293–308 K. As shown in Fig. 6a, it is noticed that an increase in temperature promotes an increase in the amount of Cr(VI) adsorbed by all adsorbents, which indicates that the adsorption process of Cr(VI) is endothermic. This is attributed to the

increment in the kinetic energy of the adsorbent molecules with the increment in temperature, the increased activated sites created on the adsorbents, and the increase in kinetic motion of Cr(VI).

The different thermodynamic parameters of adsorption can reflect its spontaneity, randomness, endothermicity or exothermicity. Thermodynamic parameters such as standard free enthalpy ΔG^0 is calculated with Equation (3), standard enthalpy ΔH^0 and standard entropy ΔS^0 are calculated from the slope and intercept of the plot of K_d versus $1/T$ (Fig. 6b) using Equation (4) .

$$K_d = \frac{aq_e}{C_e} \quad (2)$$

$$\Delta G^0 = -RT \ln K_d = \Delta H^0 - T \Delta S^0 \quad (3)$$

$$\ln K_d = \left(\frac{\Delta S^0}{R} \right) - \left(\frac{\Delta H^0}{R} \right) \frac{1}{T} \quad (4)$$

Where K_d is the distribution constant; a (g/L) is the adsorbent dose; q_e (mg/g) is the adsorption capacity at equilibrium; C_e (mg/L) is the concentration at equilibrium of adsorbate in solution; ΔG^0 (kJ/mol) is the standard Gibbs energy change; R (8.314 J/mol/K) is the ideal gas constant; T (K) is the absolute temperature; ΔH^0 (kJ/mol) is the standard enthalpy change, and ΔS^0 (J/mol/K) is the standard entropy change. The thermodynamic parameters of the adsorption at different temperatures are summarized in Table 1. ΔG^0 values are negative for adsorption of Cr(VI) onto the adsorbents. This demonstrates that the adsorption procedure is

spontaneous and thermodynamically practicable. Furthermore, the ΔG^0 values decreases as the temperature increases, demonstrating adsorption is more favorable at high temperature. Meanwhile the positive values of ΔS^0 indicate increased disorder at the adsorbate–adsorbent interface during adsorption of Cr(VI) on the adsorbent surface. Additionally, the values of ΔH^0 are positive, which suggest that the adsorption process on the surface is an endothermic process [33], and the ΔH^0 values of Fe₃O₄@SiO₂–G1, Fe₃O₄@SiO₂–G3 and Fe₃O₄@SiO₂–G5 is 37.06, 132.94 and 77.47 kJ/mol, respectively, indicating that interaction force between adsorbents and Cr(VI) increases by the sequence of Fe₃O₄@SiO₂–G1 < Fe₃O₄@SiO₂–G5 < Fe₃O₄@SiO₂–G3, which is consistent with the adsorption capacity results.

Table 1 Thermodynamic parameters for the adsorption of Cr(VI) on adsorbents at different temperatures.

Adsorbent	Gibbs free energy ΔG^0 (kJ/mol)				Enthalpy ΔH^0 (kJ/mol)	Entropy ΔS^0 (J/mol/K)
	293K	298K	303K	308K		
Fe ₃ O ₄ @SiO ₂ –G1	–0.215	–0.852	–1.488	–2.124	37.06	127.22
Fe ₃ O ₄ @SiO ₂ –G3	–3.619	–5.949	–8.279	–10.610	132.94	466.07
Fe ₃ O ₄ @SiO ₂ –G5	–3.169	–4.546	–5.922	–7.298	77.47	275.22

3.5 Kinetic studies on Cr(VI) removal

To investigate the adsorption rate of Cr(VI) on adsorbents and measure the adsorption equilibrium, the adsorption kinetics were studied.

The adsorption kinetic plots of the adsorbents for Cr(VI) are illustrated in Fig. 7a. The adsorption of the adsorbents proceeds speedily during 0–40 min. Then, it conducts relaxedly and approaches equilibrium at 60 min. The equilibrium adsorption capacity of Fe₃O₄@SiO₂–G1, Fe₃O₄@SiO₂–G3 and Fe₃O₄@SiO₂–G5 for Cr(VI) are 150.80, 240.55 and 227.55 mg/g, respectively. The sharp increase in the initial stage is mainly due to the presence of abundant active sites on adsorbents and high concentration of Cr(VI), which facilitate the contact of active adsorption sites with Cr(VI), leading to the rapid capture of Cr(VI) by the adsorbents [32]. When the adsorption time continued to extend, Cr(VI) concentration reduces, and the active adsorption sites of the adsorbent were largely occupied by Cr(VI), decreasing the contact opportunity and resulting in the decrease of adsorption rate until approach equilibrium. To ensure the system reached adsorption equilibrium, the contact time was set to 60 min in the following experiments.

