



Cite this: *RSC Adv.*, 2019, 9, 9171

# Facile preparation of amidoxime-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -*g*-PAMAM-AO magnetic composites for enhanced adsorption of $\text{Pb}(\text{II})$ and $\text{Ni}(\text{II})$ from aqueous solution

Dai Yimin, \* Liu Danyang, Zou Jiaqi, Wang Shengyun and Zhou Yi

In this paper, using amidoxime as a functional monomer, different generations of polyamidoxime dendrimer magnetic microspheres ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -*g*-PAMAM-AO) were fabricated to adsorb  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  in aqueous solution. The magnetic adsorbents were characterized by FTIR, XRD, SEM, XPS, TEM, EDS, TGA and BET. The effects of different factors (such as solution pH, adsorption time, adsorption temperature, adsorbent dosage etc.) on adsorption were evaluated.  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -*g*-PAMAM-AO has a maximum  $\text{Pb}(\text{II})$  adsorption of  $157.25 \text{ mg g}^{-1}$  ( $100 \text{ mg L}^{-1}$ ) at pH 5.5. Furthermore,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -*g*-PAMAM-AO showed an excellent adsorption performance for the removal of  $\text{Ni}(\text{II})$  with a maximum adsorption capacity of  $191.78 \text{ mg g}^{-1}$  ( $100 \text{ mg L}^{-1}$ ) at pH 8.0. The sorption isotherm data fitted the Freundlich isotherm model well. Adsorption kinetics analysis showed that it was best described by the pseudo-second-order rate model. Desorption experiment results showed that the adsorbent can be reused in the adsorption–desorption cycles.

Received 7th January 2019

Accepted 2nd March 2019

DOI: 10.1039/c9ra00128j

rsc.li/rsc-advances

## 1. Introduction

Urbanization and industrialization are the biggest cause of toxic heavy metals in the environment, including groundwater, soils, rivers, lakes, and oceans.<sup>1–5</sup> The high toxicity and bio-accumulation of heavy metal ions such as Pb, Ni, Cr, As and Hg in aqueous solution can cause terrible hazards to people.<sup>6–10</sup>  $\text{Pb}(\text{II})$  and  $\text{Ni}(\text{II})$  are heavy metal ions that are toxic to the human body because  $\text{Pb}(\text{II})$ ,  $\text{Ni}(\text{II})$  and their compounds will cause harm to many systems such as the nerves, hematopoiesis, kidneys, the cardiovascular system and the endocrine system. When the content is high enough,  $\text{Pb}(\text{II})$  and  $\text{Ni}(\text{II})$  poisoning will be caused.<sup>11</sup> Hence, the removal of pollution before discharge into the environment is an urgent matter.

In the past few decades, various methods have been applied to remove heavy metal ions, such as ion exchange,<sup>12</sup> membrane processes,<sup>13</sup> and precipitation.<sup>14</sup> However, the efficiency and economic performance of the removal of heavy metal ions using these techniques are the main obstacles to their practical application. Compared with other methods, the adsorption method is a more attractive method which is cost-effective and highly efficient.<sup>15</sup>

It is well known that amidoxime-functionalized nano-materials have outstanding ability to remove heavy metal ions. The amidoxime-functionalized groups with  $-\text{NH}_2$  and  $-\text{OH}$  have

the ability of chelation, so the functional groups on the surface of the nanohybrids can form stable chelates with heavy metal ions.<sup>16</sup>

Because different dendrimers have different cavity sizes and end functional groups, target adsorbates can be selectively adsorbed by different kinds of dendrimers.<sup>17,18</sup> Ma *et al.* prepared  $\text{GO}/\text{Fe}_3\text{O}_4$ -*g*-PAMAM for the adsorption of  $\text{Pb}(\text{II})$  in aqueous solution. The adsorption capacity of  $\text{Pb}(\text{II})$  can be up to  $181.4 \text{ mg g}^{-1}$  at  $30^\circ\text{C}$ .<sup>19</sup> From their work, the adsorption by  $\text{GO}/\text{Fe}_3\text{O}_4$ -*g*-G(3.0) of  $\text{Pb}(\text{II})$  is obviously higher than that by  $\text{GO}/\text{Fe}_3\text{O}_4$ -*g*-PAMAM (G0.5, G1.0, G1.5, G2.0 and G2.5). It was illustrated that the adsorption capacity increased with the increasing generations of PAMAM. However, one disadvantage of  $\text{GO}/\text{Fe}_3\text{O}_4$ -*g*-PAMAM is that graphene oxide (GO) has carboxyl and hydroxyl groups, and it can disturb the reaction of maleic anhydride (MAH) and ethanediamine (EDA) and thus reduce the reaction efficiency. Furthermore, these techniques generally suffer from difficult manipulation and high cost as well as long separation time.

To compensate for these disadvantages, taking advantage of the combined benefits of amidoxime and dendrimer, maleic anhydride (MAH) and ethanediamine (EDA) were alternately and repeatedly used to synthesise different generations of dendrimers. Here, we report an amidoxime-functionalized  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -*g*-PAMAM-AO magnetic composite for the enhanced ability to adsorb  $\text{Pb}(\text{II})$  and  $\text{Ni}(\text{II})$  in aqueous solution. Amidoxime and PAMAM dendrimers grafted into the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  played an important role in preventing the oxidation of  $\text{Fe}_3\text{O}_4$ .<sup>20</sup> In addition, methyl acrylate (MA) and

School of Chemistry and Food Engineering, Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, Changsha University of Science and Technology, Changsha 410114, PR China. E-mail: yimindai@sohu.com



ethanediamine (EDA) were alternated and repeated to increase the generation of dendrimers from the  $\text{Fe}_3\text{O}_4$  surface. The adsorption capacity increased with the increasing generations of PAMAM. The adsorption characteristics of  $\text{Fe}_3\text{O}_4@SiO_2$ -g-PAMAM-AO nanoparticles towards  $\text{Pb(II)}$  and  $\text{Ni(II)}$ , and the sorption kinetics, sorption capability and regeneration were investigated.

## 2. Materials and methods

### 2.1 Materials

Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), and ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) were purchased from Xiyu Chemical Reagent Co., Ltd. Polyvinyl pyrrolidone (PVP), methyl acrylate, ethanol, methanol, ethylenediamine, potassium carbonate ( $\text{K}_2\text{CO}_3$ ), tetraethyl orthosilicate (TEOS), 3-chloropropyltrimethoxysilane (APTES), hydroxylamine hydrochloride ( $\text{NH}_2\text{-OH} \cdot \text{HCl}$ ), glutaraldehyde, and 4-aminobenzonitrile were purchased from Sinopharm Chemical Reagents Co., Ltd. Unless otherwise noted, all chemicals were reagent grade and used without further purification.

