Chelating capture and magnetic removal of non-magnetic heavy metal substances from soil

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A soil remediation method based on magnetic beneficiation is reported. A new magnetic solid chelator powder, FS@IDA (core-shell Fe\(_{3}\)O\(_4\)@SiO\(_2\) nanoparticles coated with iminodiacetic acid chelators), was used as a reactive magnetic carrier to selectively capture non-magnetic heavy metals in soil by chelation and removal by magnetic separation. FS@IDA was prepared via inorganic-organic and organic synthesis reactions that generated chelating groups on the surface of magnetic, multi-core, core-shell Fe\(_{3}\)O\(_4\)@SiO\(_2\) (FS) nanoparticles. These reactions used a silane coupling agent and sodium chloroacetate. The results show that FS@IDA could chelate the heavy metal component of Cd, Zn, Pb, Cu and Ni carbonates, lead sulfate and lead chloride in water-insoluble salt systems. The resulting FS@IDA-Cd and FS@IDA-Pb chelates could be magnetically separated, resulting in removal rates of approximately 84.9% and 72.2% for Cd and Pb, respectively. FS@IDA could not remove the residual heavy metals and those bound to organic matter in the soil. FS@IDA did not significantly alter the chemical composition of the soil, and it allowed for fast chelating capture, simple magnetic separation and facilitated heavy metal elution. FS@IDA could also be easily prepared and reprocessed.

According to an official report recently released by the China Ministry of Environmental Protection\(^1\), 19.4% of the arable land in China is contaminated with heavy metals, such as cadmium, mercury, and arsenic, and organic pollutants, such as polycyclic aromatic hydrocarbons, resulting in environmental problems and food safety concerns. For example, in the “Poison Rice Incident” of May 2013, the Food and Drug Administration of Guangzhou, China, found that 44.4% of rice and related products consumed in Guangzhou were contaminated with cadmium\(^2\). The restoration of soil over large areas is urgently needed. Several strategies to remove heavy metals, such as chemical leaching\(^3\), electrokinetic remediation\(^4\), and phytoremediation\(^5,6\), have been proposed\(^7–10\) and are being used on a trial basis in China.

The use of magnetic nanoparticles (MNPs) as adsorbent materials to address environmental problems has received increasing attention due to their unique metal-ion adsorption properties and facile separation from aqueous solutions using a magnet\(^11–14\). Fe\(_{3}\)O\(_4\) MNPs with adsorptive functional groups on their surfaces are well suited to selectively extract heavy metal ions from wastewater or industrial effluents\(^15–17\) by capturing the metal ions in solution. The loaded nanoparticles can then be retrieved with a magnet, and the metal ions can be subsequently stripped from the MNPs. This process is sustainable because the MNPs are reusable and no hazardous chemicals are employed.

Recently, unique core-shell MNPs, specifically Fe\(_{3}\)O\(_4\)@SiO\(_2\) (FS), that have surface chelating groups were prepared via organic-inorganic and surface functionalization reactions\(^18\). FS particles coated with N-[(3-trimethoxysilyl)propyl] ethylenediamine triacetate acid were prepared and used to extract and separate rare-earth ions\(^19\). These materials have also been functionalized with amino, imino and sulfonic groups and used to selectively remove Pb(II) and Cr(VI) from aqueous solutions\(^19\). Porphyrin-functionalized FS particles were employed to detect, adsorb and remove aqueous Hg\(^{2+}\) ions\(^20,21\). Comparing surface-functionalized FS particles to MNPs shows that they not only have improved resistance to acidic environments during magnetic retrieval, but they also selectively adsorb some heavy metal ions, which can be easily desorbed later. To date, however, virtually all literature reports of heavy metal-ion separation by MNPs and FS particles with chelating surface groups focus