To explore the adsorption mechanism, the experimental data were fitted by kinetic equations, and the correlation coefficients were obtained. The two equations represent the pseudo–first–order kinetic model and pseudo–second–order kinetic model, which can be described below in Equation (5) and (6) [34]:

Pseudo–first–order equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_e (mg/g) is the equilibrium adsorption amount of Cr(VI), q_t (mg/g) is the adsorption amount of Cr(VI) at time t (min), k_1 and k_2 are the equilibrium rate constant of pseudo-first-order adsorption and pseudo-second-order adsorption models, respectively.

The fitting curves and related parameters of the pseudo-first-order model and pseudo-second-order model are shown in Fig. 7b, 7c and Table 2. The adsorption kinetic for the three adsorbents fit Pseudo-second-order model well as indicated by the higher correlation coefficients (R^2). The calculated equilibrium adsorption capacity ($q_{e,cal}$) that derived from pseudo-second-order model is more in agreement with the experimental value ($q_{e,exp}$), further confirms the reasonable of describing the adsorption kinetic process of Cr(VI) by pseudo-second-order model, suggesting that the chemical interactions are possibly involved in the adsorption processes. In the current work, an occurrence of chemical adsorption for the adsorbent can be understood as the complexation effect of Cr(VI) with the amine groups on adsorbents (Fig. 4). Furthermore, the generation of PAMAM with no impact on the adsorption mechanism.

Table 2 Kinetics parameters for Cr(VI).

Adsorbent	$q_{e,exp}$ (mg/g)	pseudo-first-order			pseudo-second-order		
		$q_{e,cal}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg/min)	R^2
Fe ₃ O ₄ @SiO ₂ -G1	150.80	107.23	0.06337	0.790	166.39	0.00051	0.982
Fe ₃ O ₄ @SiO ₂ -G3	240.55	147.97	0.06236	0.870	256.41	0.00052	0.992
Fe ₃ O ₄ @SiO ₂ -G5	227.55	182.00	0.06237	0.902	244.50	0.00047	0.991

3.6 Effect of initial concentration for Cr(VI) removal and adsorption isotherms

The effect of the initial Cr(VI) concentration on the adsorption capacity of adsorbents for Cr(VI) was investigated. As shown in Fig. 8, with the increase of initial Cr(VI) concentration, the adsorption capacity of the three adsorbents gradually increase. The adsorption capacity of Fe₃O₄@SiO₂-G1, Fe₃O₄@SiO₂-G3 and Fe₃O₄@SiO₂-G5 are elevated from 39.4, 49.9 and 47.4 mg/g to 213.1, 331.8 and 312.6 mg/g when the initial concentration of Cr(VI) increases from 10 to 120 mg/L. The enhanced adsorption for Cr(VI) by the raising initial concentration is due to the high concentration gradient under high concentration, which promote the diffusion of Cr(VI) to the active sites of the adsorbent. Therefore, the removal for Cr(VI) by the adsorbent is increased.

Two adsorption isotherms (i.e., Langmuir and Freundlich model) were used to describe the equilibrium adsorption according to Equation (7) and (8) [35]:

Langmuir adsorption isotherm:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad (7)$$

Freundlich adsorption isotherm:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (8)$$

where q_e (mg/g) and C_e (mg/L) are the amounts of Cr(VI) absorbed on adsorbent and the Cr(VI) concentration at adsorption equilibrium, respectively. k_L (L/mg) is the Langmuir constant related to the energy of adsorption, q_m (mg/g) refers to the maximum adsorption capacity, k_F and n are constants for the Freundlich isotherm. The fitting curves and relative parameters of each model are shown in Fig. 9 and Table 3. Compared with Freundlich model, Langmuir model provides better correlation coefficients, indicating that the process tends to be homogeneous monolayer adsorption, and there is no interaction between active sites [29]. The maximum adsorption capacity (q_m) calculated by the Langmuir model are 245.10, 334.45, and 326.80 $\text{mg} \cdot \text{g}^{-1}$ for $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$, respectively, indicating the adsorption capacity of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ is better than that of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$, which is consistent with the obtained results above. The adsorption equilibrium constant k_L increases by the sequence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1} < \text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5} < \text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$, which means that the binding strength of adsorbents and Cr(VI) increase by the same sequence. In

addition, the $1/n$ values are all less than 1 computed by Freundlich model, revealing that the adsorption process proceeded easily. The comparison of q_m between previous reported adsorbents and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ are presented in Table 4. The results show that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ has an excellent adsorption capacity for Cr(VI) and is an effective adsorbent.

Table 3 Isotherm parameters for Cr(VI).