### 2.2 Preparation of $\text{Fe}_3\text{O}_4@SiO_2\text{-NH}_2$

The magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared by the coprecipitation method.<sup>21</sup> A mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  was reacted in distilled water, which was stirred vigorously at 30 °C for 30 minutes. Afterwards, NaOH was added dropwise to keep the pH at 7 and the mixture was continuously reacted for 30 min. Finally, 2 g of PVP was added to the mixture solution and reacted at 50 °C for 2 h; then the temperature was returned to 30 °C. The  $\text{Fe}_3\text{O}_4$  was filtered with distilled water and ethanol several times to wash it. The  $\text{Fe}_3\text{O}_4$  was dried at 60 °C for 24 h in a vacuum drying oven.

The modified Stöber method<sup>22</sup> is the classic method to synthesize  $\text{Fe}_3\text{O}_4@SiO_2$ . Firstly, 0.1 g of  $\text{Fe}_3\text{O}_4$  particles was added to a mixture of water, ethanol and  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . The ratio of ethanol and water was 4 : 1. Then, 1 ml of TEOS was added to the aqueous solution and kept under stirring at 30 °C for 6 h. The  $\text{Fe}_3\text{O}_4@SiO_2$  was collected by the method of magnetic separation. The product was washed several times with distilled water and ethanol and then dried at 60 °C for 24 h in a vacuum drying oven. Finally, the  $\text{Fe}_3\text{O}_4@SiO_2$  was further modified with APTES to obtain  $\text{Fe}_3\text{O}_4@SiO_2\text{-NH}_2$ . The  $\text{Fe}_3\text{O}_4@SiO_2$  was dissolved in a solution of ethanol and water. The ratio of ethanol and water was 4 : 1. The solution was stirred for 10 minutes and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and APTES were added gradually, and the solution was reacted at room temperature for 24 h.

### 2.3 Preparation of $\text{Fe}_3\text{O}_4@SiO_2$ -g-PAMAM

Firstly,  $\text{Fe}_3\text{O}_4@SiO_2\text{-NH}_2$  was added to methanol in a three-necked flask and ultrasonicated for 10 min. The solution was stirred at 35 °C for 24 h after adding methyl acrylate (MA). This target product was named  $\text{Fe}_3\text{O}_4@SiO_2$ -g-G0.5. Secondly, the intermediate product  $\text{Fe}_3\text{O}_4@SiO_2$ -g-G0.5 was added to methanol and ultrasonicated for 10 min. And then ethanediamine

(EDA) was added dropwise to the mixture and kept under mechanical stirring at 40 °C for 2 h. The target product was named  $\text{Fe}_3\text{O}_4@SiO_2$ -g-G1.0. In order to obtain more generations of dendrimers, methyl acrylate (MA) and ethanediamine (EDA) were reacted alternately with the nanocomposites twice, respectively. The products with more generation were prepared using 10% excess volume MA and EDA of the preceding reaction during every step reaction. This experience was reacted four steps and the product  $\text{Fe}_3\text{O}_4@SiO_2$ -g-G2.0 was obtained.

### 2.4 Preparation of $\text{Fe}_3\text{O}_4@SiO_2$ -g-PAMAM-AO

The target product  $\text{Fe}_3\text{O}_4@SiO_2$ -g-G2.0 microspheres were dispersed in a solution of glutaraldehyde and ethanol. The mixture was reacted and stirred continuously at 30 °C for 3 h. Then, the particles reacted with glutaraldehyde in an aqueous solution of 4-aminobenzonitrile and ethanol. The black solid was washed and separated after 3 h at 30 °C, and then  $\text{K}_2\text{CO}_3$  and  $\text{NH}_2\text{OH} \cdot \text{HCl}$  were added into an aqueous solution of distilled water and ethanol to react at 80 °C in a three-necked flask. The final  $\text{Fe}_3\text{O}_4@SiO_2$ -g-PAMAM-AO product was obtained. A schematic presentation of the synthesis process is shown in Fig. 1.

### 2.5 Characterization of $\text{Fe}_3\text{O}_4@SiO_2$ -g-PAMAM-AO nano hybrids

The morphology and elemental distribution of the nanoparticles were characterized by transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), and scanning electron microscopy (SEM). The X-ray diffraction (XRD) patterns of  $\text{Fe}_3\text{O}_4@SiO_2$ -g-PAMAM-AO were recorded by a Philips X'Pert Pro Super X-ray diffractometer with a  $\text{Cu K}\alpha$  source ( $k = 1.54178 \text{ \AA}$ ). Fourier transformed infrared (FT-IR) spectra were recorded on a Nicolet Magna-IR 750 spectrometer with KBr pellets at room temperature.

### 2.6 Adsorption experiments

$\text{Pb}(\text{NO}_3)_2$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in distilled water to prepare the solution of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$ . For the adsorption isotherm and adsorption thermodynamic experiments with

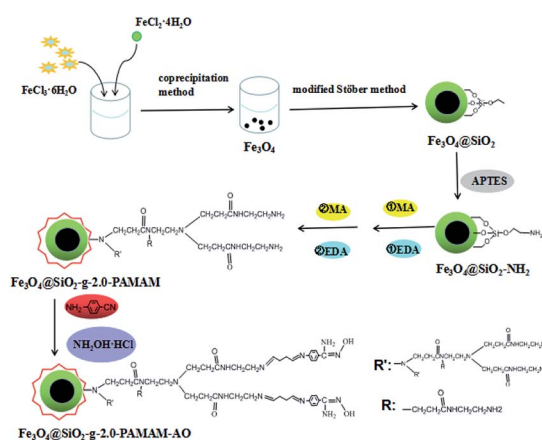


Fig. 1 A schematic presentation of the synthesis process.



$\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$ , 25 mg of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  were respectively added into solutions of different concentrations, which were 50, 100, 150, 200, 225, 250, 275 and 300  $\text{mg L}^{-1}$ . And then the mixture was reacted at 25 °C, 35 °C and 45 °C for 2 h. The above solutions were separated by a magnet and then analyzed by an atomic absorption spectrometer (AAS, AA-6800). To study the effect of pH on the adsorption reaction, 25 mg of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  was reacted with 50 ml of ionic solution (50  $\text{mg L}^{-1}$ ) at 25 °C for 2 h. 0.1  $\text{mol L}^{-1}$   $\text{HNO}_3$  and 0.1  $\text{mol L}^{-1}$   $\text{NaOH}$  were added to adjust the pH. In addition, to study the effect of contact time, the time ranged from 5 to 180 minutes. The  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  percentage removals (adsorption efficiency) were determined using eqn (1):<sup>23</sup>

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  concentrations and the equilibrium  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  concentrations, respectively.

