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β -Cyclodextrin stabilized magnetic Fe_3S_4 nanoparticles for efficient removal of Pb(II) †

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In this study, magnetic β -cyclodextrin stabilized Fe_3S_4 nanoparticles (CD- Fe_3S_4) were fabricated via a facile one-step route. The as-prepared CD- Fe_3S_4 exhibited a high Pb(II) adsorption capacity of 256 mg g^{-1} , and it also showed a surprisingly efficient adsorption toward Zn(II) , Cd(II) , and Cu(II) . XRD, FTIR and XPS analyses suggested that the mechanisms governing Pb(II) removal by CD- Fe_3S_4 were precipitation (formation of galena) and surface adsorption. Additionally, the magnetic properties of the synthesized Fe_3S_4 nanoparticles allow fast separation of sorbents from water. The sorption kinetic data were well-described by a pseudo-second-order model, whereas the adsorption isotherms followed a Langmuir isotherm model. Our experimental results proved that the β -cyclodextrin stabilized Fe_3S_4 could be a promising candidate for the removal of Pb(II) from water via simultaneously taking advantage of its magnetic properties and high affinity for heavy metals.

Introduction

Lead is a persistent and highly toxic heavy metal existing in aquatic ecosystems. It has attracted global concerns due to its adverse effects on natural ecosystems and human health via bioaccumulation and biomagnification in the food chain.^{1,2} Therefore, various technologies have been developed for the extraction of Pb(II) from wastewater, including adsorption,^{3,4} flocculation,⁵ membrane filtration,⁶ and chemical precipitation.⁷ Adsorption has been considered to be a promising technology due to its ease of operation and cost-effectiveness.⁸ Despite the fact that multiple adsorbents have been achieved, developing materials with high-performance and easy-separation still remains challenging.

In response to these challenges, various new materials have been developed.^{9–16} Among these materials, magnetic nano-adsorbents (particularly Fe_3O_4) with various surface modifications have been extensively studied because of their small size, large surface area, and convenient separation.^{11–16} Recently, we reported a magnetic adsorbent, magnetic biochar/ZnS nanocomposite, which showed a high maximum adsorption capacity for Pb(II) based on the cation exchange of ZnS nanocrystals and it can be easily separated from water by a magnet after adsorption.¹⁷ Although Zn^{2+} is less toxic than Pb^{2+} and Hg^{2+} , it still may pose a threat of Zn^{2+} release by cation exchange to the treated water,¹⁸ which restricted its large-scale application in wastewater remediation. Owing to their high affinity to heavy metal ions

similar to that of ZnS, but more environmentally friendly nature, iron sulfides can be a suitable alternative to ZnS nanocrystals as promising adsorbents. Previous reports showed that nanoscale iron sulfide adsorbents (FeS and FeS_2) exhibited superior removal capacity for divalent metals (such as Hg(II) , Cu(II) , Cd(II) , and Pb(II)).^{19–22} But similar to ZnS nanocrystals, these iron sulfide nanostructures also suffered from difficult-separation.

Unlike the nonmagnetic nature of FeS and FeS_2 , nanoscale Fe_3S_4 shows excellent magnetic properties as its counterpart oxide (Fe_3O_4),^{23–25} which is widely employed in biomedicine²³ and electrochemistry.^{24,25} It may be an ideal candidate for Pb(II) removal via simultaneously taking advantage of its magnetic properties and high affinity for heavy metals. To the best of our knowledge, rare efforts have been spent on the decontaminate potential of Fe_3S_4 previously.²⁶

Herein, we present a facile one-pot route to the preparation of β -cyclodextrin (β -CD) stabilized Fe_3S_4 nanoparticles (NPs) with excellent sorption capacity and separation properties. In our system, Fe_3S_4 plays dual-functional roles as an adsorbent and a magnetic separator, and β -CD is used to avoid the agglomeration of Fe_3S_4 . The properties of Fe_3S_4 NPs were characterized with the aid of TEM, XRD, SVM, FTIR and TGA analyses. Batch experiments were conducted to confirm the selective sorption of Fe_3S_4 for Pb(II) in the presence of Ca(II) , Mg(II) , Zn(II) , Cd(II) , and Cu(II) , respectively. The major mechanisms of Pb(II) removal by CD- Fe_3S_4 were determined by a combination of XRD, FTIR, and XPS analyses.

Experimental section

Materials

Ethylene glycol (EG, >99%), thioacetamide (>99%), β -cyclodextrin (β -CD, 98%) (the chemical structure is shown in Fig. 1), and

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lead nitrate (>99%) were purchased from Aladdin Chemical (Shanghai, China). Ferric acetylacetonate ($\text{Fe}(\text{acac})_3$, 99%) was provided by Energy Chemical (Shanghai, China). All chemicals were used without any further purification in the experiments. Distilled water (DI) (>18 M Ω cm) was used for preparing the $\text{Pb}(\text{II})$ solution.

Synthesis of Fe_3S_4 nanocrystals

In a typical procedure, 1.2 mmol of $\text{Fe}(\text{acac})_3$, 50 mL EG, and a certain amount of β -CD were placed into a 100 mL three-neck flask under magnetic stirring. The resulting mixture was heated to 160 °C for 0.5 h, and then thioacetamide EG solution (0.012 g mL⁻¹, 10 mL) was injected continuously into the reaction solution for 0.5 h by using a syringe pump at 160 °C. The mixed solution was kept stirring for 2 h at the temperature. Noticeably, the whole procedure was carried out in the atmosphere of flowing nitrogen. After magnetic separation, the black mixture was washed with water and ethanol several times and dried in a vacuum overnight at 60 °C. In this work, different amounts of β -CD (0, 1.2, and 2.4 mmol) were used in the synthesis procedure, and the obtained samples were labeled as Fe_3S_4 , $\text{CD}_1\text{-Fe}_3\text{S}_4$, and $\text{CD}_2\text{-Fe}_3\text{S}_4$, respectively.

