Acetylacetone functionalized magnetic carbon microspheres for the highly-efficient adsorption of heavy metal ions from aqueous solutions

Jie Ma, Mengya Sun, Yulan Zeng, Zhenhua Liu, Manman Zhang, Yao Xiao and Shuping Zhang

Herein, Acac-C@Fe3O4, a magnetic carbon (C@Fe3O4) modified with acetylacetone (Acac), was first prepared and used as a solid-phase adsorbent for adsorbing some heavy metal ions from aqueous solution. The adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), vibrating sample magnetometry (VSM) and BET studies. Some parameters affecting the adsorption and desorption processes were studied in Pb2+ solution, including sample pH, contact time, initial concentration, type and connection of the desorption solution. Adsorption results showed that removal of Pb2+ was 100% under optimal conditions at an initial concentration of 10.0 mg L\textsuperscript{−1}. The adsorption mechanism conformed well to a pseudo-second order kinetic model. The adsorption capacity of the sorbent also showed promising results with Hg2+, Cr3+, Fe2+, Cd2+, Mn2+, Zn2+, Cu2+ and Pb2+, where maximum adsorption capacities reached 98.0, 151.2, 188.9, 202.2, 286.3, 297.2, 305.1 and 345.3 mg g\textsuperscript{−1}, respectively. The Acac-C@Fe3O4 microsphere material was successfully applied to the adsorption of heavy metal ions in aqueous solution.

Introduction

With the growth of industrial activities, the phenomenon of highly toxic heavy metal ions release to water resources becomes more and more serious.\textsuperscript{1} Heavy metals are difficult to biodegrade and can be enriched hundreds of times during biological amplification of the food chain before entering the human body. Eventually, they will make proteins and enzymes inactive and also cause chronic poisoning.\textsuperscript{2} Thus, it becomes even more necessary to establish a facile and reliable method to deal with environmental pollution of heavy metal ions. Over decades, several technologies have been developed to remove heavy metal ions from wastewaters such as chemical precipitation (including hydroxide precipitation,\textsuperscript{3} sulphide precipitation\textsuperscript{4} and chelating precipitation\textsuperscript{5}), ion exchange,\textsuperscript{6} membrane filtration (including ultrafiltration,\textsuperscript{7} reverse osmosis and nanofiltration\textsuperscript{8} and electrodialysis\textsuperscript{9}), coagulation and flocculation,\textsuperscript{10} flotation,\textsuperscript{11} electrochemical treatment\textsuperscript{12} and adsorption.\textsuperscript{13} Adsorption methods draw more attention, because they are simple to pursue without additional consumption, high performing and cost-effective.

With all of the absorbing materials, magnetic nanomaterials are different from others as they can be collected by external magnetic fields.\textsuperscript{14} This performance provides both adsorption and desorption post-processing for convenience. Meanwhile, low-cost nanosized ferric oxides (Fe3O4 or γ-Fe2O3) possess non-toxicity and superparamagnetism and therefore they have gained even more interest.\textsuperscript{15} Aggregation of these particles can be regulated and controlled by a surface modified process and so far abundant materials have been used as a modified layer including silicon, carbon, synthetic polymers and metals. Among these materials, carbon-based materials are popularly selected because they are easily synthesized and eco-friendly, especially when they have numerous hydrophilic groups and can provide favourable conditions for further modification.\textsuperscript{16} Wang et al. prepared two different structures of carbon-coated Fe3O4 for lithium storage; both composite materials have good performance and represent a good future for applications. There are also many applications of Fe3O4/C nanomaterials in the environmental treatment fields.\textsuperscript{17} Liu et al. designed 1D Fe3O4/C/CdS coaxial nanochains for the degradation of RhB.\textsuperscript{18} Bystrzewski et al. prepared carbon-encapsulated magnetic nanoparticles to adsorb Cu2+, Co2+ and Cd2+ and their adsorption capacities were 3.21, 1.23 and 1.77 mg g\textsuperscript{−1}, respectively.\textsuperscript{19} Chen et al. synthesized magnetic core–shell Fe3O4@C nanoparticles with SO3H–COOH groups modified for adsorbing Pb2+, Hg2+ and Cd2+ ions and their maximum adsorptions were 90.7, 83.1 and 39.7 mg g\textsuperscript{−1}, respectively.\textsuperscript{20} The above-mentioned carbon coated magnetic nanomaterials could be used to adsorb heavy metal ions, but their absorption
capacities are limited, which may be improved by some new methods.

