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Extraction of Pb^{2+} from dilute solution by paramagnetic Fe_3O_4 @ SiO_2 @ Clpr-silica @ dithizone solid-phase nanoextractant

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ABSTRACT

A paramagnetic solid phase nanoextractant, Fe_3O_4 @ SiO_2 @ Clpr-silica @ dithizone, is firstly constructed for separating Pb^{2+} from dilute solution. The special extractant is composed of a paramagnetic Fe_3O_4 nanomaterials core, amorphous silica, chloro-propyl silane coupling agent, and dithizone from inside to outside. The experimental results demonstrate the as-obtained extractant fine adsorbability, high adsorption and desorption speed, wide acidic resistance, facile separability, and admirable reusability. The adsorption capacity of the extractant exceeds $63.4\,mg\,g^{-1}$, and the adsorption process is accomplished in 25 s. Pb^{2+} ions are completely eluted from the extractant immersed into 2 M HNO_3 solution in 20 s. After five times of adsorption-regeneration cycles, no significant loss of adsorption capacity is observed, indicating the good stability of the extractant.

Keywords: Magnetic separation; Nanocomposite; Solid-phase extracting; Lead ion; Heavy metal ions

1. Introduction

Heavy metal ions pollutions have attracted extensive attentions due to diverse harms and damages for the environment and human beings. Many diseases are related to these pollutions, such as minamata and bone pain. However, many heavy metals, as an important kind of industrial materials, have been widely applied in many fields such as machinery, shipping, and electrical industry. Among them, lead metal is utilized in battery industry, electromagnetic, and radiation protection field. However, lead is one of the most toxic heavy metal elements, which seriously threatens the ecological environment and human health. So, it has aroused widespread attention on how to eliminate the pollution from heavy metal ion and recycle them [1–3].

In a few decades, many technologies have been developed for governing heavy metal ions contamination, such as, chemical precipitation, adsorption, ion exchange, membrane separation, and solvent extraction method [4–11]. Some traditional methods have exposed some insufficiency, though they are widely applied in industry. For instance, the ion exchange resin methods and membrane separation methods require many complex devices and tedious procedures, which are accompanied by high costs, and emergence of secondary contamination; the chemical precipitation method is cheap and facile, but heavy

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metal ions cannot be eliminated by them thoroughly by one time. Recently, many nanocomposites are applied to absorb and separate heavy metal ions due to wide surface area, high dispersibility, and absorptive speed [12–15]. For example, silica gel bounded dithizone as a solid-phase extraction has been used to absorb Cu^{2+} from complex matrix [16]; The amino-functionalized mesoporous silicas are used to absorb Cu^{2+} and Pb^{2+} [17]; Barium-strontium titanate powder coated by dithizone is used to extract Pb^{2+} ion from wastewater with good absorbing speed [18]. Though non-magnetic solid-phase nanoextractants show high dispersibility and stability in solution, it still is a tough problem how to accomplish their efficient and fast separation from media solution system.

The magnetic substance can be separated conveniently from medium by ex-magnetism, so it is an alternative method that applied magnetic nanomaterial as matrix of an extractant for approaching the extractant separation problem. According to this idea, many magnetic extractants have been constructed such as: Fe_3O_4@ SiO_2@ IIP [19], functional silica-coated magnetic Fe_3O_4 nanoparticles [20]. However, as we know, it is disadvantageous to the application of the as-reported magnetic nanoabsorbents due to poor acid and alkali resistance, small adsorption capacity, low selectivity, and bad reusability. So, it is still a challenging task to prepare a magnetic solid phase nanoabsorbent with good reusability, high selectivity, good capacity, and high acid resistance.

Dithizone, as an ideal Pb^{2+} recognition receptor, has been widely used as a liquid–liquid extractor of lead ions due to indication and selectivity [18,21]. However, as far as we know, it is rarely that dithizone is banded on magnetic nanoparticles to prepare a solid-phase nanoextractant. Compared to a liquid–liquid extraction by dithizone, the solid extractant with dithizone shows many advantages including the simplified separation procedure, no need for organic solvent, and high speed with efficiency.