Characterization

Morphologies of the samples were characterized using a transmission electron microscope (TEM, JEM-2100F operating at 200 kV). The X-ray diffraction (XRD) patterns were recorded by using a Shimadzu XRD-6100 diffractometer. Fourier transform infrared (FTIR) spectra were collected by using a Thermo Nicolet 6700 spectrometer (USA) over the wavenumber range of 4000–400 cm⁻¹, using KBr as a reference. Thermogravimetry analysis (TGA) was conducted on a Mettler Toledo analyzer from 30 °C to 600 °C at a heating rate of 10 °C min⁻¹ with an Ar flow rate of 50 mL min⁻¹. The magnetic properties were obtained using a physical property measurement system (PPMS-9T, EC-II, Quantum Design/USA). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra-DLD spectrometer with a monochromatic Al K α radiation source ($h\nu = 1486.6$ eV).

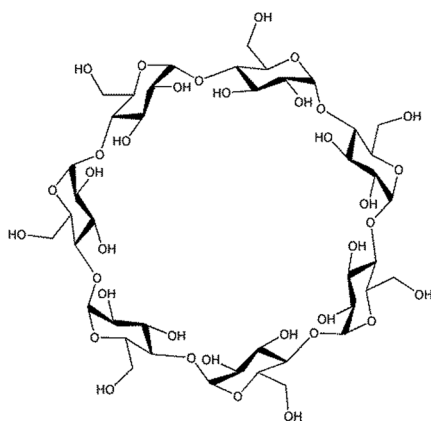


Fig. 1 The chemical structure of β -CD.

Adsorption experiments

To determine the optimum pH for $\text{Pb}(\text{II})$ adsorption experiments, the influence of solution pH on adsorption was examined first. The sorption tests were conducted under different pH conditions (2.0–6.0) adjusted using 0.1 M HNO_3 and 0.1 M NaOH . An adsorbent (20 mg) was added to 40 mL of 100 mg L⁻¹ $\text{Pb}(\text{II})$ solution under continuous stirring at 25 °C for 24 h.

For kinetic studies, the pH was fixed at the obtained optimum value. A typical adsorption experiment was performed in vials by mixing 30 mg of sorbent with 50 mL of $\text{Pb}(\text{II})$ solution (100 mg L⁻¹) under continuous stirring at 25 °C. Solution was sampled and filtered through a 0.22 μm membrane to determine the $\text{Pb}(\text{II})$ concentration at certain time intervals.

Adsorption isotherm experiments were conducted by adding 20 mg of sorbent to 40 mL $\text{Pb}(\text{II})$ solution with concentrations ranging from 5 to 500 mg L⁻¹. The vials were sealed and shaken for 24 h to attain the equilibrium state. The amount of $\text{Pb}(\text{II})$ adsorbed on the adsorbent under equilibrium conditions was obtained from the following equation:

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

where C_0 and C_e are the initial and equilibrium concentrations of $\text{Pb}(\text{II})$ solution (mg L⁻¹), respectively; V is the volume of $\text{Pb}(\text{II})$ solution (L); m denotes the mass of the sorbent (g).

To test the effect of ion competition, the competing ions (*i.e.*, $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Cu}(\text{II})$) were separately added into the tested $\text{Pb}(\text{II})$ solution. The tests were conducted at the competing ion concentration of 0.48 and 0.96 mM, respectively. A control test was conducted in the absence of competing ions and otherwise identical to the conditions described above.

The residual concentration of $\text{Pb}(\text{II})$ in the filtrates was analyzed using an atomic adsorption spectrometer (ControlAA 700, Analytik Jena AG, Germany). The filtered adsorbent was then dried in a vacuum and investigated to identify the removal mechanisms. To avoid oxidation of the NPs, the $\text{Pb}(\text{II})$ solutions were purged with purified N_2 (>99%) for 10 min to remove dissolved oxygen before use.

Results and discussion

Characterization

The structure and morphology of the Fe_3S_4 NPs prepared with or without β -CD were examined by XRD, TEM, FTIR, and TGA analyses. Fig. 2 shows the XRD patterns of Fe_3S_4 and β -CD modified Fe_3S_4 NPs. The diffraction peaks at 25.43°, 29.96°, 36.34°, 47.81°, and 52.36° matched well with the (220), (311), (400), (511), and (440) planes of the standard XRD data for greigite Fe_3S_4 (JCPDS 16-0713), which proved that the Fe_3S_4 NPs were prepared successfully and well crystallized. No obvious differences were observed between bare Fe_3S_4 and β -CD modified Fe_3S_4 NPs, implying that the existence of β -CD did not result in any structure change of Fe_3S_4 . However, the corresponding TEM images (Fig. 3) of the resulting Fe_3S_4 NPs clearly illustrated the morphological differences between the bare Fe_3S_4 NPs and $\text{CD-Fe}_3\text{S}_4$ NPs. For the Fe_3S_4 NPs, a certain degree

of conglomeration was observed (Fig. 3a). While the CD-Fe₃S₄ NPs were monodisperse and exhibited uniform bulk-like shapes perhaps due to the β -CD serving as a surfactant and a stabilizer in the growth of Fe₃S₄ crystals (Fig. 3b and c). This indicated that the existence of β -CD prevented the aggregation of Fe₃S₄ NPs. And the CD₁-Fe₃S₄ NPs have a size ranging from 49 to 122 nm with a statistical average size of 90 ± 16 nm, which was slightly larger than that of the CD₂-Fe₃S₄ NPs (74 ± 14 nm). It seemed that the increasing amount of β -CD corresponded to the decrease of the sizes of CD-Fe₃S₄ NPs. The CD₂-Fe₃S₄ NPs were well crystallized according to the HR-TEM image in Fig. 3d, and the clear lattice fringes with a d -spacing of 0.298 nm would be assigned to the (311) plane of Fe₃S₄. The appearance of an amorphous layer in the HR-TEM image of CD₂-Fe₃S₄ NPs suggested the introduction of β -CD onto the surfaces of Fe₃S₄ NPs.