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The number of solvated divalent metal ions adsorbed on FS@IDA was affected by the pH, adsorption time, FS@IDA quality, initial cadmium concentration and presence of other ions. Initially, 1 g of FS@IDA was added to 100 mL of 0.89 mM and 2.67 mM cadmium solutions, which were then maintained at room temperature for 12 h. The effects of the pH, the initial cadmium concentration and the presence of other ions on the amount of Cd$^{2+}$ adsorbed were determined, and the results are shown in Fig. 4.
As shown in Fig. 4a, b, the amount of Cd\(^{2+}\) adsorbed increased with increasing pH and reached a maximum when pH was between 6 and 7. Above pH 7, the amount adsorbed decreased. The H\(^+\) concentration decreased with increasing pH, resulting in a decrease in the reactions between the carboxylate radicals, nitrogen atoms and H\(^+\) ions and increased chelation of Cd\(^{2+}\). However, the cadmium ion easily formed a hydrate under alkaline...
conditions, hindering its adsorption. When the initial Cd\(^{2+}\) concentrations were 0.89 mM and 2.67 mM, the maximum adsorption capacities of FS@IDA were about 6.40 mg g\(^{-1}\) and 22.5 mg g\(^{-1}\), respectively.

The adsorption behavior included both chemical and physical adsorption, and the maximal amount of Cd\(^{2+}\) adsorption was related to the initial Cd\(^{2+}\) concentration. Generally, the higher the initial concentration, the greater the adsorption quantity. So the adsorption of Cd\(^{2+}\) was higher than the nitrogen load. Where, as, the nitrogen concentration of the sample was measured by a semi-micro Kjeldahl determination, and the results from this method were usually low, resulting in the adsorption capacity of the actual dynamic adsorption curve being larger than the nitrogen load, which denoted the quantity of the chelation group of the FA@IDA material.

Furthermore, Ca\(^{2+}\), Mg\(^{2+}\), Zn\(^{2+}\) and Hg\(^{2+}\) adsorption might compete with Cd\(^{2+}\) adsorption. The effects of Ca\(^{2+}\) and Mg\(^{2+}\) on the amount of Cd\(^{2+}\) adsorbed were the same and slightly greater than those of Zn\(^{2+}\) and Hg\(^{2+}\). In addition, when a solution containing equal amounts of Cd\(^{2+}\) and Pb\(^{2+}\) was used, the amount of Cd\(^{2+}\) adsorbed decreased by approximately 50%, showing that the presence of Pb\(^{2+}\) had a larger impact on cadmium adsorption than the other ions. These results indicate that FS@IDA can be used to selectively capture and separate solvated Cd\(^{2+}\) and Pb\(^{2+}\) ions.

Chelating capture of several sparingly soluble heavy metals. Several insoluble carbonate powders (M = Cd, Zn, Pb, Cu, Ni), lead sulfate and lead chloride were added to 100 mL of aqueous solutions at pH 7. The heavy metal-ion concentrations in the solutions were 100 mg·L\(^{-1}\) (Cd: 0.89 mM, Zn: 1.53 mM, Pb: 0.49 mM, Cu: 1.57 mM, Ni: 1.69 mM). FS@IDA (3.5 g, the chelating group concentration was greater than 1.75 mmol·g\(^{-1}\)) was added to the solution, which was intermittently stirred for 12 h at room temperature. The magnetic solid was separated using a magnet; the insoluble carbonate, sulfate and chloride powders were removed; and the suspension was filtered and dried.

### Table 1. Results for the dissolution of several insoluble compounds suspended in solution and the corresponding metal ion capture. s is the solubility of the insoluble salt. \(K_p\) and \(K_{sp}\) denote the solubility and concentration product constants, respectively.