In this study, a four-layer structured paramagnetic material, Fe_3O_4@ SiO_2 @ Clpr-silica @ dithizone, is firstly constituted and used as solid phase nanoextractant to isolate lead ion from solution. The dithizone is fixed on a paramagnetic Fe_3O_4 nanocomposited microsphere (400–500 nm) via silane coupling agent. The paramagnetic Fe_3O_4 self-assembled nanomicrospheres with 500 nm diameter are selected as a core due to its high magnetic response and structure stability; the magnetic core is modified by silica and γ-chloropropyl-trimethoxysilane (KH-230) in turn; then the dithizone molecules are grafted on the surface of the particles. The as-prepared nanoextractant demonstrates good adsorption capacity beyond $63\,mg\,g^{-1}$, fast absorption and desorption speed, and fine reusability. This paper may provide an alternative strategy to design and prepare similar solid-phase nanoextractant on heavy metal ion extraction and separation.

2. Experimental

2.1. Reagents and solution

All chemical reagents, except of aqueous ammonium solution (25–28%), γ-chloropropyl-trimethoxysilane (KH-230) (98%), and nitric acid (65%), are of analytical grade and used without further purification in this study. The lead (Ⅱ) ion solutions are prepared with lead (Ⅱ) acetate and ultrapure water are distilled by a Milli-Q instrument (Millipore Co. Ltd., USA). Nitric acid aqueous solution is used as elution solutions. $NH_3{\cdot}H_2O/NH_4Cl$ buffer solution is prepared to control the pH value of solution in some adsorption procedures. Sometimes the pH value of solution is adjusted by some aqueous nitric acid or ammonia.

2.2. Preparation of paramagnetic solid phase nanoextractant

The scheme for preparing the Fe_3O_4 @ SiO_2 @ Clpr-silica @ dithizone extractant including four basic stages is listed in Fig. 1. These stages are briefly described as follows:

2.2.1. Synthesis of Fe_3O_4 nanocomposited microspheres

Fe_3O_4 microspheres are synthesized via a classic solvothermal method [22]. The procedures of the synthesis method are sketched as follows: $FeCl_3{\cdot}6H_2O$ (0.036 mol), sodium acetate anhydrous (0.2 mol), and ethylene glycol (350 ml) are mixed and continuous stirred at room temperature to obtain a homogeneous precursor solution, then the precursor is transferred into a 500 ml Teflon-lined autoclave. The autoclave is sealed and heated at 200℃ for 24 h and then cooled naturally. The resulting product is separated from system by magnetism, washed with ethanol, and distilled water to ensure total removal of the inorganic ions and organic impurities, and then dried under vacuum at 60℃ for 4 h.

2.2.2. Fe_3O_4 nanospheres modified by tetraethyl orthosilicate and KH-230

The magnetite nanospheres are coated by silica via a proven hydrolysis technique of tetraethyl orthosilicate (TEOS) based on reference [23]. It includes some typical procedures as follows: In a tri-necked flask

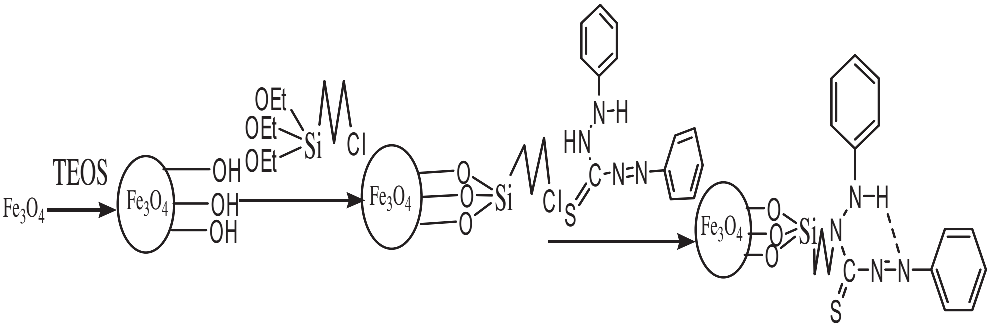

Fig. 1. The preparation routes of the paramagnetic solid phase nanoextractant.