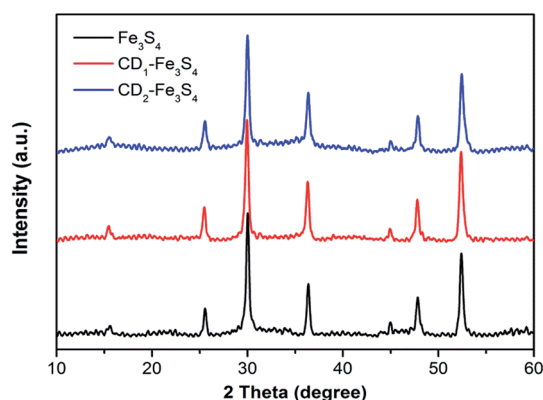


Fig. 2 XRD patterns of Fe₃S₄ NPs with and without β -CD modification.

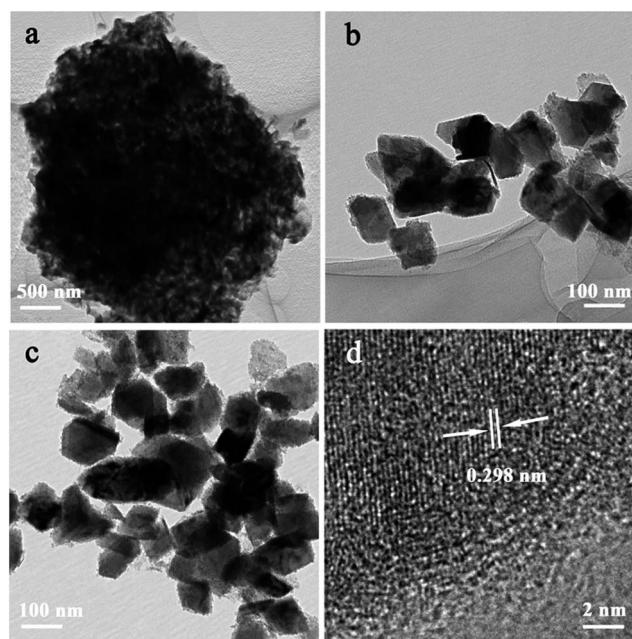


Fig. 3 TEM images of Fe₃S₄ NPs. (a) TEM image of bare Fe₃S₄ NPs. (b) TEM image of CD₁-Fe₃S₄ NPs. (c) TEM image of CD₂-Fe₃S₄ NPs. (d) High-resolution TEM (HR-TEM) image of CD₂-Fe₃S₄ NPs.

Fig. 4 presents the FTIR spectra of β -CD, Fe₃S₄ NPs, and CD₂-Fe₃S₄ NPs. It can be seen that several clear peaks were obtained for CD₂-Fe₃S₄ NPs compared to those of Fe₃S₄ NPs and the characteristic peaks of β -CD exhibited in the spectrum of CD₂-Fe₃S₄ NPs with certain shifts at 1116, 1021, and 915 cm⁻¹, respectively.²⁷ This can be attributed to the surface β -CD modified on Fe₃S₄ NPs. The peaks at 1116 cm⁻¹ and 1021 cm⁻¹ in the spectrum of CD₂-Fe₃S₄ corresponded to the coupled ν (C-C/C-O) stretching vibration and C-O-C.²⁸ The band at 915 cm⁻¹ can be assigned to R-1, 4-bond skeleton vibration.²⁷ In addition, the broad bands at 3390 cm⁻¹ and 1623 cm⁻¹ belong to the O-H valence vibration of primary hydroxyl groups and OH in-plane bending vibration,²⁹ respectively. Notably, the characteristic -OH band shifted from 3368 cm⁻¹ of β -CD to a higher frequency at 3390 cm⁻¹ for the spectrum of CD₂-Fe₃S₄, which suggested that the hydroxyl groups may respond to the link between β -CD and Fe₃S₄.^{30,31} Thus, it could be concluded that β -CD has been introduced onto the surface of the Fe₃S₄ successfully.

Moreover, thermogravimetric analysis further confirmed that the β -CD was successfully introduced onto the Fe₃S₄ NPs (Fig. 5). The thermogravimetric curve of bare Fe₃S₄ NPs shows a weight loss about 0.68% at 150 °C, which can be ascribed to the loss of absorbed water on the sorbent surface. However, a drastic weight loss about 11.50% was observed in the temperature range of 150–600 °C, which can be explained by the thermodynamic meta-stability of Fe₃S₄. This result was similar to the findings that greigite (Fe₃S₄) began to decompose beyond 260 °C under vacuum conditions.³² As for the CD₁-Fe₃S₄ and CD₂-Fe₃S₄, the weight losses showed certain increase compared with that of Fe₃S₄ over the temperature range of 150–600 °C with 14.76% and 17.56%, respectively. The β -CD content of CD₁-Fe₃S₄ and CD₂-Fe₃S₄ was calculated to be 3.69% and 6.85%, which clearly demonstrated the presence of β -CD in CD-Fe₃S₄ NPs.

The magnetization properties of Fe₃S₄ were characterized by using a physical property measurement system at 3 T, and the results are depicted in Fig. 6. The hysteresis loops confirmed that there were no obvious hysteresis and coercivity which illustrated the superparamagnetism of the NPs. Saturation magnetizations of Fe₃S₄, CD₁-Fe₃S₄, and CD₂-Fe₃S₄ were 27.1,

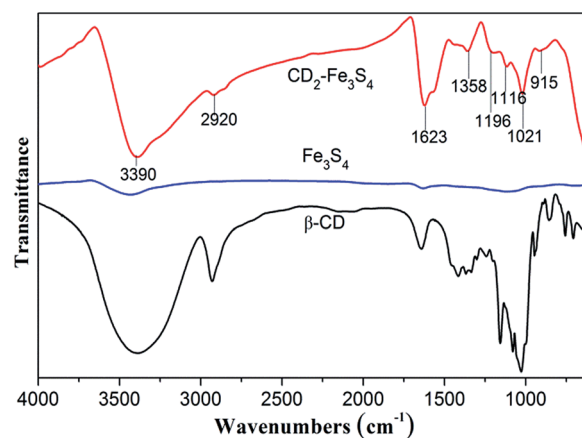


Fig. 4 FTIR spectra of β -CD, Fe₃S₄, and CD₂-Fe₃S₄.