| Metal form | \(K_p = [M^{2+}] / [CO_3^{2-}]\) | \([M^{2+}] = s (M)\) | \([CO_3^{2-}] = \frac{s}{K_p}\) | Ion concentration | \(K_{sp} = [M^{2+}] [CO_3^{2-}]\) | Comparison | Dissolution observed? |
|------------|---------------------------------|-------------------|-----------------|-----------------|-----------------|-------------|---------------------|
| CdCO\(_3\) | 5.20 × 10\(^{-14}\) | 5.60 × 10\(^{-4}\) | 9.30 × 10\(^{-1}\) | 1.20 × 10\(^{-4}\) | 1.12 × 10\(^{-14}\) | \(K_p < K_{sp}\) | yes |
| ZnCO\(_3\) | 1.40 × 10\(^{-11}\) | 1.75 × 10\(^{-4}\) | 8.00 × 10\(^{-4}\) | 1.75 × 10\(^{-3}\) | 1.40 × 10\(^{-12}\) | \(K_p < K_{sp}\) | yes |
| PbCO\(_3\) | 7.40 × 10\(^{-18}\) | 1.20 × 10\(^{-3}\) | 5.78 × 10\(^{-1}\) | 1.01 × 10\(^{-8}\) | 5.93 × 10\(^{-15}\) | \(K_p < K_{sp}\) | yes |
| CuCO\(_3\) | 1.40 × 10\(^{-10}\) | 5.56 × 10\(^{-4}\) | 2.52 × 10\(^{-7}\) | 3.17 × 10\(^{-5}\) | 7.99 × 10\(^{-12}\) | \(K_p < K_{sp}\) | yes |
| NiCO\(_3\) | 6.60 × 10\(^{-9}\) | 3.82 × 10\(^{-3}\) | 1.73 × 10\(^{-4}\) | 6.10 × 10\(^{-5}\) | 1.56 × 10\(^{-10}\) | \(K_p < K_{sp}\) | yes |
| PbSO\(_4\) | 1.6 × 10\(^{-8}\) | 1.26 × 10\(^{-4}\) | 1.26 × 10\(^{-4}\) | 1.01 × 10\(^{-8}\) | 1.27 × 10\(^{-10}\) | \(K_p < K_{sp}\) | yes |
| PbCl\(_2\) | 1.6 × 10\(^{-7}\) | 0.0252 | 0.0504 | 1.01 × 10\(^{-6}\) | 1.03 × 10\(^{-10}\) | \(K_p < K_{sp}\) | yes |
At pH 7, \( \partial_{CO_3^{2-}} = 2.2 \times 10^3 \).

In this study, lead carbonate was used as an example to demonstrate precipitate dissolution.

For PbCO_3, \( K_p = 7.4 \times 10^{-14} \),

\[
K_p' = K_p \cdot \partial_{CO_3^{2-}} = 7.4 \times 10^{-14} \times 2.2 \times 10^3 = 1.63 \times 10^{-10} = s^2,
\]

\( s = 1.28 \times 10^{-5} \).

\[
CO_3^{2-} = \frac{K_p}{s} = 5.78 \times 10^{-9}.
\]

The \([Pb^{2+}]'\) concentration of the solution was 1.01 \( \times 10^{-6} \) M 12 h after the FS@IDA powder was added. Because

\[
K_p' = [Pb^{2+}'][CO_3^{2-}] = (1.01 \times 10^{-6})(5.87 \times 10^{-9}) = 5.93 \times 10^{-15} < K_p,
\]

PbCO_3 was dissolved in the solution, leading to the formation of FS@IDA-Pb.

The dissociation constants of H_3PO_4 in water are \( K_{a1} = 7.6 \times 10^{-3}, K_{a2} = 6.3 \times 10^{-8} \) and \( K_{a3} = 4.4 \times 10^{-13} \). The acid effect coefficient of PO_4^{3-} is

\[
\partial_{PO_4^{3-}} = 1 + \beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3 = 1 + \frac{[H^+]}{K_{a1}} + \frac{[H^+]^2}{K_{a2}K_{a1}} + \frac{[H^+]^3}{K_{a3}K_{a2}K_{a1}}.
\]

At pH 7, \( \partial_{PO_4^{3-}} = 5.89 \times 10^{-5} \).

In this study, Zn_2(PO_4)_3 was used as an example to demonstrate why precipitate dissolution did not occur.

With \( K_p = 9.1 \times 10^{-33}, K_{p'} = 1.02 \times 10^{-25}, \) and \( K_p' > K_p \), the precipitate did not dissolve.

Lead sulfate and lead chloride were not hydrolyzed, and for these compounds, \( K_p' < K_p \); therefore, these precipitates dissolved.