(250 ml volume), 1 g Fe_3O_4 microspheres are dispersed into ethanol/water mixed-solution (80/20 ml) to form a homogeneous mixture. When the system is heated at 45℃, 5 ml ammonia (25%) are added into the mixture, then 1 ml TEOS are added dropwise into the suspension after 30 min treatment, and then the system is further heated at 45℃ for 60 min and cooled to room temperature. The magnetic nanomaterials are separated by a magnet, washed with ethanol and water, and then the Fe_3O_4 @ silica nanomaterials are obtained after drying at 60℃ for 2 h. The similar hydrolysis route is adopted to fix the KH-230 molecular on the surface of Fe_3O_4 @ silica nanomaterials: firstly, the mixture including 1 g Fe_3O_4 @ silica, 100 ml water-ethanol, and 1 ml ammonia (25%) is heated at 45℃; then 3 ml KH-230 are added dropwise into the system and maintained at the temperature for 1 h; and then the system is further heated at 60℃ for another 1 h under mechanical stirring; finally, after the magnetic samples are separated by magnetism and rinsed thoroughly with water and ethanol, the γ-chloropropyl functionalized magnetic nanocomposite (Fe_3O_4@ SiO_2 @ Clpr-silica) is constructed.

2.2.3. Immobilized dithizone on the nanocomposites

1.0 g Fe_3O_4@ SiO_2 @ Clpr-silica, 0.1 g dithizone, 0.3 ml triethylamine and 80 mL trichloromethane are added into a 250 ml tri-neck flask to form turbid liquid under continuous stirring, then the mixture is continually refluxed at 40℃ for 24 h. The as-obtained magnetic nanoextractant sample is separated by magnetism and rinsed thoroughly with ethanol to remove residual dithizone, and then dried under vacuum at 60℃ for 5 h.

2.3. Structure characterization

The infrared adsorption spectrum of a sequenced sample obtained at different preparation steps are identified by Fourier transform infrared spectra (FT-IR, Nicolet 380). The typical morphologies of Fe_3O_4, Fe_3O_4@ SiO_2 nanocomposites, and Fe_3O_4@ SiO_2 @ Clpr-silica @ dithizone nanocomposites are characterized by a scanning electron microscope (Quanta FEG 450, USA). The room-temperature M-H curve of a typical sample is obtained by a vibrating sample magnetometer (VSM, Lake Shore 735VSM, USA) in the range from −6,000 to 6,000 Oe.

2.4. Investigation of the extracting capacity of the extractant

The typical adsorption procedures are performed as follows: 5 mg of as-prepared extractant is dispersed into a given 100 ml Pb^{2+} diluted solutions in flasks at room temperature. The extractants in different test samples are collected and separated by magnetism before the residual concentrations of Pb^{2+} in them are measured by an atomic adsorption spectrometer (TAS-990AFG).

The adsorption kinetics of the extractant is investigated by the follow procedures: Lead ion solution 100 ml (20 μg Pb^{2+}) is poured into a 250 ml beaker, which is placed in ultrasonic condition. Timing begins with 5 mg adsorbent addition. A series of 1 ml samples is pipetted out rapidly at 5, 20, 30, 40, 60, 120 s, and the adsorbent is quickly isolated with a strong magnet from samples at the same time. The residual lead ions concentration in the samples is used to measure the extractant adsorption dynamic performance.

The used extractants are rinsed and regenerated by 2 M HNO_3 solution. The regenerated extractant is further rinsed by ultrapure water until the pH of leachate is neutral, then the extractant is dried and reused as extractant to absorb Pb^{2+} again. The procedures of adsorption and desorption are repeated at least five times to test the reusability of the extractant.