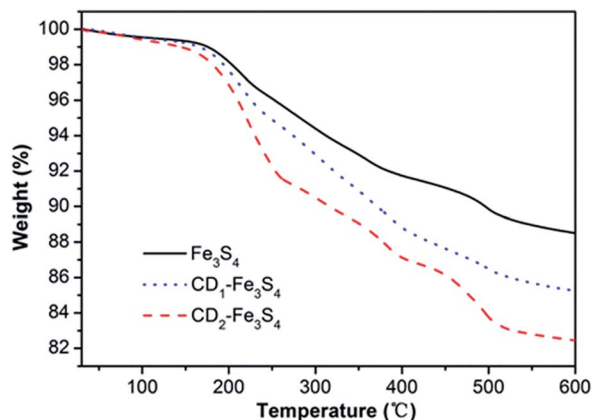


Fig. 5 TGA curves of Fe_3S_4 NPs, $\text{CD}_1\text{-Fe}_3\text{S}_4$ NPs, and $\text{CD}_2\text{-Fe}_3\text{S}_4$ NPs.

35.1, and 31.4 emu g^{-1} , respectively. The lower saturation magnetization of $\text{CD}_2\text{-Fe}_3\text{S}_4$ compared to $\text{CD}_1\text{-Fe}_3\text{S}_4$ should be mainly attributed to the dilution effect of more $\beta\text{-CD}$ coating or the smaller particle sizes of $\text{CD}_2\text{-Fe}_3\text{S}_4$. After Pb(II) adsorption, the magnetization of $\text{CD}_2\text{-Fe}_3\text{S}_4$ was lowered to 26.1 emu g^{-1} which may result from the released Fe ion and Pb(II) adsorption on the surface (the initial Pb(II) concentration was 500 ppm), while the magnetic intensity still can be assured of magnetic separation. We examined the separation properties of $\text{CD}_2\text{-Fe}_3\text{S}_4$ after 24 h of the reaction with 500 mg L^{-1} Pb(II) solution. The $\text{CD}_2\text{-Fe}_3\text{S}_4$ NPs were attracted toward a permanent magnet quickly (inset) which confirmed that the $\text{CD}_2\text{-Fe}_3\text{S}_4$ NPs can be used as magnetic adsorbents.

Effect of pH on Pb(II) adsorption

Fig. 7 shows the influence of pH value on Pb(II) adsorption by $\text{CD}_2\text{-Fe}_3\text{S}_4$. It was measured over a pH range of 2.0 to 6.0, due to the fact that Pb(II) hydroxide precipitation may occur when the pH value is higher than 6.0 (ref. 33) and dissolution of $\text{CD}_2\text{-Fe}_3\text{S}_4$ sharply increased at pH below 2.0 (Fig. 7b). The Pb(II) adsorption by $\text{CD}_2\text{-Fe}_3\text{S}_4$ depended strongly on the solution pH.

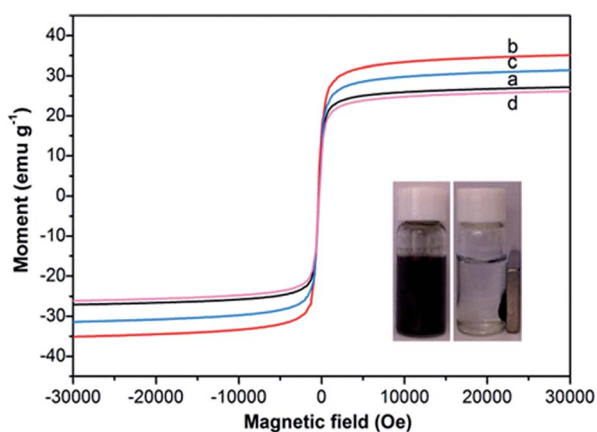


Fig. 6 Magnetization curves of (a) Fe_3S_4 NPs, (b) $\text{CD}_1\text{-Fe}_3\text{S}_4$ NPs, (c) $\text{CD}_2\text{-Fe}_3\text{S}_4$ NPs, and (d) $\text{CD}_2\text{-Fe}_3\text{S}_4$ NPs after Pb(II) adsorption. The inset images are the photograph of dispersion of $\text{CD}_2\text{-Fe}_3\text{S}_4$ in aqueous solution (left) and its response to a magnet (right).

It increased dramatically from 30.58 mg g^{-1} to 142.73 mg g^{-1} with increasing pH over the investigated range. The adsorption capacity of Pb(II) at pH 6.0 was more than four times greater than that at pH 2.0. The lowest adsorption of Pb(II) occurred at pH 2.0, which may be attributed to the competition between H^+ and Pb(II) ions for adsorption sites, enhanced electrostatic repulsion between Pb(II) and $\text{CD}_2\text{-Fe}_3\text{S}_4$, and partial dissolution of $\text{CD}_2\text{-Fe}_3\text{S}_4$ NPs leading to the loss of partial binding sites. Because of the pH-dependent sorption of $\text{CD}_2\text{-Fe}_3\text{S}_4$, here, we choose the pH at 6.0 for further adsorption studies, where the dissolution of $\text{CD}_2\text{-Fe}_3\text{S}_4$ can be partly avoided.