The equilibrium sorption capacity was determined using eqn (2):<sup>24</sup>

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where  $q_e$  is the equilibrium amount of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  adsorbed per unit mass of adsorbent ( $\text{mg g}^{-1}$ ) and  $V$  is the sample volume (L). All experimental data were determined by repeated experiments.

## 2.7 Desorption experiment

To test the reusability and regenerability of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$ , 25 mg of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  was respectively added into solutions of  $\text{Pb}(\text{II})$  and  $\text{Ni}(\text{II})$  (50 ml, 50  $\text{mg L}^{-1}$ ). Then using  $\text{NaOH}$  to adjust the pH, the pH of  $\text{Pb}(\text{II})$  and  $\text{Ni}(\text{II})$  were 5.5 and 8.0, respectively. The desorption experiment was reacted at 30 °C for 2 h. After desorption, the mixture was collected in a conical flask. The  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  was washed with  $\text{HNO}_3$  and distilled water until the solution reached a pH of 7. To test the reusability of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$ , this was repeated using five-consecutive adsorption-desorption cycles.

# 3. Results and discussion

## 3.1 Characterization

Fig. 2 shows the FT-IR spectra of  $\text{Fe}_3\text{O}_4$  (a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-G2.0}$  (c),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM}$  (d) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  (e). The vibrating characterization at 575  $\text{cm}^{-1}$  was associated with the Fe–O stretching vibration (Fig. 2a). Two peaks of 1049  $\text{cm}^{-1}$  and 1091  $\text{cm}^{-1}$  are relevant to the stretching vibration of Si–O–Si, and the absorption peak at 463  $\text{cm}^{-1}$  corresponds to the O–Si–O bending vibration. All the evidence indicated that silica was successfully coated onto the surface of  $\text{Fe}_3\text{O}_4$ . In the spectrum of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (Fig. 2b), the absorption peak at 3424  $\text{cm}^{-1}$  is attributed to the H–O stretching vibration. A broad and strong peak at 3430  $\text{cm}^{-1}$  is related to the O–H stretching vibration. In addition, the peak at 3430  $\text{cm}^{-1}$  is related

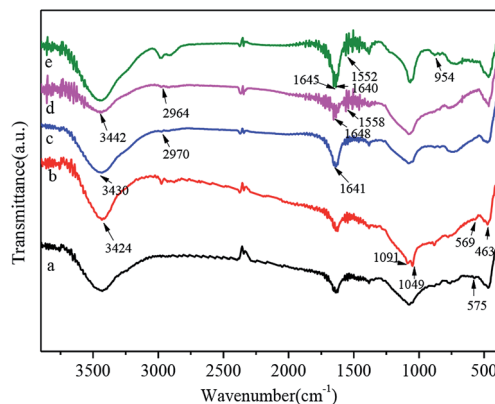


Fig. 2 FT-IR spectra of  $\text{Fe}_3\text{O}_4$  (a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-G2.0}$  (c),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM}$  (d),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  (e).

to the N–H stretching vibration of the  $-\text{NH}_2$  groups. The peak at 2970  $\text{cm}^{-1}$  corresponds to the  $-\text{CH}_2$  asymmetric stretching vibration. The characteristic band at 1641  $\text{cm}^{-1}$  is attributed to the secondary amide stretching of C=O, which indicated the existence of the acylamino group ( $-\text{NHCO}-$ ) in PAMAM (Fig. 2c). The peaks observed at 1558  $\text{cm}^{-1}$  and 1552  $\text{cm}^{-1}$  are ascribed to the C=C stretching vibrations of benzene. After modification with 4-aminobenzonitrile, the existence of new peaks at 2365  $\text{cm}^{-1}$  and 2344  $\text{cm}^{-1}$  is related to the stretching vibration of  $\text{C}\equiv\text{N}$  (Fig. 2d). The disappearance of the absorption bands of  $\text{C}\equiv\text{N}$  and the appearance of two new bands at 1640  $\text{cm}^{-1}$  and 954  $\text{cm}^{-1}$  are explained well by the C=N and N–O stretching vibrations of the amidoxime groups, respectively (Fig. 2e).

Fig. 3 shows the XRD patterns of  $\text{Fe}_3\text{O}_4$  (a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (c) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  (d). In Fig. 3a, the diffraction peaks in curve a at the bands (220), (311), (400), (422), (511) and (440) can be indexed as characteristic of  $\text{Fe}_3\text{O}_4$  with a face-centered cubic (fcc) phase (JCPDS no. 75-0033).<sup>25</sup> After coating with the silica layer, the diffraction peaks in curve b at 20–30° were observed, confirming the formation of silica. Moreover, the diffraction peaks of  $\text{Fe}_3\text{O}_4$  in Fig. 3b–d are very similar to Fig. 3a, indicating that the  $\text{Fe}_3\text{O}_4$  crystal structure did not change during the process of APTES and grafting by PAMAM.

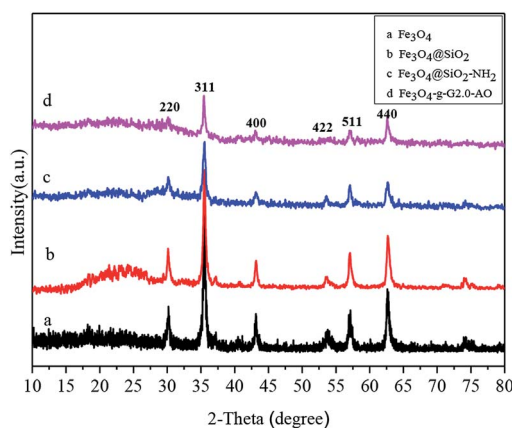


Fig. 3 The XRD pattern of  $\text{Fe}_3\text{O}_4$  (a),  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  (b),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  (c),  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  (d).



To better analyze the electronic structure and chemical composition, a fine-scan XPS of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  was performed. The high-resolution deconvoluted C 1s spectrum in Fig. 4a confirmed three different peaks at 284.6, 285.9 and 288.0 eV, respectively, representing the typical XPS characteristics of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$ . The binding energy peak at 284.6 eV is ascribed to the removal of the oxygen groups' carbon component of C-C ( $\text{sp}^2$ -hybridized); the peaks at 285.9, 288.0 eV represent C-O bonding, and O=C-N bonding, respectively. The bonding of -NHCO- is also indicative of the successful combination between the -COOH groups and the -NH<sub>2</sub> groups, demonstrating that PAMAM underwent a successful grafting reaction on the  $\text{Fe}_3\text{O}_4$  surface. The high-resolution spectrum of Fe 2p shown in Fig. 4b can be deconvoluted into two obviously different peaks at 724.4 and 711.2 eV, corresponding to Fe 2p<sub>1/2</sub> and Fe 2p<sub>3/2</sub>, respectively, which are in accordance with the reported values for  $\text{Fe}_3\text{O}_4$  (ref. 26 and 27). As shown in Fig. 4c, the binding energy peak appearing at 398.2 eV is ascribed to the quinoid imine (=N-) for  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-G2.0-AO}$ . The binding energy peaks appearing at 398.8 eV and 399.7 eV are related to -NH- and -NH<sub>2</sub>, respectively. The fine-scan XPS spectrum (Fig. 4d) of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-G2.0-AO}$  illustrates that  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  includes Fe, N, O, Si and C elements.