3. Results and discussion

3.1. Characterization of the as-prepared nanoextractant

The infrared adsorption spectra of the samples are listed in Fig. 2. The characteristic lattice vibrations of Fe–O in Fe_3O_4 are obviously indicated in the four spectra with the peaks around 590 and 448 cm^{-1}; Compared to the adsorption spectrum of Fe_3O_4, the spectrum of is shown in, the adsorption bands from silica are unclear in Fe_3O_4 @ silica (Fig. 2(b)), except the stretching vibrations bands of Si–O–Fe and Si–OH are weakly appeared at 838 and 889 cm^{-1}, respectively. It indicates that the paramagnetic Fe_3O_4 nanoparticles are coated by thin silica layer. Fig. 2(c) shows the spectrum of the Clpr-silica sample, the strong adsorption bands with the peak at 1,094 cm^{-1} demonstrates the stretching vibration adsorption bands of Si–O–Si, meanwhile, the adsorption bands around 2,957 and 794 cm^{-1} further indicate that the existence of C–H, C–C, and C–Cl groups. It shows that KH-230 molecules are successfully grafted on the surface of the magnetic nanomaterials. The spectrum of the as-prepared nanoextractant is listed in Fig. 2(d), some new adsorption bands including 1,544, 1409, and 1312 cm^{-1} appears and belongs to the bending vibration of –N–H, the stretching vibration of –N=N–, and the stretching vibration of –N–H and –C=S. Besides, the adsorption bands in the range from 1,600 to 1,450 cm^{-1} in Fig. 2(d) indicate the existence of benzene ring in the materials. These detection results confirm dithizone molecules are effectually fixed the surface of magnetic nanomaterials by the coupling reagent KH-230.

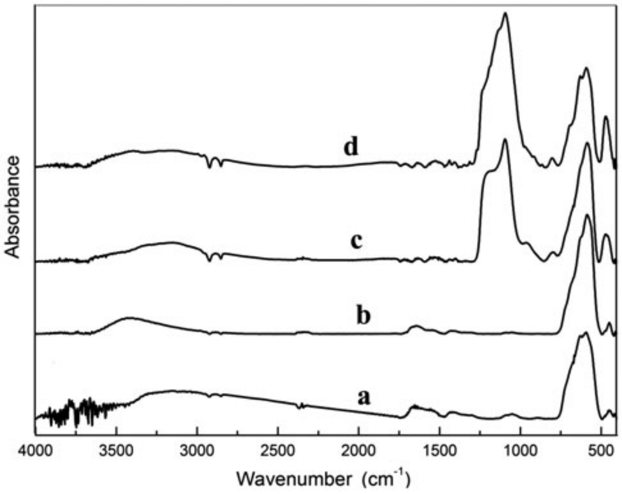

Fig. 2. FTIR spectra of Fe_3O_4 (a), Fe_3O_4 @ silica (b), Fe_3O_4 @ silica@ Clpr-silica (c), Fe_3O_4@ SiO_2 @ Clpr-silica @ Dithizone, and (d).

The typical SEM images of samples are shown in Fig. 3. The diameter of the sphere-like Fe_3O_4 core is about 400–500 nm (Fig. 3(A)), which are self-assembled by numbers of nanoparticles. After Fe_3O_4 microspheres are modified by silica, the obtained image (Fig. 3(B)) indicates the size of samples slightly increases due to the increase of its surface roughness. It further suggests the very thin silicon layer is formed at the surface of magnetic sphere. The SEM image shown in Fig. 3(C) demonstrates that the as–prepared nanoextractant has sphere-like shape with smooth surface. The reason for formation of smooth surface should be assigned to the Clpr-silica layer and many dithizone molecules, which are fixed to the surface and fill some surface defects of Fe_3O_4 @ SiO_2 nanocomposite.

Fig. 4 shows the hysteresis curve of the nanoextractant. The curve suggests the extractant is ascribed to super-paramagnetic materials because the coercivity of the samples is about zero with the saturation magnetization (Ms) around 50 emu g^{-1}. Compared to ferromagnetic particles, the interaction among paramagnetic particles is quite feeble, the dispersibility and stability of the particles are better than ferromagnetic particles. So the as-prepared nanoextractant may keep good dispersibility in Pb^{2+} diluted solution without magnetism. The enough magnetic response capability of the extractant with the Ms about 50 emu g^{-1} ensures the extractant can be quickly separated from solution system by magnetism.