Adsorption kinetics

The adsorption capacities (q_t) of Pb(II) on Fe_3S_4 , $\text{CD}_1\text{-Fe}_3\text{S}_4$, and $\text{CD}_2\text{-Fe}_3\text{S}_4$ vs. time at 100 mg L^{-1} initial concentrations are shown in Fig. 8a. A rapid initial Pb(II) adsorption was observed for all three sorbents and then the rate decreased until it reached equilibrium. The amount of Pb(II) adsorbed varied with different adsorbents, and $\text{CD}_2\text{-Fe}_3\text{S}_4$ exhibited a more efficient removal of Pb(II) than the other two which indicated that the addition of $\beta\text{-CD}$ may influence the adsorption capacity of sorbents.

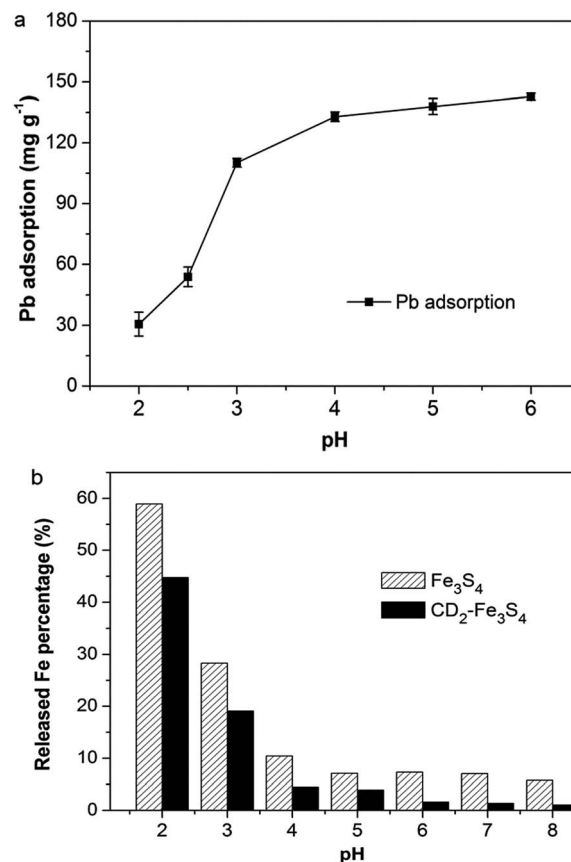


Fig. 7 (a) The influence of initial pH on the adsorption of Pb(II) by $\text{CD}_2\text{-Fe}_3\text{S}_4$. Experimental conditions: initial Pb(II) concentration 100 mg L^{-1} (40 mL), sorbent 20 mg, pH 2.0–6.0, contact time 24 h, and temperature 25 $^{\circ}\text{C}$; (b) released Fe percentage as a function of the solution pH. Experimental conditions: water 40 mL, sorbent 20 mg, and pH 2.0–8.0.

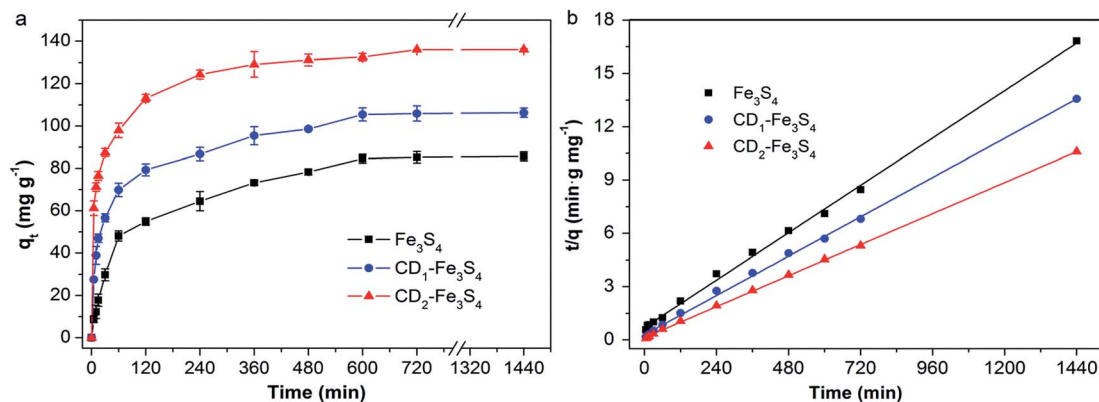


Fig. 8 (a) Adsorption kinetics of the adsorption of Pb(II) on Fe₃S₄. Experimental conditions: initial Pb(II) concentration 100 mg L⁻¹ (50 mL), sorbent 30 mg, pH 6.0, contact time 24 h, and temperature 25 °C; (b) test of the pseudo-second-order model for adsorption of Pb(II) on different adsorbents. The symbols indicate experimental data and the solid lines represent the fitted curves.

The kinetics of Pb(II) removal was examined in order to understand the adsorption process of Fe₃S₄. Two different kinetic models, the pseudo-first-order model and pseudo-second-order model, were employed to simulate the experimental data. The equations can be expressed in the forms:³⁴

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where q_t and q_e denote the amount of adsorption at any time t (min) and equilibrium (mg g⁻¹). k_1 (min⁻¹) and k_2 (g (mg min)⁻¹) are the rate constant of pseudo-second-order sorption, respectively. From these two models, the adsorption parameters and regression coefficients (R^2) were obtained and are summarized in Table 1. The pseudo-second-order kinetic model provided a good linearity for the plots of t/q versus t (Fig. 8b), suggesting that the adsorption should be controlled by the sorption process rather than diffusion.³⁵ In this study, it means that the transport of Pb(II) to the Fe₃S₄ surface was faster than the interactions between Pb(II) and Fe₃S₄. A similar adsorption behavior was reported for the Hg(II) adsorption kinetics by carboxymethyl cellulose stabilized iron sulfide nanoparticles.²⁰

At pH 6.0 and with 100 mg L⁻¹ Pb(II), the q_e of Pb(II) is 136.07 mg g⁻¹ for CD₂-Fe₃S₄, ~1.28 times higher than that of CD₁-Fe₃S₄ and ~1.59 times higher than that of Fe₃S₄. The rate constant k_2 was 5.31×10^{-4} g (mg min)⁻¹ for CD₂-Fe₃S₄, 4.39×10^{-4} g (mg min)⁻¹ for CD₁-Fe₃S₄, and 2.07×10^{-4} g (mg min)⁻¹ for Fe₃S₄, respectively. These results indicated that CD₂-Fe₃S₄ exhibited the highest adsorption rate and q_e . The most efficient

adsorption performance of CD₂-Fe₃S₄ may come from its minor particle size, greater surface area and hydroxyl groups after bonding with β -CD, which provided more active sites to adsorb Pb(II),⁸ which confirmed its promising potential for wastewater treatment.