Fig. 5 shows the TEM, SEM, SAED and EDS images of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$ . From Fig. 5a, we can see that  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  has an obvious core-shell structure with a core of about 25 nm and a shell of about 10 nm. The HRTEM image (Fig. 5b) shows well-resolved lattice fringes with an interplane distance of 0.417 nm. The SAED pattern (Fig. 5c) shows that  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  is polycrystalline in nature, confirming that the nanoparticles have the magnetic cubic structure of the  $\text{Fe}_3\text{O}_4$  phase and consist of small nanocrystals. As can be seen from the SEM image (Fig. 5d), this product contains more sphere-like shapes and has a narrower size distribution. The EDS image (Fig. 5e) of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  suggests that Fe is the major constituent of

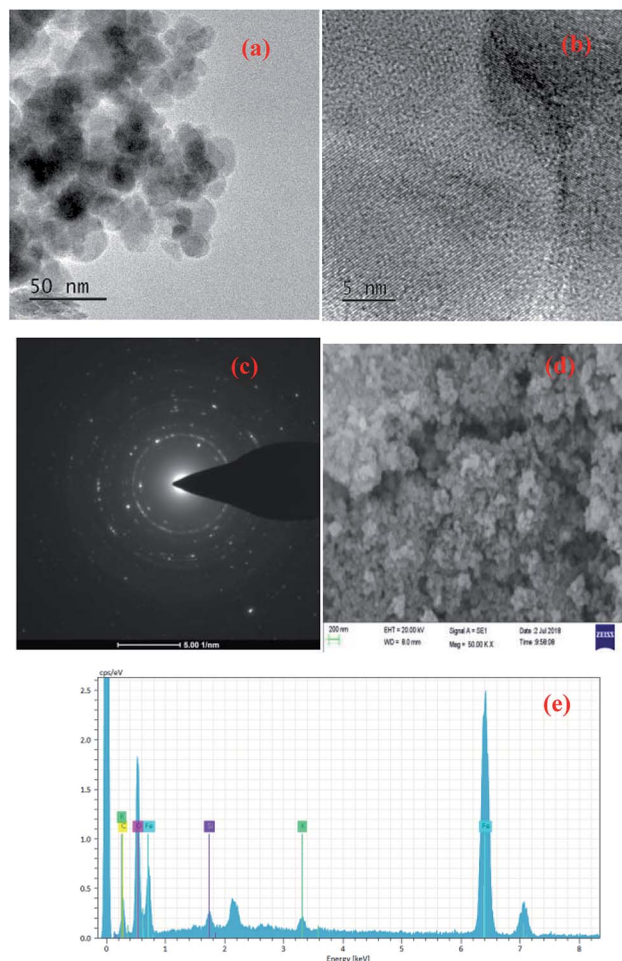


Fig. 5 The TEM of (a) sample  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  and the HRTEM image of (b) sample  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  and the SAED pattern of (c) sample  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  and the SEM of (d) sample  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  and the EDS of (e).

$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$ . Other elements are oxygen, carbon, silicon and potassium.

The TGA curve and DSC curve are shown in Fig. 6. In the TGA curve of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$  (Fig. 6a), the weight loss is divided into two distinct sections. In the first section, between

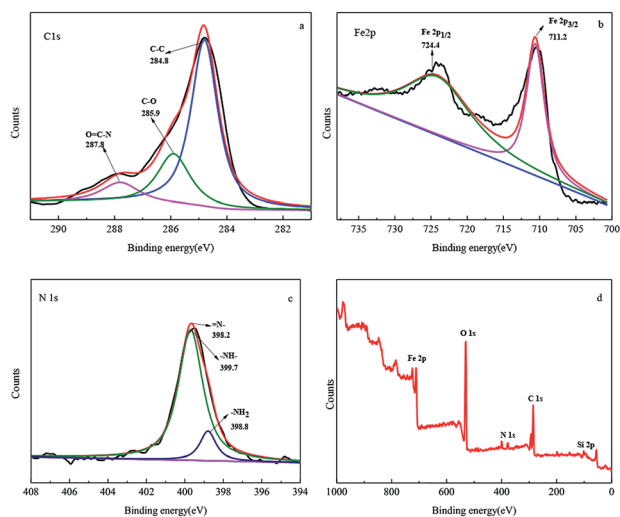


Fig. 4 The high-resolution scan XPS spectra of C 1s (a), Fe 2p (b), N 1s (c), and the survey scan XPS spectra (d) of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$ .

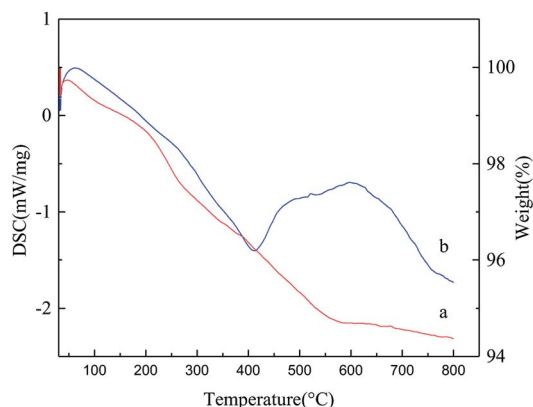


Fig. 6 Thermogravimetric analysis (TGA) curve (a) and differential scanning calorimetry (DSC) curve (b) of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-g-PAMAM-AO}$ .



32 °C and 200 °C, the weight loss of 1.08% is ascribed to the loss of bound water adsorbed on the microspheres. The second section of weight loss (close to 3.95%), at temperatures from 200 °C to 580 °C, was also indicative of the thermal decomposition of the surface amidoxime groups. The DSC curves recorded during the endothermic and exothermic processes of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO are shown in Fig. 6b. The first endothermic peak is less than 400 °C, accompanied by a significant mass loss on the TGA curve, which can be attributed to the oxidation of carbon on the silicon surface. The second endothermic peak between 400 °C and 700 °C was largely related to the pyrolysis of organic molecules on the shell surface.