3.2. Influence of pH on the adsorbent efficiency

The influence of pH value on the extractant is totally investigated and the corresponding results are shown in Fig. 5(A). The adsorption process is performed with multiple parts extractants with equal mass (5 mg) that are added into a series of different acidity solutions in volume of 100 ml with 20 μg Pb^{2+}. The change curve indicates some important information as follow: at high acidic conditions, the absorbing capability of the extractant is almost negligible and only tiny Pb^{2+} is transferred; the absorbed amount of Pb^{2+} is boosted with the pH value, acidic degree changing from 1 to 4; over 90% of lead ions is adsorbed at acidic degree equaled 4; after that the efficiency of absorbed lead ion is slightly increasing with the raise of acidic degree until the acidic degree reaches 7; when the system is performed in basic setting, the adsorption capability of the extractant obviously declines with the increase of pH value, but the absorption efficiency of the lead ion still maintained over 90% at the pH value equaled 9. Based on the above experimental results, the extractant can be

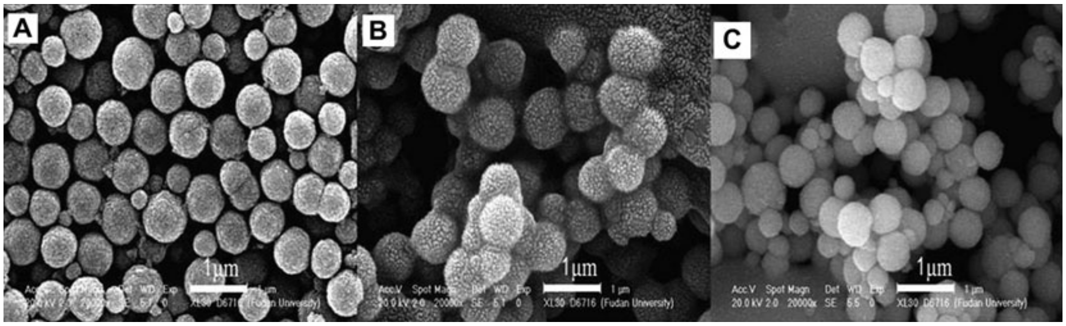

Fig. 3. SEM images of Fe_3O_4 (A), Fe_3O_4@ SiO_2 (B), and Fe_3O_4@ SiO_2 @ Clpr-silica @ Dithizone (C).

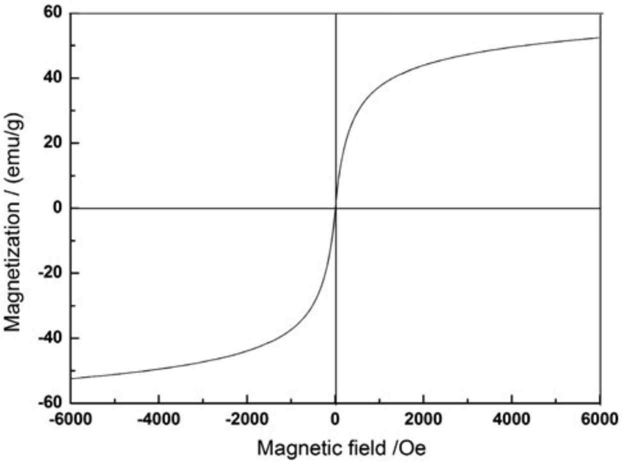

Fig. 4. The hysteresis curve of the as-obtained solid-phase nanoextractant.

applied to the solution with acidity range from 4 to 9. In a strong acidic medium, the "–NH" group in the dithizone preferentially bond with H^+ and restrain the coordination with the metal ion, so the absorbed efficiency of the extractant is very inferior. This result may provide an applicable method to recycle the extractant for the metal ion that can be eluted by H^+ ion-exchange in strong acidic system. However, if the system performs in the solution with high alkalinity, lead ions react with OH^- and form $Pb(OH)_2$ precipitation. For common wastewaters containing heavy metal ions showing weak or neutral acidity, the extractant can meet the applicant need for absorbing lead ion from them.