Adsorption isotherms

Fig. 9 presents the typical adsorption isotherms of Pb(II) on Fe₃S₄, CD₁-Fe₃S₄, and CD₂-Fe₃S₄ NPs at a fixed pH of 6.0 in the studied concentration ranges. All the Fe₃S₄ adsorbents showed a good adsorption performance toward Pb(II). Obviously, CD₂-Fe₃S₄ NPs exhibited higher adsorption capacity than the other two, which increased with the increasing equilibrium concentration. The obtained isotherm data were fitted using the classical Langmuir model and Freundlich model, respectively.

The two typical adsorption isotherms can be expressed as:³⁶

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (4)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where C_e is the equilibrium concentration (mg L⁻¹), q_e is the adsorption capacity at equilibrium, and q_m represents the maximum adsorption capacity of Pb(II) (mg g⁻¹). K_L and K_F refer to the affinity parameter of Langmuir sorption constant and Freundlich adsorption capacity, respectively. $1/n$ relates to the Freundlich adsorption intensity parameter.

Table 1 Adsorption kinetics parameters for the adsorption of Pb(II)

Adsorbent	Pseudo-first-order model			Pseudo-second-order model		
	$K_1 \times 10^{-2}$ (min ⁻¹)	q_e (mg g ⁻¹)	R^2	$K_2 \times 10^{-4}$ (g (mg min) ⁻¹)	q_e (mg g ⁻¹)	R^2
Fe ₃ S ₄	0.51	70.00	0.936	2.07	85.47	0.996
CD ₁ -Fe ₃ S ₄	0.54	69.09	0.893	4.39	101.01	0.997
CD ₂ -Fe ₃ S ₄	0.71	72.39	0.910	5.31	133.33	0.999

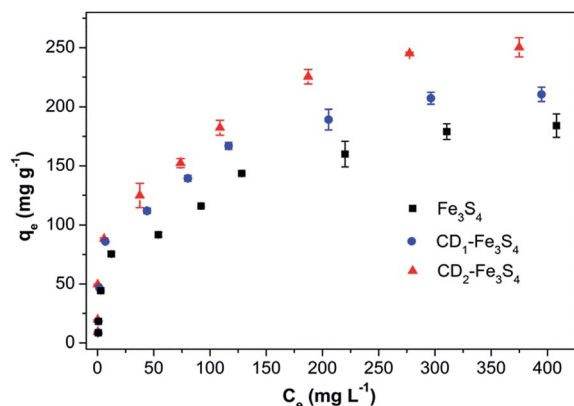


Fig. 9 Adsorption isotherms of Pb(II) on Fe₃S₄, CD₁-Fe₃S₄, and CD₂-Fe₃S₄. Experimental conditions: initial concentration 5–500 mg L⁻¹ (40 mL), sorbent 20 mg, pH 6.0, contact time 24 h, and temperature 25 °C.

The fitting results based on the two isotherm models are listed in Table S1 and Fig. S2.† It can be seen that the adsorption of Pb(II) on Fe₃S₄ was better estimated by the Langmuir model with the correlation coefficient (R^2) in the range of 0.979–0.987 under the Pb (II) concentration ranging from 5 mg L⁻¹ to 500 mg L⁻¹, implying that the Pb(II) adsorption process is mainly monolayered.³⁷

The feasibility of the adsorption can be described by a separation factor (R_L), which is defined by the following equation:³⁷

$$R_L = \frac{1}{K_L C_0 + 1} \quad (6)$$

where C_0 (mg L⁻¹) is the initial Pb(II) concentration. The value of R_L indicates the shape of the Langmuir isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). In this study, the initial concentration of Pb(II) is 5 mg L⁻¹ and the calculated values of R_L were 0.851, 0.816, and 0.804 within the range of 0–1. Thus, the removal of Pb(II) by all three adsorbents appeared to be a favourable process.³⁷

The maximum adsorption capacity of CD₂-Fe₃S₄ for Pb(II) was calculated to be 256.41 mg g⁻¹, which was higher than those of Fe₃S₄ (190.11 mg g⁻¹) and CD₁-Fe₃S₄ (217.39 mg g⁻¹). The surface β-CD with hydroxyl groups may partially be responsible for the enhanced adsorption performance.³⁸ The as-prepared nanoparticles showed a considerably higher adsorption capacity for Pb(II), in comparison to previously reported adsorbents, such as Fe₃S₄ hollow spheres (92.1 mg g⁻¹),²⁶ Fe₃O₄/cyclodextrin polymer nanocomposites (64.5 mg g⁻¹),³⁹ MWCNT/Fe₃O₄ nanocomposites (41.77 mg g⁻¹),⁴⁰ and MWCNT/iron oxide/CD nanostructures (12.29 mg g⁻¹).⁸ These results indicated that the β-CD stabilized Fe₃S₄ could be a prospective adsorbent for Pb(II) removal in contaminated water due to its easy-separation and efficient-adsorption.

Effect of competing ions

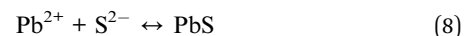
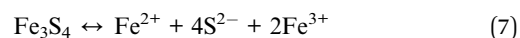
Competing ions such as Ca(II), Mg(II), and Zn(II) are expected to be present in natural water, and always have effects on the

adsorption of a particular metal ion (in this study, the metal ion is Pb(II)). Thus, we determined the influence of competing ions (Ca(II), Mg(II), Zn(II), Cd(II), and Cu(II)) on the adsorption of Pb(II) by varying their concentrations.