In order to improve adsorption properties of adsorbents, some chelate molecules, especially multideterminate ligands, were selected to modify nanomaterials, such as ethylenediamine tetraacetic acid (EDTA), ethanediamine (EDA) and acetylacetone (Acac), which showed strong coordination with metal ions. Among them, the Acac molecules are superior to other molecules because their active hydrogen and the dicarbonyl structures can be retained during the modification process.\textsuperscript{24} In this work, the magnetic carbon composite (C@Fe\textsubscript{3}O\textsubscript{4}) was synthesized by a hydrothermal method and functionalized with Acac for adsorbing heavy metal ions in an aqueous solution. Behaviours of the adsorption in different analytical conditions and performance under optimized conditions were investigated by FAAS determination. Meanwhile, the adsorption capacities of the as-prepared composites for Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Mn\textsuperscript{2+}, Cd\textsuperscript{2+}, Fe\textsuperscript{2+}, Hg\textsuperscript{2+} and Cr\textsuperscript{3+} were measured and had ideal results. Thus the Acac modified C@Fe\textsubscript{3}O\textsubscript{4} microspheres (Acac-C@Fe\textsubscript{3}O\textsubscript{4}) may be used in the metal ion wastewater treatment.

**Experimental**

**Materials**

All reagents were of analytical grade including FeCl\textsubscript{3}·6H\textsubscript{2}O, Pb(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, FeSO\textsubscript{4}·7H\textsubscript{2}O, CuSO\textsubscript{4}·5H\textsubscript{2}O, ZnCl\textsubscript{2}, HgCl\textsubscript{2}, CrCl\textsubscript{3}·6H\textsubscript{2}O, MnSO\textsubscript{4}, CdCl\textsubscript{2}·2.5H\textsubscript{2}O, NaOH, CH\textsubscript{3}COONa, ethylene glycol (C\textsubscript{2}H\textsubscript{6}O\textsubscript{2}), \( \rho \) (+) glucose monohydrate (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}, C\textsubscript{2}H\textsubscript{6}O\textsubscript{2}, H\textsubscript{2}O), ethanediamine (C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}), (3-chloropropyl) triethoxysilane (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}Si, KH\textsubscript{23}O), acetylacetone (Acac), and HCl solution and all were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China). A target stock solution of Pb\textsuperscript{2+} with 1000.0 mg L\textsuperscript{-1} was prepared by dissolving proper amounts of Pb(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and nitric acid in distilled water. Then the solution was further diluted to the given concentrations for testing adsorption capacity and analysing the pre-concentration process.

**Instrumentation**

The morphology of a sorbent was detected by a field emission scanning electron microscope (SEM, VEGA3 TESCAN, CZ) and a transmission electron microscope (TEM, H800EM Hitachi, JP). Surface area was measured by a BET instrument (TriStar 3020 Micromeritics, CN). XPS spectra were measured by an X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, CN). A Fourier transform infrared spectrophotometry analysis was performed using a FTIR spectrophotometer (FTIR, Nicolet, USA) equipped with a KBr beam splitter. X-ray diffraction patterns of the samples were recorded by an X-ray powder diffractometer (XRD, D8 advance, DE). Magnetic properties of the sorbent were tested using a vibrating sample magnetometer (VSM, EZ-VSM, MicroSense, USA) at room temperature. Concentrations of metal ions were measured using a flame atomic absorption spectrophotometer with air-acetylene (FAAS, TAS990, China). A digital pH meter was used for pH adjustment of the solutions.