The N<sub>2</sub> adsorption and desorption isotherm of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO is demonstrated in Fig. 7. From the BET results, the isotherm of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO accords with the IV adsorption isotherm, which illustrates that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO is a mesoporous structure. Furthermore, it is clear that the surface area is 73.493 m<sup>2</sup> g<sup>-1</sup>. This illustrates that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO has a large surface area.

Fig. 8 depicts the magnetization hysteresis loop of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO at room temperature. The saturation magnetization (SM) value of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO nanoparticles is 47.7 emu g<sup>-1</sup>. It is worth noting that the nanoparticles have no obvious coercivity and remanence in the magnetization curves,

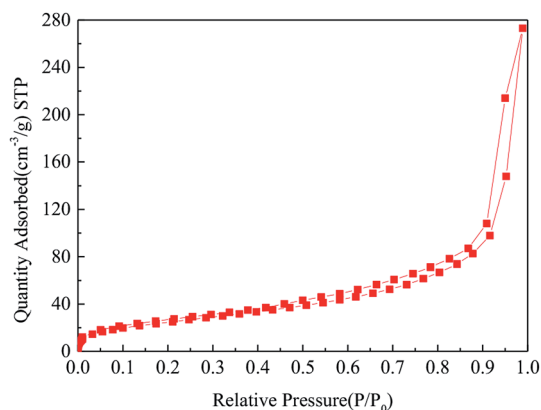


Fig. 7 N<sub>2</sub> adsorption and desorption isotherm of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO.

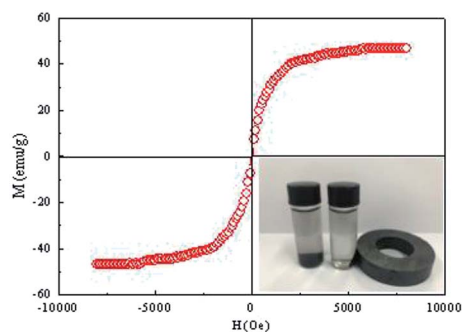


Fig. 8 Magnetization curve of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO; the inset shows a photograph of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO dispersion in ethanol and its magnetic response when placed in an external magnetic field (right).

illustrating that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO possesses superparamagnetism. As shown in the inset of Fig. 8, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO nanoparticles were uniformly dispersed in aqueous solution, which was then placed in an external non-magnetic field. Because Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO has strong ferromagnetic behavior, an external magnet can make the absorbed contaminant easily separable from the solution.

### 3.2 Adsorption studies

**3.2.1 Effect of pH.** The effect of pH is a key factor in determining the adsorption performance for Pb(II) and Ni(II) in aqueous solutions. As shown in Fig. 9, with the pH increasing from 2.0 to 3.0, the adsorption capacity for Pb(II) increased slowly. However, with the pH increasing from 3.0 to 5.5, the adsorption ability for Pb(II) increased enormously. As shown in the inset of Fig. 9, in the pH range 6.0–7.0, the adsorption ability of Pb(II) reached a plateau. Because of the pH range from 6.0 to 7.0, a white sediment appeared in the aqueous solution. For the adsorption of Ni(II), adsorption experiments were investigated in the pH range between 2.0 and 9.0. It can be seen from Fig. 8 that the adsorption capacity for Ni(II) increased enormously from 2.0 to 8.0, then reached a maximum value with the pH reaching 8.0–9.0. Comparing the adsorption performances for Pb(II) and Ni(II), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO has higher adsorption ability for Ni(II) all over the ranges of pH. The relative distribution of Pb(II) in the aqueous solution and the surface properties of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO can be affected by the pH. For the adsorption of Pb<sup>2+</sup> and Ni<sup>2+</sup>, the amidoxime group can have a bidentate ligand effect. The lone pairs of electrons on the amino nitrogen and the oxime oxygen induced the positive Pb(II) and Ni(II) centers to construct a new five-membered ring including the metal ion. It is worth noting that the oxime oxygen can undergo metal-assisted deprotonation:

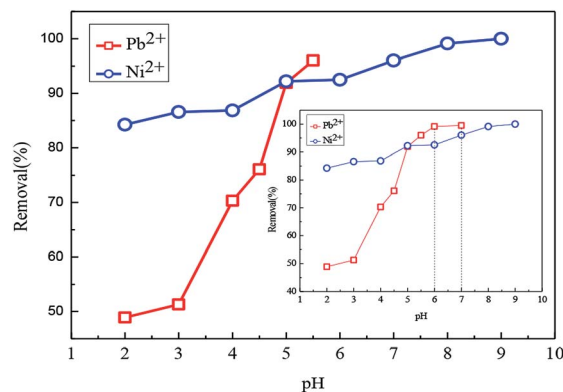
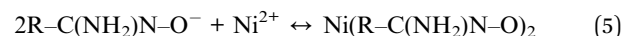
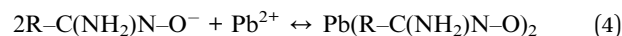


Fig. 9 Effect of pH on the adsorption of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO for Pb(II) and Ni(II) (Co = 50 mg L<sup>-1</sup>, T = 298 K, t = 2 h).



With the pH increasing, the emitted  $H^+$  ions can be neutralized under the chelation reaction environment. When the functional groups were deprotonated, the repulsion between  $Pb^{2+}/Ni^{2+}$  and  $Fe_3O_4@SiO_2-g-PAMAM-AO$  decreased. Therefore, the sorption amounts of the samples for  $Pb(II)$  and  $Ni(II)$  were increased. The main reason is ascribed to the fact that amidoxime chelating functional groups on the surfaces of  $Fe_3O_4@SiO_2-g-PAMAM-AO$  can construct stable chelates with  $Pb(II)$  and  $Ni(II)$ .

**3.2.2 Effect of contact time and adsorption kinetics.** Then we employed the nanoparticles  $Fe_3O_4@SiO_2-g-PAMAM-AO$  as adsorbents to investigate the impact of contact time on the removal of  $Pb(II)$  and  $Ni(II)$ . As shown in Fig. 10, the adsorption ability increased slowly. However, the adsorption ability of  $Fe_3O_4@SiO_2-g-PAMAM-AO$  for  $Pb(II)$  and  $Ni(II)$  approaches equilibrium after 10 min. As shown in Fig. 10, the adsorption ability of  $Fe_3O_4@SiO_2-g-PAMAM-AO$  for  $Ni(II)$  is higher than for  $Pb(II)$  under the same conditions ( $C_0 = 50 \text{ mg L}^{-1}$ ,  $T = 298 \text{ K}$ ,  $t = 180 \text{ min}$ ).