From the results illustrated in Fig. 10, it is clear that Mg(II) and Zn(II) ions have no obvious effect on the adsorption capacity of CD₂-Fe₃S₄ NPs, while the addition of Cu(II) and Cd(II) decreased the adsorption capacity to a large extent. When the molar ratio of competing ions vs. Pb(II) was 2, the CD₂-Fe₃S₄ showed 74.27% and 50.82% Pb(II) adsorption in the presence of Cd(II) and Cu(II) compared to the control, respectively. The influence sequence of competitive ions on Pb sorption by CD₂-Fe₃S₄ is Cu(II) > Cd(II) > Ca(II) > Mg(II) ≈ Zn(II). Note that CD₂-Fe₃S₄ also exhibited high removal efficiencies of 94.37%, 60.234%, and 43.77% toward Cu(II), Zn(II) and Cd(II) (Fig. S3†). This facilitates us to extend the adsorbent for other metal remediation in the future study.

Removal mechanism

XRD, FTIR, and XPS analyses were conducted to elucidate the major mechanism of Pb(II) removal by CD-Fe₃S₄ (Fig. 11–13). Fig. 11 depicts the XRD spectra of CD₂-Fe₃S₄ nanoparticles before and after equilibration with Pb(II). We chose 24 h as a standard reaction time for the equilibrium experiments. Three new peaks appeared at 43.06°, 50.98°, and 53.4°, corresponding to the characteristic peaks of galena PbS. The lower solubility of PbS ($K_{sp} = 3.4 \times 10^{-28}$) could promote the sorption reaction between Fe₃S₄ and Pb²⁺.



Hence, it is reasonably concluded that Pb(II) was removed from water through the formation of lead sulfide precipitates (galena). This is similar to the previous reports which used FeS

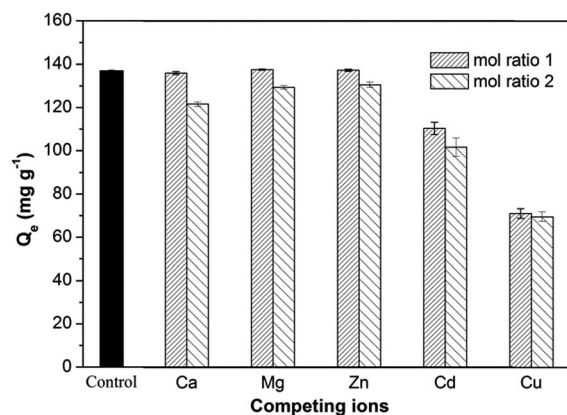


Fig. 10 The effects of competing ions on the Pb(II) adsorption of CD₂-Fe₃S₄. Experimental conditions: initial Pb(II) concentration 100 mg L⁻¹ (50 mL), sorbent 35 mg, pH 6.0, contact time 24 h, and temperature 25 °C.

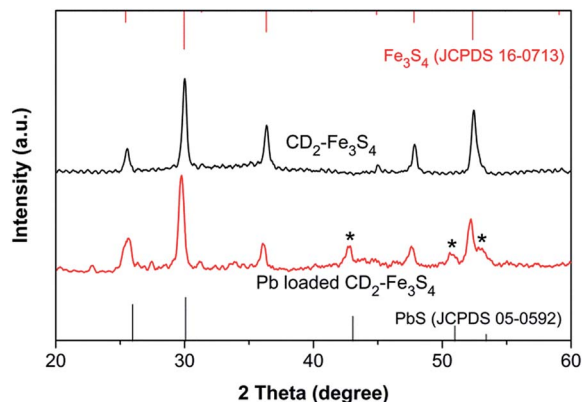


Fig. 11 XRD spectra of $\text{CD}_2\text{-Fe}_3\text{S}_4$ NPs before and after Pb(II) adsorption. Diffraction patterns of Fe_3S_4 and PbS are indicated by black lines and red lines, respectively. XRD powders were prepared under the conditions: initial Pb(II) 500 mg L^{-1} (40 mL), sorbent 20 mg, pH 6.0, contact time 24 h, and temperature 25°C .

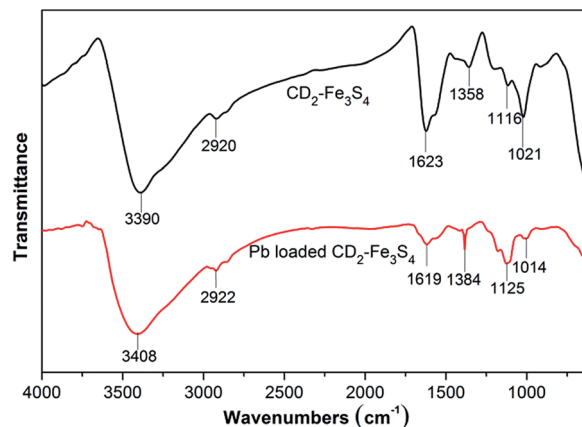


Fig. 12 FTIR spectra of $\text{CD}_2\text{-Fe}_3\text{S}_4$ NPs before and after Pb(II) removal. Preparation conditions were the same as above.

to scavenge Hg and observe the formation of HgS through precipitation.^{20,41}

The possible substitution of Pb(II) into the Fe sites in Fe_3S_4 was also considered. No formation of $(\text{Pb}, \text{Fe})\text{S}$ crystals has been observed under the experimental conditions. Although this may owe to the fact that the crystals are not abundant to detect, removal of Pb(II) through this mechanism was not expected to be the predominated part.