The adsorption kinetics, as an important characteristic, defines the adsorption efficiency of an extractant. Fig. 5(B) exhibits the change between the residual Pb^{2+} concentration and the adsorption time in neutral solution. The curve suggests the adsorption equilibrium has been achieved in 20 s due to hardly changing residual Pb^{2+} concentration after the mentioned time. This result suggests the extractant shows a fast adsorption rate property, which provides a guarantee for rapid adsorbing the lead ion from waste solution.

3.3. The adsorption capacity of the extractant

The adsorption isotherm data of the extractant is measured at room temperature. The experiments are performed in 100 ml neutral solution containing different series of concentration Pb^{2+} and 10 mg extractant.

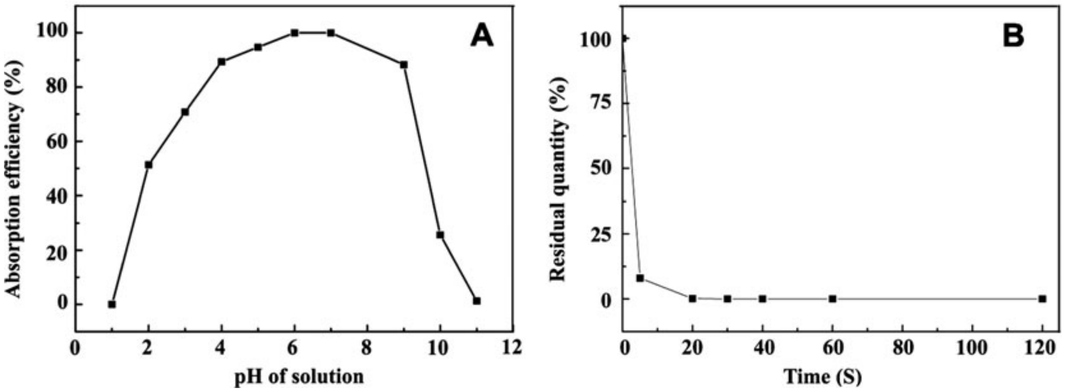

Fig. 5. The effect of pH value (A) and adsorption time (B) on absorbed efficiency of the extractant.

According to the above result, to the adsorbing time of all experiments is given 30 s. According to the reference [24], the adsorption capacity value (Q) (mg g^{-1}) is calculated by the following equation: $Q_t = (C_0 - C_t) V/W$; where C_0 is the initial Pb^{2+}concentration; C_t is the residual Pb^{2+} concentrations; V is the volume of the initial Pb^{2+} solution, and W is the dry weight of the extractant. The corresponding experimental results are shown in Fig. 6. The isotherms have remarkable increase at low-lead ion concentration, which indicates the high adsorption potential of the extractant adsorbent to the metal ions. The adsorption capacity of the extractant is enhanced with the increase of Pb^{2+} concentration. When the mass of the lead ion C_0 is lower than 10 mg L^{-1}, the lead ion is almost completely absorbed by the extractant. The extracting capacity of the extractant increases with the increase of concentration of lead ions until 80 mg L^{-1}, but the amount of absorbed lead ions declines from 100 to 90% and 79%, meanwhile, the extractant almost reaches saturated adsorption capacity about 63.4 mg g^{-1}. After that, the capacity of it does not change with the increasing concentration of Pb^{2+} ions. According to the experimental results, the maximum adsorption capacity of the extractant is around 63.4 mg g^{-1}. The isotherm data can be appropriately described by the Sips model [25]. It is an ideal process where the extractant is applied into the diluted Pb^{2+} ion solution. Based on the above experimental results, the high adsorption capacity of the extractant should be ascribed to the dithizone, which can coordinate with Pb^{2+} ion. This adsorption process of the extractant conforms to the coordination equilibrium: with the mass of Pb^{2+} ion increases, more and more dithizone molecules are bonded to Pb^{2+}. When the concentration of the lead ion exceeds the proper value, all dithizone molecules are coordinated with Pb^{2+} ion, so that the adsorption capacity of the extractant reaches maximum and remains constant in spite of the increase of the ion concentration.