To gain further insight into the adsorption kinetics, the pseudo-first-order equation and pseudo-second-order equation were adopted to explain the adsorption mechanism. The pseudo-first-order and pseudo-second-order equations are defined as eqn (6) and (7),<sup>28,29</sup> respectively.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \left(\frac{1}{Q_e}\right) t \quad (7)$$

where  $Q_e$  ( $\text{mg g}^{-1}$ ) and  $Q_t$  ( $\text{mg g}^{-1}$ ) are the  $Pb(II)$  and  $Ni(II)$  adsorption capacities at equilibrium, respectively,  $t$  (min) is the constant time,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

Fig. 11 and Table 1 provide more intuitive depictions of the statistical results. From the values of the correlation coefficients,  $Pb(II)$  and  $Ni(II)$  adsorptions are more consistent with the pseudo-second-order model in comparison with the pseudo-first-order model. The results indicated that the chemical

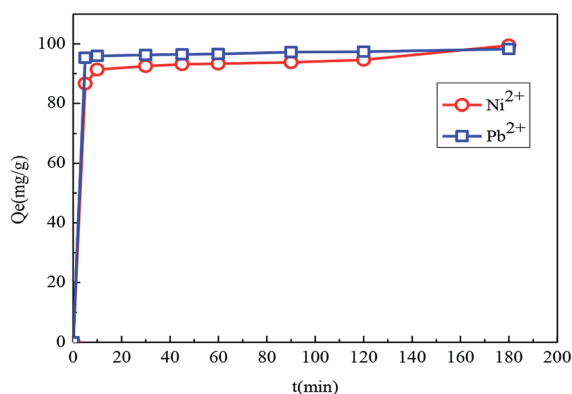


Fig. 10 The effect of contact time on the adsorption of  $Fe_3O_4@SiO_2-g-PAMAM-AO$  for  $Pb(II)$  ( $C_0 = 50 \text{ mg L}^{-1}$ ,  $T = 298 \text{ K}$ ,  $pH = 5.5$ ) and  $Ni(II)$  ( $C_0 = 50 \text{ mg L}^{-1}$ ,  $T = 298 \text{ K}$ ,  $pH = 8$ ).

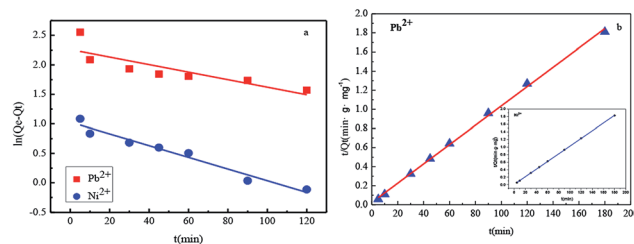


Fig. 11 Pseudo-first-order (a) and pseudo-second-order (b) kinetics of  $Pb(II)$  and  $Ni(II)$  adsorption on  $Fe_3O_4@SiO_2-g-PAMAM-AO$ . ( $C_0 = 50 \text{ mg L}^{-1}$ ,  $T = 298 \text{ K}$ ,  $pH(Pb^{2+}) = 5.5$ ,  $pH(Ni^{2+}) = 8$ ).

Table 1 The parameters of the kinetics of  $Pb^{2+}$  and  $Ni^{2+}$  adsorption onto  $Fe_3O_4@SiO_2-g-PAMAM-AO$

Model	Parameter	$Pb^{2+}$	$Ni^{2+}$
Pseudo-first-order model	$Q_e$ ( $\text{mg g}^{-1}$ )	10.3605	4.0678
	$k_1$	0.0064	0.0099
	$R^2$	0.7272	0.9631
Pseudo-second-order model	$Q_e$ ( $\text{mg g}^{-1}$ )	49.0294	49.143
	$k_2$	0.01012	0.01018
	$R^2$	0.99843	0.99994

adsorption is the main adsorption mechanism of  $Fe_3O_4@SiO_2-g-PAMAM-AO$  for  $Pb(II)$  and  $Ni(II)$ .

**3.2.3 Adsorption isotherm.** In order to illustrate the adsorption mechanism of  $Fe_3O_4@SiO_2-g-PAMAM-AO$ , the interaction between adsorbent and adsorbate was studied. The adsorption data were analyzed according to the well-known Langmuir and Freundlich isotherm models, whose equations are respectively expressed by eqn (8) and (9).<sup>30,31</sup>

$$\frac{C_e}{Q_e} = \left(\frac{1}{Q_{\max}}\right) C_e + \frac{1}{k_L Q_{\max}} \quad (8)$$

$$\log Q_e = \log k_F + \frac{1}{n} \log C_e \quad (9)$$

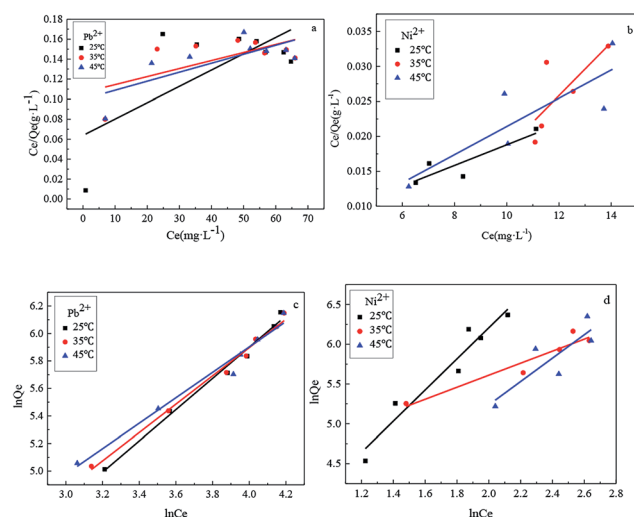


Fig. 12 The Langmuir (a), (b) and Freundlich (c), (d) isotherms of  $Pb(II)$  and  $Ni(II)$  adsorption onto  $Fe_3O_4@SiO_2-g-PAMAM-AO$ .



Table 2 Langmuir and Freundlich isotherm parameters for Pb<sup>2+</sup> and Ni<sup>2+</sup> adsorption onto the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO nanocomposite

Heavy metal ions	Temperature (°C)	Langmuir model			Freundlich model		
		$k_L$	$Q_e$ (mg g <sup>-1</sup> )	$R^2$	$k_F$	$N$	$R^2$
Pb <sup>2+</sup>	25	0.023	150.3588	0.6913	118.15	13.895	0.9946
	35	0.021	153.846	0.6506	121.78	8.876	0.9950
	45	0.017	157.2578	0.7475	133.25	6.729	0.9881
Ni <sup>2+</sup>	25	0.026	191.7856	0.8864	137.46	15.138	0.9678
	35	0.024	191.2116	0.7538	125.18	11.257	0.9576
	45	0.019	184.6080	0.8409	123.29	7.623	0.8493

Table 3 Comparison of adsorption capacity of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO composite nanoparticle adsorbent with other nanoparticles adsorbents