**Preparation of Acac-C@Fe\textsubscript{3}O\textsubscript{4}**

The synthetic process is shown in Scheme 1. First, a solvothermal method was adopted for synthesizing Fe\textsubscript{3}O\textsubscript{4} magnetic composites according to a previously reported procedure.\textsuperscript{22} In a typical procedure, 36 mmol of FeCl\textsubscript{3}·6H\textsubscript{2}O and 200 mmol of CH\textsubscript{3}COONa were dissolved in 350.0 mL ethylene glycol. The mixture was sonicated for 30 min and then stirred at room temperature for 2 h. Afterward, the homogeneous solution was transferred into a 500 mL Teflon-lined stainless-steel autoclave and reacted at 200 °C for 10 h followed by cooling down to room temperature naturally. The product was washed with ethanol and distilled water for several times, and then dried in a vacuum freeze-drying apparatus for 5 h.

Secondly, C@Fe\textsubscript{3}O\textsubscript{4} was prepared by a facile hydrothermal method.\textsuperscript{23,24} Concretely, 0.5 g Fe\textsubscript{3}O\textsubscript{4} nanoparticles were dispersed in 0.1 mol L\textsuperscript{-1} HNO\textsubscript{3} solution and sonicated for 10 min, then were rinsed with distilled water several times until neutral. Subsequently, 8.2 g glucose was dissolved in 80.0 mL distilled water, followed by the addition of 0.5 g Fe\textsubscript{3}O\textsubscript{4} under sonication. The pH value of the mixture was adjusted to 8.0 by a 0.1 mol L\textsuperscript{-1} NaOH solution. Afterwards, the mixture solution was transferred into a Teflon-lined stainless-steel autoclave (100 mL capacity) and heated at 170 °C for 4 h. The precipitate was washed with distilled water for several times and dried in a vacuum freeze-drying apparatus for 5 h, and then the carbon coated Fe\textsubscript{3}O\textsubscript{4} nanomaterials were obtained.

Thirdly, 1.0 g C@Fe\textsubscript{3}O\textsubscript{4} was dissolved in 100.0 mL water–ethanol under mechanical stirring. Then, 1.0 mL ammonia (25%) and 3.0 mL KH\textsubscript{2}3O\textsubscript{4} were added dropwise to the reaction mixture under constant stirring at 45 °C. After 1 h, the reaction mixture was heated to 60 °C and stirred constantly for 1 h, and then cooled to room temperature. Finally, the magnetic samples (KH\textsubscript{2}3O·C@Fe\textsubscript{3}O\textsubscript{4}) were isolated by using an external magnet, washed thoroughly with distilled water and ethanol several times, and then dried in a vacuum freeze-drying apparatus.

Finally, 1.0 g NaOH was dissolved in 10.0 mL distilled water and then was added to 40.0 mL ethanol in an ice-water bath, 10.0 mL Acac was added into the mixture, followed by 1.0 g KH\textsubscript{2}3O·C@Fe\textsubscript{3}O\textsubscript{4} which was dispersed into the suspension under constant stirring for 0.5 h. Then the mixture was heated to 33 °C for 7 h. The sample was separated using an external magnetic field and washed several times with distilled water and ethanol and dried in a vacuum freeze-drying apparatus. Finally, Acac-C@Fe\textsubscript{3}O\textsubscript{4} composites were prepared successfully.

**Adsorption procedure**

Aqueous solutions with different Pb\textsuperscript{2+} concentrations were prepared and adjusted to a given pH value by HCl and NaOH, and then 5.0 mg sorbent was dispersed into the above solution (25.0 mL). The time dependence of the adsorption capacity was also examined as a function of contact time from 1 to 8 min at room temperature using 25.0 mL of Pb\textsuperscript{2+} solution (20.0 mg g\textsuperscript{-1}) mixed with 5.0 mg of sorbent. The Pb\textsuperscript{2+} concentration of a sample was measured by FAAS. The adsorption capacity of the material for Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Mn\textsuperscript{2+}, Cd\textsuperscript{2+}, Fe\textsuperscript{3+}, Hg\textsuperscript{2+} and Cr\textsuperscript{3+} were researched under the same conditions. The adsorption process is shown in Fig. 1.
Result and discussion

Characterization of the magnetic microspheres

VSM analysis. Fig. 2a depicts the magnetization hysteresis loops of typical samples including Fe₃O₄, C@Fe₃O₄ and Acac-C@Fe₃O₄ microspheres at room temperature. The curves indicated that all prepared samples had superparamagnetic properties with negligible magnetic remanence and coercivity. Saturation magnetization of samples decreased from 30 to 14 emu g⁻¹ with an increase of coating layer which showed that the obtained samples had enough magnetic response characteristics to meet magnetic separation process.