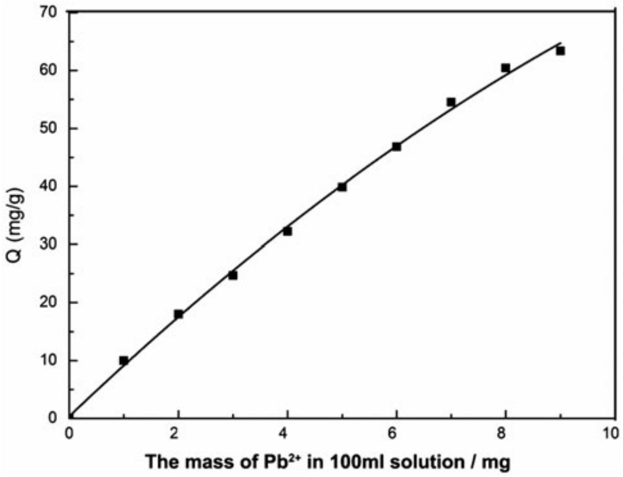

Fig. 6. The adsorption capacity changed with the volume of 10 mg/L Pb^{2+} ion solution.

3.4. The regeneration of the extractant

The used extractant is regenerated by HNO$_3$ solution. The sequential HNO$_3$ solutions are investigated to search the proper acidic degree for efficiently desorbing the lead ion from the extractant in case of maintaining its structural stability. The change curve between the desorbing efficiency of Pb^{2+} ion and the acidic degree of HNO$_3$ solution is shown in Fig. 7(A). The curve demonstrates the removal rate of the lead ion in the adsorbent that reaches maximum about 99% in 2 M HNO$_3$ solution. At low acidic degree, for the concentration of H$^+$, it is insufficient to completely replace the lead ion, the elution efficiency increases with acidic degree increasing. Contrarily, when the acidic degree of HNO$_3$ solution exceeds the proper value, the strong oxidizability of the solution is significantly reflected and results into a change in the structure and performance of the extractant. The experimental result is in accordance with some references in terms of the regeneration of some extractants [26–28]. The elution rate, as an important factor, is demonstrated in Fig. 7(B). The curve shows that the elution efficiency changes with the immense time. The curve indicates that the best desorption efficiency reaches 99% within 20 s, and the elution efficiency of the extractant decreases with the elution time exceeding 20 s. This result may be attributed to some secondary reactions occurred in strong acidic system.

According to the above experimental results, the adsorption and desorption mechanism of the as-prepared paramagnetic solid-phase nanoextractant are deduced and shown in Fig. 8. At low acidic condition, the extractant demonstrates good absorbability on lead ion; meanwhile, Pb^{2+} ion is eluted from the extractant in high acid solution.

3.5. The reusability of the extractant

The reusability of an adsorbent is crucial in practical applications. Fig. 9 shows the results of five adsorption-regeneration cycles of Pb^{2+} for the extractant. It is clearly seen from the general trends shown in the curves that the adsorption and desorption efficiency of the extractant slightly declines with the increase of reused times number, but the values of the two important parameters are still higher than 95%