Adsorbent	Adsorbate	Adsorption capacity	References
Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	Pb <sup>2+</sup>	23.75 (mg g <sup>-1</sup> )	29
Magnetic Fe <sub>3</sub> O <sub>4</sub> yeast treated with EDTA dianhydride	Pb <sup>2+</sup>	99.26 (mg g <sup>-1</sup> )	30
Chain-like Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @chitosan magnetic nanoparticles	Pb <sup>2+</sup>	6.899 (μg mg <sup>-1</sup> )	31
Magnetic multiwalled carbon nanotube nanocomposite	Ni <sup>2+</sup>	2.11 (mg g <sup>-1</sup> )	32
Iron oxide nanoparticles	Ni <sup>2+</sup>	11.1 (mg g <sup>-1</sup> )	33
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -g-PAMAM-AO magnetic nanoparticles	Pb <sup>2+</sup>	157.25 (mg g <sup>-1</sup> )	This work
	Ni <sup>2+</sup>	191.78 (mg g <sup>-1</sup> )	This work

where  $Q_e$ ,  $Q_{max}$  (mg g<sup>-1</sup>) are the equilibrium adsorption capacity and the maximum adsorption capacity of Pb(II) and Ni(II) on the adsorbent, respectively.  $C_e$  (mg L<sup>-1</sup>) is the Pb(II) and Ni(II) concentration residual in solution at equilibrium,  $K_L$  (L mg<sup>-1</sup>) is the Langmuir adsorption constant, and  $K_F$  and  $n$  are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

As shown in Fig. 12, it can be observed that the adsorption isotherms of Pb(II) and Ni(II) could be fitted with both Langmuir (a), (b) and Freundlich (c), (d) models. The parameters calculated by the model are listed in the support information to Table 2. For the adsorption isotherms of Pb(II) and Ni(II), the Freundlich model showed a higher correlation coefficient, indicating that the adsorption data of the Freundlich model is a better fit than the adsorption data of the Langmuir model. Therefore, the Freundlich isotherm can be applied for non-ideal adsorption on multilayer adsorption and heterogeneous surfaces in nature.<sup>32</sup>

Compared with other magnetic adsorbents, the adsorption capacities on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO for Pb(II) and Ni(II) are higher than those for Pb(II) and Ni(II) sorption on other related materials, as listed in Table 3. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO with such a high ability for Pb(II) and Ni(II) sorption exhibits a potential for real applications in the removal of Pb(II) and Ni(II) from large volumes of aqueous solutions. The main reason for the high adsorption capacity is that the dendritic graftings have a large surface area. Furthermore, the amidoxime-functionalized groups have multivariate coordination characteristics.

Fig. 13 shows the effects of adsorbent dose on the removal efficiency of Pb(II) and Ni(II) in aqueous solution. For Pb(II),

when the adsorbent dose increased from 0 to 30 mg, the removal efficiency quickly increased from 0 to 96%. For Ni(II), the removal efficiency rapidly increased from 0 to 99.1% with the adsorbent dose under the same conditions. Because an increase in the adsorbent dose meant an improvement, there are relatively more active sites and greater surface area.

The regeneration and reuse of adsorbent materials play a decisive role in practical applications.<sup>33-37</sup> In this work, the Pb(II)-loaded adsorbent was desorbed using a 0.1 mol L<sup>-1</sup> NaOH solution and then washed with distilled water to a pH of 7.0 for reuse in the next run. For Pb(II), it was found that the removal efficiency was approximately 93.74%, and the removal capacity was still over 91.256% after five adsorption-desorption cycles. Furthermore, for Ni(II), it was found that the

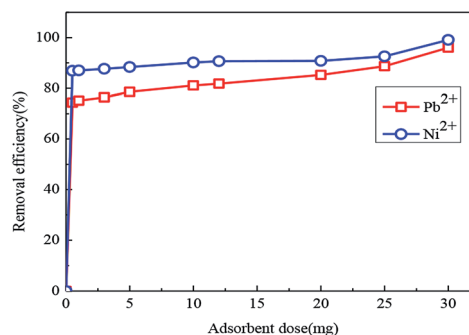


Fig. 13 Effect of adsorbent dose on the removal efficiency of Pb(II) and Ni(II) by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO. ( $C_0 = 50$  mg L<sup>-1</sup>,  $T = 298$  K, pH (Pb<sup>2+</sup>) = 5.5, pH (Ni<sup>2+</sup>) = 8,  $t = 2$  h).



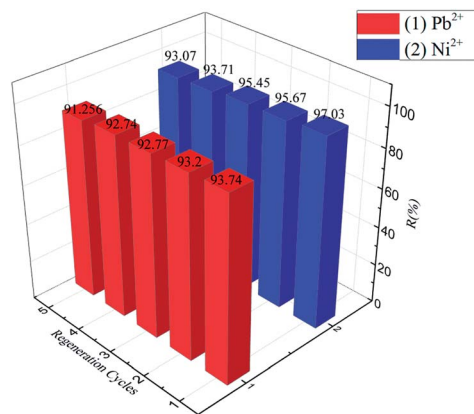


Fig. 14 Removal efficiency of five adsorption–desorption cycles of regenerating Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO on Pb(II) and Ni(II). (Co = 50 mg L<sup>-1</sup>, T = 298 K, pH (Pb<sup>2+</sup>) = 5.5, pH (Ni<sup>2+</sup>) = 8, t = 2 h).

removal efficiency was approximately 97.03%, and the removal capacity was still over 93.07% after five adsorption–desorption cycles (Fig. 14). These results indicated that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO has good ability of regeneration, and it can be reused in the application of Pb(II) and Ni(II) removal from wastewater.

## 4. Conclusions

In summary, magnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO was successfully synthesized and used as an adsorbent for the adsorption of Pb(II) and Ni(II) from several environmental waters. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO exhibits enhanced adsorption capacities for both Pb(II) and Ni(II) because of the larger surface area and the strong chelation of amidoxime to Pb(II) and Ni(II). The adsorption process was pH dependent. FT-IR and XPS studies revealed the amidoxime-functionalized groups formed on the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO. Magnetic measurement revealed the superparamagnetic behavior of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO with a saturation magnetization of 47.7 emu g<sup>-1</sup>. The adsorption processes of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO for Pb(II) and Ni(II) were in good agreement with the pseudo-second-order kinetics model and the Freundlich isotherm model. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO has a maximum Pb(II) adsorption of 157.25 mg g<sup>-1</sup> (100 mg L<sup>-1</sup>) at pH 5.5. Furthermore, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO showed an excellent adsorption performance for the removal of Ni(II) with a maximum adsorption capacity of 191.78 mg g<sup>-1</sup> (100 mg L<sup>-1</sup>) at pH 8.0. The adsorption capacities of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO nanohybrids grafted with amidoxime-functionalized groups for Pb(II) and Ni(II) are very high. All the results suggested that the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-g-PAMAM-AO composites are effective adsorbents for the removal of Pb(II) and Ni(II).