Meanwhile, the coercivities of samples were almost stable below 20 Oe. The above suggested the modified layer did not affect the superparamagnetic feature of the composites, but just reduced the saturation magnetization of a sample due to the decreased content of Fe₃O₄ component in the microspheres.

X-ray diffraction analysis. The XRD patterns of Fe₃O₄, C@Fe₃O₄ and Acac-C@Fe₃O₄ magnetic particles are presented in Fig. 2b. The similar diffraction peaks of all patterns, including 30.1°, 35.5°, 43.0°, 53.6°, 57.0° and 62.6°, indicated the crystal structures of all composites were coincided with a Fe₃O₄ standard specimen as a cubic spinel structure (JCPDS, no. 19-0629). The X-ray diffraction patterns of C@Fe₃O₄ and Acac-C@Fe₃O₄ were similar with the pattern of Fe₃O₄ magnetic particles, which illuminated that they had the same crystal structure and it was not changed during the modification procedures.

FTIR analysis. Composition of the Acac-C@Fe₃O₄ composite was further characterized by FT-IR spectrophotometry, and the relevant results are shown in Fig. 2c. The specific stretching vibration absorption peak of Fe-O in Fe₃O₄ was obviously visible in four spectra at 586 cm⁻¹, which indicated all samples contained Fe₃O₄. The peaks at 1623 cm⁻¹ and 1689 cm⁻¹ were attributed to C≡C and C=O vibrations and illustrated that carbon was successfully coated on the magnetic core. Meanwhile, the absorption peak at 3434 cm⁻¹ implied the existence of residual hydroxyl groups, which confirmed that some hydrophilic groups (-OH) and carbonyl group (-C=O) remained after the process of hydrothermal carbonization treatment. The peak at 802 cm⁻¹ shown in Fig. 2c indicated the existence of C-Cl groups and suggested that KH230 were grafted on the surface of C@Fe₃O₄ composites. Curves of Acac-C@Fe₃O₄, KH230-C@Fe₃O₄ and Fe₃O₄ are compared and shown in Fig. 2c and the enhancement of a peak at 1623 cm⁻¹ is attributed to the carbonyl stretching vibration while the peak at 2915 cm⁻¹ indicated the existence of -CH₃ of Acac. These FTIR data indicated that Acac successfully functionalized the C@Fe₃O₄ magnetic microspheres.

BET analysis. The ratio surface areas of Fe₃O₄ and Acac-C@Fe₃O₄ were analyzed by nitrogen adsorption–desorption techniques. As Fig. 2d shows, the nitrogen adsorption–desorption isotherms of Fe₃O₄ and Acac-C@Fe₃O₄ have representative type-IV curves. The hysteretic loop in the range of 0.6–0.9 P/P₀ is a type of H1 hysteresis. The BET specific surface area of Acac-C@Fe₃O₄ was measured to be 68.41 m² g⁻¹, which is higher than that of Fe₃O₄ (37.41 m² g⁻¹). This change might be

Fig. 1 Schematic diagram of the adsorption process.
attributed to the porous structure of Acac-C@Fe₃O₄ coming from carbon coating.