Adsorbent	Langmuir model			Freundlich model		
	q_m (mg/g)	k_L (L/mg)	R^2	k_F (mg/g)	$1/n$	R^2
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$	245.10	0.0819	0.9990	33.16	0.461	0.9510
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$	334.45	1.0034	0.9988	147.80	0.243	0.9520
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$	326.80	0.3214	0.9993	86.88	0.369	0.8534

Table 4 Comparison of q_m for Cr(VI) between the adsorbents.

Adsorbents	q_m (mg/g)	Ref
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$	334.45	This work
chitosan/ NiFe_2O_4 (CNF)	31.52	[14]
GO-DIL	260.92	[32]
ZFA-350	52.63	[33]
$\text{Fe}_3\text{O}_4\text{-FeB}$	38.9	[36]
Q-APEI	334.00	[37]
MBC/PPE	227.9	[38]
Co-Al-LDH/ Fe_2O_3 /3DPCNF	400.40	[39]
PPy/HMSNs	322	[40]
FSBC(1:1:1)	103.93	[41]

3.7 Reusability

Reusability is an important parameter property for evaluating the performance of the adsorbent. The adsorption/desorption process of Cr(VI) on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ was investigated using 0.5 mol/L NaOH solution as eluent. The reusability property was determined by considering five adsorption–desorption cycles. Fig. 10 shows that the Cr(VI) adsorption capacity of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ gradually decreased with the number of cycles, but not significantly. After five cycles of use, the removal ration of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ for Cr(VI) remained above 89.5%, indicating that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ has good stability and reusability.

4 Conclusions

In this work, three different generations of PAMAM dendrimer immobilized on magnetic Fe_3O_4 composites ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5}$) were successfully prepared and used to remove Cr(VI). The solution pH of 3.0 is favored for Cr(VI) removal. Adsorption approaches equilibrium at 60 min for all the adsorbents. The results of adsorption kinetics and isothermal studies indicate that the adsorption behavior conform to both the pseudo–second–order kinetic model (chemical interaction) and Langmuir isotherm model (homogeneous monolayer adsorption). Furthermore, the thermodynamics model demonstrates that adsorption is endothermic and spontaneous. More interestingly, we found that the uptake of Cr(VI) obey the sequence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G1} < \text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G5} < \text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$, indicating that

the affinity of the composites increases with dendrimer generation increases only in low generation range, but excessively high generation of PAMAM is unfavourable for the adsorption due to the large steric hindrance and serious surface defects of PAMAM. As-synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ exhibit competitive adsorption capacity (334.45 mg/g) for Cr(VI) than most alternative adsorbents. Regeneration suggests the removal ration of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ for Cr(VI) remained above 89.5% after five cycles of adsorption–desorption. This work shows that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ is an efficient and reusable adsorbent for the adsorption of Cr(VI) from aqueous solution, and the obtained results could be useful for the generation optimization during fabrication of dendrimer modified adsorbents.

Conflicts of interest

There are no conflicts to declare.

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Scheme 1 The synthetic procedures for adsorbents.

Fig. 1 The FTIR (a), XRD (b) and TGA (c) characterization.

Fig. 2 TEM micrographs of Fe₃O₄ nanoparticles (a) and Fe₃O₄@SiO₂-G3 (b).

Fig. 3 Effect of pH on adsorption capacity. ($C_0 = 50$ mg/L; adsorbent dosage = 10mg; $t = 60$ min; $T = 303$ K)

Fig. 4 Mechanism illustrating the removal of Cr(VI).

Fig. 5 Effect of adsorbent dosage on adsorption capacity. ($C_0 = 50$ mg/L; pH = 3.0; $t = 60$ min; $T = 303$ K)

Fig. 6 Effect of temperature on the adsorption capacity (a) and evolution of $\ln K_d$ as function of $1000/T$ (b). ($C_0 = 50$ mg/L; pH = 3.0; adsorbent dosage = 10mg; $t = 60$ min)

Fig. 7 Adsorption kinetics (a), pseudo-first-order fitting plots (b) and pseudo-second-order fitting plots (c) for Cr(VI). ($C_0 = 50$ mg/L; pH = 3.0; adsorbent dosage = 10 mg; $T = 303$ K)

Fig. 8 Effect of Cr(VI) initial concentration on adsorption capacity. (pH = 3.0; adsorbent dosage = 10 mg; $T = 303$ K; $t = 60$ min)

Fig. 9 Linearized form plot of Langmuir adsorption isotherm (a-c) and Freundlich adsorption isotherm (d-f) for the adsorption of Cr(VI).

Fig. 10 $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G3}$ continuous adsorption-desorption cycles to remove Cr(VI). ($C_0 = 50$ mg/L; pH = 3.0; adsorbent dosage = 10 mg; $T = 303$ K; $t = 60$ min)