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors greatly acknowledge the financial support provided by the National Natural Science Foundation of China (21671026), the Natural Science Foundation of Hunan Province (2019JJ40310), the Science and Technology Key Project of Hunan Province (2015SK20823), Scientific Research Key Fund of Hunan Provincial Education Department (15A001).

## Notes and references

- 1 Y. G. Zhao, H. Y. Shen, S. D. Pan, M. Q. Hu and Q. H. Xia, *J. Mater. Sci.*, 2010, **45**, 5291–5301.
- 2 N. H. Rashidi, I. W. Wan, I. Ali and M. M. Sanagi, *Environ. Sci. Pollut. Res.*, 2016, **23**, 9759–9773.
- 3 Y. Dai, L. Niu, J. Zou, T. Chen, H. Liu and Y. Zhou, *Chin. Chem. Lett.*, 2018, **29**, 887–891.
- 4 W. Hou, X. Yuan, W. Yan, X. Chen, L. Leng and W. Hui, *Chem. Eng. J.*, 2015, **262**, 597–606.
- 5 G. Liu, Q. Deng, H. Wang, S. Kang, Y. Yang and D. H. Ning, *Chem.–Eur. J.*, 2012, **18**, 13418–13426.
- 6 J. H. Wang, S. R. Zheng, Y. Shao, J. L. Liu, Z. Y. Xu and D. Q. Zhu, *J. Colloid Interface Sci.*, 2010, **349**, 293–299.
- 7 X. Sun, L. Yang, H. Xing, J. Zhao, X. Li and Y. Huang, *Chem. Eng. J.*, 2013, **234**, 338–345.
- 8 V. Chandra, J. Park, Y. Chun, J. W. Lee, I. C. Huang and K. S. Kim, *ACS Nano*, 2010, **4**, 3979–3986.
- 9 H. Shi, J. Yang, L. Zhu, Y. Yang, H. Yuan and Y. Yang, *J. Nanosci. Nanotechnol.*, 2016, **16**, 1871–1882.
- 10 Z. Fan, Y. Shi, Z. Zhao, B. Ma, L. Wei and L. Lu, *J. Mater. Sci.*, 2014, **49**, 3478–3483.
- 11 Y. Li, L. Cao, L. Li and C. Yang, *J. Hazard. Mater.*, 2015, **289**, 140–148.
- 12 N. H. Shaidan, U. Eldemerdash and S. Awad, *J. Taiwan Inst. Chem. Eng.*, 2012, **43**, 40–45.
- 13 L. A. Wei, A. W. Mohammad, N. Hilal and C. P. Leo, *Desalination*, 2015, **363**, 2–18.
- 14 I. Mobasherpour, M. S. Heshajin, A. Kazemzadeh and M. Zakeri, *J. Alloys Compd.*, 2007, **430**, 330–333.
- 15 R. Donat, A. Akdogan, E. Erdem and H. Cetisli, *J. Colloid Interface Sci.*, 2005, **286**, 43–52.
- 16 Y. Zhao, J. Li, L. Zhao, S. Zhang, Y. Huang and X. Wu, *Chem. Eng. J.*, 2014, **235**, 275–283.
- 17 N. Lu, M. Zhang, L. Ding, J. Zheng, C. X. Zeng, Y. L. Wen and G. Liu, *Nanoscale*, 2017, **9**, 4508–4515.
- 18 J. P. Wang, M. Zhang, J. L. Xu and J. Zheng, *Dalton Trans.*, 2018, **47**, 2791–2798.
- 19 Y. X. Ma, Y. L. Kou, D. Xing, P. S. Jin, W. J. Shao and X. Li, *J. Hazard. Mater.*, 2017, **340**, 407–416.
- 20 P. Zhao, L. Tian, X. Li, Z. Ali, B. Zhang and H. Zhang, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1–28.
- 21 M. Anbarasu, M. Anandan, E. Chinnasamy, V. Gopinath and K. Balamurugan, *Spectrochim. Acta, Part A*, 2015, **135**, 536–539.
- 22 Y. Kobayashi, H. Katakami, E. Mine, D. Nagao, M. Konno and L. M. Lizmarzán, *J. Colloid Interface Sci.*, 2005, **283**, 392–396.



- 23 K. Zhu, Y. Duan, F. Wang, P. Gao, H. Jia and C. Ma, *Chem. Eng. J.*, 2017, **311**, 236–246.
- 24 Q. Peng, M. Liu, J. Zheng and C. Zhou, *Microporous Mesoporous Mater.*, 2015, **201**, 190–201.
- 25 J. Mu, B. Chen, Z. Guo, M. Zhang, Z. Zhang and P. Zhang, *Nanoscale*, 2011, **3**, 5034–5040.
- 26 A. B. Albadarin, M. N. Collins, M. Naushad, S. Shirazian, G. Walker and C. Mangwandi, *Chem. Eng. J.*, 2017, **307**, 264–272.
- 27 M. Zhang, L. F. Chen, J. Zheng and W. Z. Li, *Dalton Trans.*, 2017, **46**, 9172–9179.
- 28 J. P. Simonin, *Chem. Eng. J.*, 2016, **300**, 254–263.
- 29 V. P. Mahida and M. P. Patel, *RSC Adv.*, 2016, **6**, 21577.
- 30 K. Y. Foo and B. H. Hameed, *Chem. Eng. J.*, 2010, **156**, 2–10.
- 31 B. S. Kaith, R. Jindal and R. Sharma, *RSC Adv.*, 2015, **5**, 43092.
- 32 Z. Wang, S. Zhu, S. Zhao and H. Hu, *J. Alloys Compd.*, 2011, **509**, 6893–6898.
- 33 A. R. Keshtkar, M. Irani and M. A. Mousavian, *J. Radioanal. Nucl. Chem.*, 2013, **295**, 563–571.
- 34 X. Meng, Y. Zhang, Z. Zhang, Y. Shen, M. Zhao and G. Pan, *Chem. Eng. J.*, 2011, **168**, 737–745.
- 35 H. Shi, J. Yang, L. Zhu, Y. Yang, H. Yuan, Y. Yang and X. Liu, *J. Nanosci. Nanotechnol.*, 2016, **16**, 1871–1882.
- 36 W. Konicki, I. Pelech and E. Mijowska, *Pol. J. Chem. Technol.*, 2014, **16**, 87–94.
- 37 S. E. Ebrahim, A. H. Sulaymon and H. S. Alhares, *Desalin. Water Treat.*, 2015, **62**, 1–15.