**XPS analysis.** The surface element composition of Acac-C@Fe₃O₄ was determined by XPS spectra. As shown in Fig. 3a, the elements of Fe, C, O, and Si were detected on the surfaces of the nanocomposites. The signals of Fe and Si were weaker than that of C, indicating that the Fe₃O₄ core is coated completely by the carbon shell and a small amount of KH₂₃O₇ was modified. The high-resolution XPS spectrum of Fe 2p can be fitted into two main doublet peaks, as shown in Fig. 3b. In the high-resolution spectrum, it can be seen that the doublet peak at 710.8 eV and 724.2 eV are assigned to Fe 2p₃/2 and Fe 2p₁/2, which can be attributed to Fe(II) and Fe(III) of the Fe₃O₄ core. These results were consistent with the XRD analysis. In Fig. 3c, there are more than one chemical state of C in the C 1s region; there peaks were identified and assigned to C–C and C–H (284.8 eV), C–O (286.5 eV), and C≡O species (288.4 eV), respectively. These may be ascribed to a carbon shell and acetylacetone. The XRD results and previous conclusions were combined and provide supportive evidence for the successful modification of carbon and Acac.

**SEM and TEM analysis.** Morphology and structures of the Fe₃O₄, C@Fe₃O₄ and Acac-C@Fe₃O₄ microspheres were characterized by scanning electron microscopy and transmission electron microscopy. Fig. 4 indicated the as-prepared Fe₃O₄ materials were monodispersed microspheres, which were further proved by the relative TEM image of Fe₃O₄ shown in Fig. 5. The average size of a microsphere is about 260 nm. Fig. 4 also confirmed that the Acac-C@Fe₃O₄ sample still kept spherical morphology with a broader size distribution. The particle distribution range increased slightly, and the average of size of a microsphere increased to 400 nm. The increase of particle sizes and edges of C@Fe₃O₄ and Acac-C@Fe₃O₄ looked like a light shadow layer should be attributed to the carbon coating on the surface of the magnetic core, which was confirmed directly by the TEM image in Fig. 5. This further indicated that the Acac-C@Fe₃O₄ composite was prepared successfully.

**Optimization of pre-concentration conditions**

**Effect of pH.** Acidity of a solution shows strong influence on the adsorption capacity of the adsorbent. To detect influence of the acidity of a solution, Pb²⁺ was used as the target ion, and the adsorption process was performed at 25 °C for about 20 minutes. The pH of the solution was set in a range from 2.0 and 10.0, and concentrations and amounts of solutions were given at 20 mg L⁻¹ and 25.0 mL in turn with the same amounts of sorbent. The relevant results are shown in Fig. 6a. The curves obviously indicated the absorptivity of C@Fe₃O₄ was more than Fe₃O₄ microsphere in a set range and this may be due to the porous structure of the carbon layer where there are rich oxygenic groups on the surface. The absorptivity of Acac-C@Fe₃O₄ was higher than C@Fe₃O₄. The absorptivity of Acac-C@Fe₃O₄ was raised from 25% to 90% with pH values from 2.0 to 6.0 and it slightly declined when the pH changed from 6.0 to 9.0 so the absorptivity was obviously decreased with a pH beyond 9.0. The above indicated that the proper pH range should be controlled between 6.0 and 9.0 for better performance of the adsorbent. Compared with the three curves, the result should be attributed to Acac modified on the surface of C@Fe₃O₄ composites. Acac has convertible enolyl and dicarbonyl structures with the change in acidity. It is beneficial to resist acidity, which helps to form coordination with lead ions. However, the maximum absorptivity of Fe₃O₄ and C@Fe₃O₄
microspheres ca. 80% appeared at an acidity around 8.0. Since Pb$^{2+}$ ions can precipitate under basic conditions, this cannot indicate the as-prepared Fe$_3$O$_4$ microsphere are a suitable lead ion absorbent although the adsorption capacity is higher in an alkaline setting.