These results show that FS@IDA could promote the dissolution of some insoluble metal salts by capturing the metal ions with their chelating surface groups (Fig. 1), allowing for the targeted magnetic separation of multi-phase non-magnetic metal.

**Energy spectrum characterization of FS@IDA-Cd.** In this study, the FS@IDA-Cd powder sample was obtained by magnetic separation. After drying the sample at 105 °C, its surface elements were analyzed with SEM-EDS22. The red dots (Fig. 5d) and green dots (Fig. 5e) in the full energy spectrum represent carbon and nitrogen atoms, respectively, which were introduced during the grafting reaction. The purple dots represent cadmium ions chelated by FS@IDA (Fig. 5f). Based on the energy spectrum, the nitrogen and cadmium loadings were found to be 3.57 and 1.07 wt%, respectively (Fig. 5c).

**Chelation and magnetic separation of Cd and Pb in soil.** Heavy metals are found in different chemical forms in soils, and those forms have different activities in reactions such as dissolution, precipitation, coagulation and complex formation. Tessier et al.23 classified sediments and heavy metals in soils into different fractions: water-soluble, interchangeable, carbonate-bound, iron-manganese oxide-bound, organic-bound and residual fraction. The chemical stability of the different heavy metal fractions is as follows: residual > organic-bound > iron-manganese oxide-bound > carbonate-bound > interchangeable > water-soluble.

The topsoil near a lead and zinc refinery in Zhuzhou, Hunan Province, was chosen because it is representative of soils that are significantly contaminated by heavy metals. This factory specializes in heavy metals such as Pb, Zn, and Cu and their alloys and combines non-ferrous heavy metals such as Au, Ag, Cd, In, Ge, Ga, Se and Te, with chemical industry products such as vitriol. The cadmium and lead concentration was determined to be 10.91 ± 2.06 mg·kg^{-1} and 190.0 ± 33.2 mg·kg^{-1} (Table 2), respectively, using the GB/T17138–1997 standard method24. The heavy metal forms were analyzed using the Tessier method25.

To measure the amount of cadmium and lead removed from the soil, a slurry of 50 g of soil and 150 g of distilled water was prepared. The pH was adjusted between 6 and 7, and 5 g of FS@IDA was added to the slurry at room temperature. The magnetic solids were separated using a magnet after intermittent stirring for 7 d. The cadmium and lead concentration in the solution was reduced to 1.639 and 52.7 mg·kg^{-1} at room temperature. The magnetic solids were separated using a magnet after intermittent stirring for 7 d. The distilled water was prepared. The pH was adjusted between 6 and 7, and 5 g of FS@IDA was added to the slurry at room temperature. The magnetic solids were separated using a magnet after intermittent stirring for 7 d. The distilled water was prepared. The pH was adjusted between 6 and 7, and 5 g of FS@IDA was added to the slurry at room temperature. The magnetic solids were separated using a magnet after intermittent stirring for 7 d. The distilled water was prepared. The pH was adjusted between 6 and 7, and 5 g of FS@IDA was added to the slurry at room temperature. The magnetic solids were separated using a magnet after intermittent stirring for 7 d. The distilled water was prepared. The pH was adjusted between 6 and 7, and 5 g of FS@IDA was added to the slurry at room temperature. The magnetic solids were separated using a magnet after intermittent stirring for 7 d. The distilled water was prepared. The pH was adjusted between 6 and 7, and 5 g of FS@IDA was added to the slurry at room temperature.
Related studies have reported that MNPs with high efficiencies can be used to remove heavy metals, such as Cd, Pb, Cu, Hg, in aqueous solution. In this study, it was not emphasized that FS@IDA was a nanometer material. In fact, it was a multi-core, core-shell structure and the average particle size was not of nanomaterial particle size. Moreover, the nanoscale magnetic adsorption material is too small, while in the soil-liquid system and heterogeneous soil system, because of the fixation effect of soil clay, it is difficult for it to be completely separated, so the FS@IDA size was controlled in the range of a few microns to dozens of micrometers. The FS@IDA material was applied in a solid-liquid soil system and a heterogeneous soil system. The condition of the soil system was more complicated than in an aqueous solution. It was demonstrated that the FS@IDA had the potential to chelate sedimentary heavy metals (M) such as carbonates, sulfates, phosphates, and iron-manganese oxide-bound fractions, into soluble magnetic solids that were easy to separate magnetically.