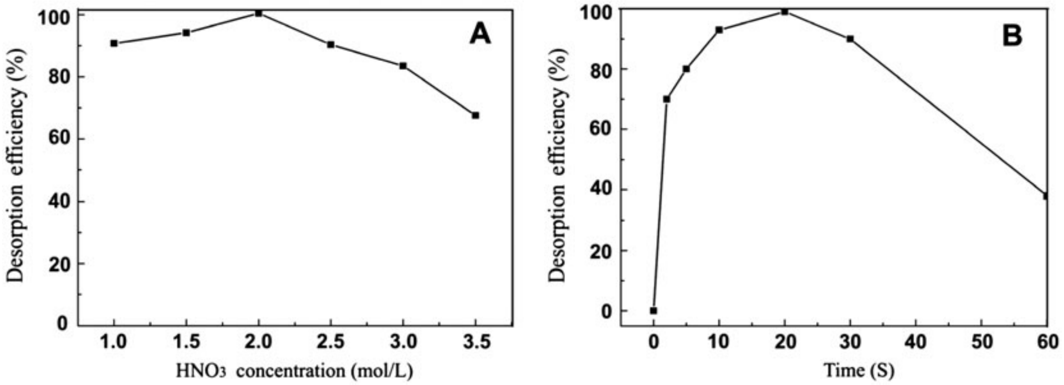

Fig. 7. The elution efficiency changed with acidity of HNO_3 (A) and desorption time (B).

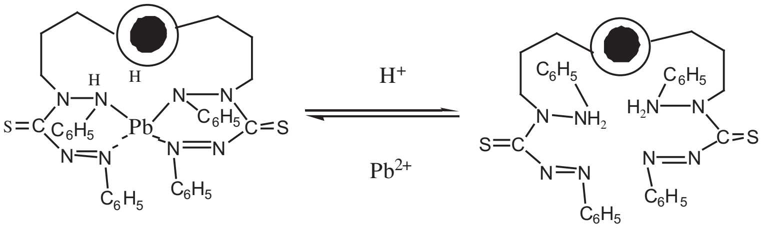

Fig. 8. Adsorption mechanism of the paramagnetic solid phase nanoextractant.

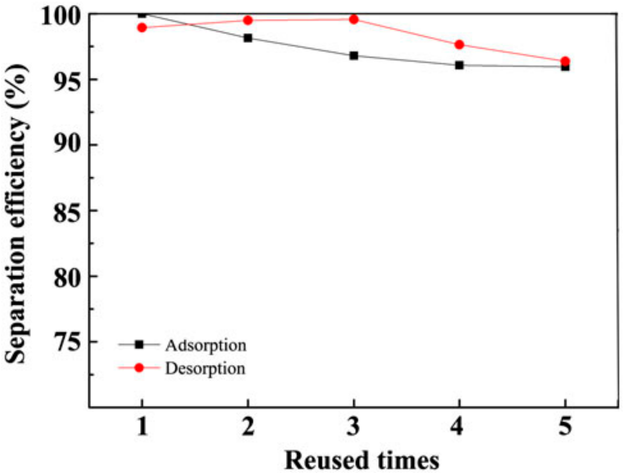

Fig. 9. The experiment investigation of the reusability of the as-prepared extractant.

after five cycles. The above experimental results suggest the as-prepared solid-phase nanoextractant possesses fine reusability. The decrease of adsorption and desorption efficiencies of the extractant should be ascribed to the loss of mass or few lost functional groups of the extractant in the process of separation in the recycling application.

4. Conclusion

In summary, a four-layer structure paramagnetic solid-phase nanoextractant, Fe_3O_4@ SiO_2 @ Clpr-silica @ dithizone, is successfully constructed with sphere-like shape around 500 nm. The extractant can rapidly absorb Pb^{2+} ion from diluted wastewater with adsorption capacity beyond 63.4 mg g^{-1} at room temperature. Pb^{2+} ion can also be quickly eluted from the extractant by 2 mol L^{-1} HNO_3 solution. The extractant has high reusability and its removal efficiency and desorption efficiency still keep above 95 and 97% after five cycles, respectively. Meanwhile, the extractant shows good magnetic responding feature, acids stability, and dispersibility in the aqueous system.

It can be anticipated that the adsorption capacity of the extractant should be improved with the increase of chemisorption group and decrease of magnetic nanoparticles size. Meanwhile, it is important to find effective active groups bonded to magnetic nanomaterial for selectively absorbing of special heavy metal ion.

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