**Effect of adsorption time.** Adsorption time is an important factor in the application of the as-prepared sorbent. Fig. 6b demonstrates the results about absorptivity versus adsorption time at given conditions including the pH at 6.0, temperature at 25 °C and concentration of Pb$^{2+}$ at 20 mg L$^{-1}$. These three curves indicated that the absorptivity increased rapidly within 7 min but after that it remained almost unchanged. The adsorption equilibrium of the adsorbing system was reached after around 7 minutes, which suggests the Acac-C@Fe$_3$O$_4$ adsorbent can achieve the maximum adsorption efficiency within 7 minutes in the testing system, and the adsorption rate of lead ions under the conditions investigated was more than 90%. Relatively, the adsorption rate of lead ions was 61% absorbed by the C@Fe$_3$O$_4$ microsphere and only 54% by naked Fe$_3$O$_4$ at the same time. Above indicated that the as-prepared Acac-C@Fe$_3$O$_4$ adsorbent had excellent capacity for lead ions, so it could reach the absorption equilibrium quickly. It is beneficial to use the sorbent in the field of separation of heavy metal ions. As the initial concentration of lead ions was raised, the adsorption amount of Acac-C@Fe$_3$O$_4$ sorbent also increased gradually and reached to a maximum value greater than 345.3 mg g$^{-1}$ with a lead ion concentration at 70 mg L$^{-1}$, thus basically remaining unchanged. Meanwhile, the adsorption capacity of C@Fe$_3$O$_4$ and Fe$_3$O$_4$ microspheres only reached 205.0 mg g$^{-1}$ and 138.4 mg g$^{-1}$, respectively. The maximum adsorption amount of Acac-C@Fe$_3$O$_4$ was obviously higher than C@Fe$_3$O$_4$ and the naked Fe$_3$O$_4$ compared to the three curves. This indicated the saturated adsorption capacity of the Acac-C@Fe$_3$O$_4$ can be acquired with a lead ion concentration beyond 70.0 mg L$^{-1}$. Because all available adsorption sites of as-prepared sorbent were occupied by ions in a high concentration ion solution, it cannot achieve more amounts of ionic adsorption. This suggested the adsorption process should belong to chemical absorption.

**Adsorption kinetics study.** An adsorption isotherm expresses the relationship between adsorption capacity and time equilibrium. The experimental data were obtained by detecting the adsorbing amount with a series of given adsorbing times with the concentration of Pb$^{2+}$ ions at 70 mg L$^{-1}$. The corresponding data were calculated according to two Langmuir isotherm model formula including pseudo-first-order (1) and pseudo-second-order eqn (2):  

$$
\log (Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303}
$$  \hspace{1cm} (1)

$$
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}
$$  \hspace{1cm} (2)

where $Q_e$ and $Q_t$ refer to the adsorption amount of Pb$^{2+}$ at equilibrium and time $t$, respectively, and $k_1$, $k_2$ are the rate constants of pseudo-first-order and pseudo-second-order.

According to the model formula, two linear fitting curves and equations are separately shown in Fig. 6d. The analysis results suggested that the pseudo-second-order model ($R^2 = 0.9915$) provided a better description of the Pb$^{2+}$ adsorption isotherm process than the pseudo-first-order model based on the fitted correlation coefficients ($R^2 = 0.996$ for the second order and 0.933 for the first order model). These results further suggested the adsorbing process belongs to a chemical process.

**Adsorption of other heavy metal ions.** Due to Acac having a strong coordination capacity with many metal ions, the sorption capacity of the as-prepared absorbent for various common metal ions (Hg$^{2+}$, Cr$^{3+}$, Fe$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$) were investigated in parallel under the same conditions. The concentration of all them was given at 70 mg L$^{-1}$ with the same optimal conditions as the Pb$^{2+}$ adsorbing procedures. All data are shown in Fig. 7. This showed that the adsorbing capacities of the Acac-C@Fe$_3$O$_4$ sorbent on Hg$^{2+}$, Cr$^{3+}$, Fe$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ were 98.0, 151.2, 189.9, 202.2, 286.3, 297.2 and 305.1 mg g$^{-1}$, respectively. These results illustrated that the Acac-C@Fe$_3$O$_4$ composites can be applied as a highly efficient sorbent for absorbing some common metal ions, which was beneficial for enriching some metal ions in aqueous solution. In order to measure the quality of the prepared adsorbents, saturated adsorbents were compared with some reported metal ion adsorbents and are shown in Table 1. These data indicated that the as-prepared Acac-C@Fe$_3$O$_4$ adsorbent presented outstanding advantages in adsorption capacity which should be attributed to the functionalization of Fe$_3$O$_4$ microspheres by Acac and carbon.