Chelation mechanism. The reaction between cadmium ions and FS@IDA illustrates the chelation mechanism. Both the nitrogen and oxygen atoms of the iminodiacetic acid chelating group have electron pairs that can coordinate with metal ions, resulting in a tridentate chelator structure. The FS@IDA surface has many alkyl iminodiacetic acid chelating groups that can coordinate with metal ions via the nitrogen and oxygen atoms to form stable four-coordinate, three-coordinate, and double five-membered ring chelates. In addition, the cadmium ion has an 18-electron shell structure with an unoccupied orbital, a relatively small ionic radius and a relatively strong...
electronegativity and can therefore readily form six-coordinate or four-coordinate complexes. Possible chelation reaction equations and the resulting FS@IDA-Cd structure showing the coordination of the FS@IDA chelating groups to the cadmium ion are shown in Fig. 1.

The magnetic solid chelate FS@IDA-Cd had cadmium ions coordinated with four atoms, the nitrogen and two oxygen atoms of a chelating group and solution species. H$_2$O, OH$^-$ or halogen ion in a double five-membered ring configuration. Therefore, it was assumed that the cadmium ions were captured via a chelating adsorption reaction on the FS@IDA surface or at the solid-liquid interface.

The effect of the adsorption time on the amount of Cd$^{2+}$ adsorbed on FS@IDA at different temperatures was measured. FS@IDA (1 g) was added to a 100 mg·L$^{-1}$ Cd$^{2+}$ solution (100 mL) and the pH was adjusted to 7. The temperature was set to 293, 303, or 313 K. The cadmium adsorption increased rapidly within the first 0.5 h, reaching over 75% of the maximum adsorption, indicating that these ions can be quickly captured by FS@IDA (Fig. 6a).

The formation of chemical bonds during the adsorption process was the key factor affecting the secondary dynamic adsorption and it was further assumed that cadmium was mainly adsorbed on FS@IDA via chelation (Fig. 6b).

Conclusions
To achieve highly selective, efficient heavy metal removal from contaminated soil, a novel inorganic-organic hybrid material, magnetic solid chelator powder FS@IDA, was prepared. The inorganic FS particles displayed soft magnetism, and the organic alkyl iminodiacetic acid groups on the particle surface can capture heavy metals via chelation. Specifically, FS@IDA can coordinate with the heavy metals (M) of Cd, Zn, Pb, Cu and Ni carbonates, lead sulfate and lead chloride, which were insoluble in the aqueous systems tested, to form FS@IDA-M for magnetic separation. Only the organic-bound and the residual metal species in the soil cannot be chelated by FS@IDA. Moreover, FS@IDA-M could be easily reprocessed and recycled via acid treatment. This material has the potential to be used to selectively remove non-magnetic heavy metals from multi-phase soil systems under natural conditions via magnetic separation and could potentially be used to purify and manage large areas of farmland contaminated with heavy metals.

Methods
Materials. Fe$_3$O$_4$ powders (Tianjin Bodi Chemical Engineering Co., Ltd., Tianjing, China), tetraethoxysilane (TEOS) (Tianjin Fuchen Chemical Reagent Factory, Tianjing, China), APTES (Hubei Wuda Organosilicon New Material Co., Ltd., Wuhan, China), and sodium chloroacetate (Tianjin Guangfu Fine Chemical Research Institute, Tianjing, China) were employed.

Apparatus. TEM (Hitachi H-800), SEM (Hitachi SU-8010), XRD (Bruker AXS D8 Focus), Avatar 370 FTIR (US Nicolet), VSM (HH-10, Nanjing Nanda Instrument Plant), and Z-2000 AAS (Hitachi) instruments were employed.