FTIR spectra of $\text{CD}_2\text{-Fe}_3\text{S}_4$ after Pb adsorption are illustrated in Fig. 12. It exhibited that the peaks of $\text{CD}_2\text{-Fe}_3\text{S}_4$ at 3390 , 2920 , 1116 , and 1021 cm^{-1} showed a certain change to 3408 , 2922 , 1125 , and 1014 cm^{-1} respectively after Pb(II) adsorption. These shifts may be attributed to the involvement of these groups in Pb(II) adsorption. Also a peak almost disappeared after Pb(II) adsorption at 1358 cm^{-1} , suggesting that a structural change of the groups may happen under the Pb(II) adsorption. It should be noted that after Pb(II) adsorption a sharp peak appeared at 1384 cm^{-1} , a similar band has been confirmed by other investigators and ascribed to the stretching vibration of the NO_3^- ions.⁴² There was no band observed for the characteristic of PbS after Pb(II) adsorption though it can be detected by the XRD analysis, because galena, an ionic material, showed weak infrared features.⁴³ The FTIR spectra demonstrated that the removal of Pb(II) was somehow dependent on the surface adsorption, not merely by the formation of PbS .

The $\text{CD}_2\text{-Fe}_3\text{S}_4$ samples before and after Pb adsorption were also analyzed by XPS. As shown in the full-range XPS spectra (Fig. 13a), the appearance of Pb species confirmed the successful adsorption of Pb on the $\text{CD}_2\text{-Fe}_3\text{S}_4$. A more detailed structure of Pb species could be obtained in the high resolution XPS spectrum in the region of Pb 4f (Fig. 13b). It can be deconvoluted into four peaks at 137.3 , 138.5 , 142.2 , 143.4 eV , from which two distinct components can be resolved. The binding energies of Pb $4f_{5/2}$ at 137.3 eV and Pb $4f_{7/2}$ at 142.2 eV corresponded to the crystalline PbS ^{44–46} further confirming the formation of PbS under the adsorption process, and another two fitted peaks of Pb $4f_{5/2}$ and Pb $4f_{7/2}$ at 138.5 eV and 143.4 eV

may be associated with the presence of Pb-O bonding,^{47,48} respectively. The corresponding S 2p XPS spectra further indicated the existence of PbS at the surface of $\text{CD}_2\text{-Fe}_3\text{S}_4$ (Fig. S4†). It can be clearly found that the S 2p spectra are quite different after Pb adsorption, indicating that the S constituents of $\text{CD}_2\text{-Fe}_3\text{S}_4$ significantly changed after adsorption. Two new fitted peaks at a binding energy of 159.3 eV and 161.3 eV emerged corresponding to the presence of Pb-S after Pb

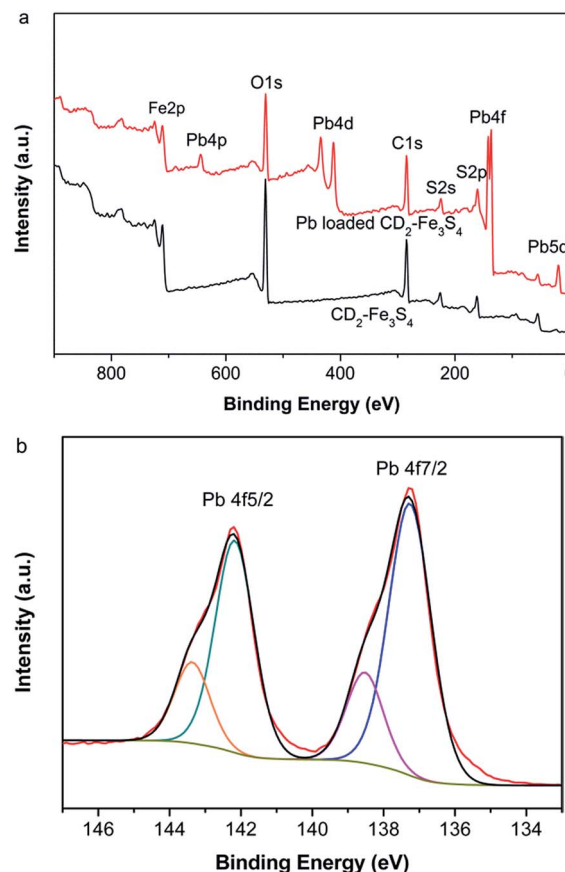


Fig. 13 (a) Full range XPS spectra of $\text{CD}_2\text{-Fe}_3\text{S}_4$ before and after Pb(II) adsorption. (b) Pb 4f XPS spectrum of Pb -loaded $\text{CD}_2\text{-Fe}_3\text{S}_4$.

adsorption.^{49,50} The XPS spectra supported the formation of PbS and the surface adsorption process, which was consistent with the XRD and FTIR analyses.

From the aforementioned analyses, it is rational to conjecture that Pb(II) was immobilized from water due to a combination of precipitation (formation of galena) and surface adsorption. The different performance between bare Fe₃S₄ and CD-Fe₃S₄ comes from the extended adsorption sites (multiple hydroxyl groups) and the monodispersed morphology of CD-Fe₃S₄ via grafted β -CD which improved the efficient utilization of adsorbent.

Conclusion

A monodispersed β -CD stabilized nano-adsorbent (CD-Fe₃S₄) was prepared through a facile one-step method. The grafted β -CD plays an important role in the morphology formation of Fe₃S₄ nanoparticles. Batch sorption studies proved that the CD-Fe₃S₄ exhibited an enhanced removal capacity toward Pb(II) (256 mg g⁻¹) in comparison with bare Fe₃S₄ NPs. The dominant mechanisms of Pb(II) removal were verified to be precipitation (formation of galena) and surface adsorption through XRD, FTIR, and XPS analyses. Moreover, high removal efficiencies toward Cu(II), Zn(II), and Cd(II) by CD-Fe₃S₄ were observed, which is expected to widen its application in the wastewater treatment. This research demonstrated that β -CD stabilized magnetic Fe₃S₄ can be a potential material for Pb(II) removal from wastewater.

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