**Regeneration of the sorbent**

**Selection of a desorption solution.** Regeneration property and method are important parameters to evaluate an adsorbent. Regeneration of the Acac-C@Fe$_3$O$_4$ composite materials was investigated. First, the type of desorption solution was...
selected from four kind of common solutions (H₂SO₄, HNO₃ and HCl at 1 mol L⁻¹ and EDTA at 0.5 mol L⁻¹). They were used to desorb Pb²⁺ from the magnetic sorbent and the desorption efficiencies of them are shown in Fig. 8a. This proved that a HCl solution was the most suitable for use for desorption because it had the highest effective desorption among those tested. On this basis, the influence of the concentration of a HCl solution was further explored and the data are shown in Fig. 8a. With an increase of the HCl concentration desorption efficiency increased as the solution concentration changed from 0.2 to 2.0 mol L⁻¹, and then the desorption efficiency decreased slightly. The above results indicated that desorption solution acidity was an important factor for desorbing lead ion from the as-prepared magnetic sorbent. The coordination sites with Pb²⁺ were more and more occupied by H⁺ with increased concentration of the HCl solution, so high acidity was an advantage to regenerate the sorbent. However, when concentration of desorption solution was beyond 2.0 mol L⁻¹, the desorption performance could keep a high level, but the colour of the desorption solution changed to pale yellow, which might be due to Fe³⁺ ion being generated and suggesting that Acac-C@Fe₃O₄ materials were damaged in a high acidic setting. So, the concentration of the HCl solution used as a desorption solution should be controlled between 1.0 and 2.0 mol L⁻¹ when desorption efficiency of Acac-C@Fe₃O₄ sorbent is beyond 95%.

Meanwhile, the effects of HCl solution volume and desorption time on desorption were also studied. The desorbed efficiency was observed higher with the increase of HCl solution volume under 50.0 mL as shown in Fig. 8b. There was no change when the volume was more than 50.0 mL. Hence, 50.0 mL desorption solution was used in subsequent research. The desorbed time also affects the desorption process. Fig. 8c showed the recovery of the lead ions was up to 97% when the desorbed time was 5 min. And then, the desorption efficiency kept stable even if time was increased. So we choose 5 min as optimum desorption.

Reuse studies. The reusability of a sorbent is crucial in practical applications. Fig. 8d indicated the results from five time’s consecutive adsorption–desorption cycles of Pb²⁺ on the Acac-C@Fe₃O₄ microspheres. The desorption efficiency still maintained beyond 90% after 5 times which clearly indicated that absorption capacity just decreased slightly and this decrease of sorption efficiency may be ascribed to loss of adsorbents in a recycled application. The above experimental results suggest our as-prepared Acac-C@Fe₃O₄ microspheres sorbent possess fine reusability.

Conclusions

An Acac-C@Fe₃O₄ magnetic adsorbent was successfully prepared by a simple and sustainable procedure and its structure and properties were detected via numerous instrumental
measurements. The adsorbent demonstrated outstanding adsorption capacity for some metal ions. Under given conditions, the maximum adsorption capacities for Hg$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Cd$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cu$^{2+}$ and Pb$^{2+}$ were 98.0, 151.2, 188.9, 202.2, 286.3, 297.2, 335.1 and 345.3 mg g$^{-1}$, respectively. The adsorption process reached adsorption equilibrium within 7 min and conforms to a pseudo-second-order kinetics model. The adsorbent had excellent stability and reusability. The Acac-C@Fe$_3$O$_4$ magnetic adsorbent may provide an alternative for adsorption process reached adsorption equilibrium within 286.3, 297.2, 335.1 and 345.3 mg g$^{-1}$, respectively. Used as a substrate and in the further synthesis of metal ions in aqueous solutions. What's more, the material can be applications in the adsorption and separation of heavy metal ions in aqueous solutions. What's more, the material can be used as a substrate and in the further synthesis of metal-organic frameworks.

Conflicts of interest

There are no conflicts to declare.

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