Preparation of FS. TEOS (9 g) and Fe$_3$O$_4$ powder (10 g) were stirred into 70 mL of anhydrous ethanol at 50°C. Then, a solution of 12 mL of ammonium hydroxide, 30 mL of ethanol, and 14.4 mL of deionized water was added dropwise to the suspension under stirring, and the mixture allowed to react for 8 h. The product was separated using a magnet and washed with water. Finally, the resulting FS powder was vacuum-dried at 70°C to a constant weight.
Synthesis of FS-N. The FS powder (5 g) was added to 150 mL of anhydrous ethanol, and 1 g of APTES was added after stirring. The reaction solution was adjusted to pH 5. The reaction was maintained at 40 °C for 5 h. After the reaction, the product was separated using a magnet and washed with water. The magnetic FS-N particles were dried at 105 °C to generate the aminated multi-core core-shell structure.

Carboxymethylation reaction on the FS-N surface. FS-N (5 g), 3 wt% sodium chloroacetate (100 mL), and a 10 v/v% ammonia solution (10 mL) were dissolved in 100 mL of distilled water. The reaction solution was maintained at 70°C for 8 h. Then, the product was separated using a magnet and washed with distilled water. The FS@IDA powder was obtained by the nucleophilic substitution reaction of FS@-N with sodium chloroacetate after drying at 105°C.

The reutilization measurement of FS@IDA. Soil samples (30 g, 100-mesh sieved) were added to 75 mL of distilled water and stirred for 10 min to prepare a soil suspension with a soil water ratio of 2.5. A columnar magnet with a magnetic field intensity of 5000 gauss was used to remove magnetic materials from the soil suspension. FS@IDA (3 g) was added to the soil suspension and stirred for 30 min. Then, the samples were magnetically separated after standing for 120 min, and the soil particles from the FS@IDA surface were washed with distilled water, dried at 70°C and weighed.

Calculating the cadmium concentration in the solution. A cadmium solution with a given concentration was placed in a beaker and FS@IDA added. The pH was adjusted. After reacting at room temperature, the final product was separated using a magnet. The residual cadmium concentration in the solution was measured to calculate the amount adsorbed on FS@IDA and the cadmium removal rate.

The formula for calculating the amount adsorbed is

\[ q = \frac{C_0 V_0 - C_1 V_1}{m_0} \]  

The formula for calculating the cadmium removal rate is

\[ n = \frac{C_0 V_0 - C_1 V_1}{C_0 V_0} \]  

The initial concentration and volume of the cadmium solution are denoted by \( C_0 (\text{mg·L}^{-1}) \) and \( V_0 (\text{mL}) \), respectively. The concentration and volume of the cadmium solution after the adsorption reaction are designated \( C_1 (\text{mg·L}^{-1}) \) and \( V_1 (\text{mL}) \), respectively. The mass of FS@IDA used is \( m_0 (\text{g}) \).

Calculating the FS@IDA desorption rate. Saturated FS@IDA-Cd (1 g) was immersed in 100 mL of 1 M hydrochloric acid and the magnetic substances were separated using a magnet after the cadmium was allowed to desorb by stirring at room temperature for 1 h. The cadmium concentration in the solution was measured, and the desorption rate was calculated as:

\[ s = \frac{C_1 V_2}{m_2} \]  

The concentration and volume of the cadmium solution after desorption were denoted by \( C_1 (\text{mg·L}^{-1}) \) and \( V_2 (\text{mL}) \), respectively. The mass of cadmium adsorbed by FS@IDA was denoted \( m_1 (\text{g}) \).

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Author Contributions
F.-L.R. conceived and designed the application of FS@IDA, analyzed its chemical principle and chelating mechanism, and wrote the paper. S.-J.Q. designed the application of FS@IDA to the treatment of soil pollution and wrote the manuscript with F.-L.R., B.-W.B. performed some of the soil experiments and wrote some paragraphs of the manuscript. L.-X.M. performed most of the experiments, including the FS@IDA preparation, structure characterization and performance study. W.-S.P. participated in the material characterization, performance study and conception of the soil pollution treatment. Z.-M. was involved in the material preparation and edited the English text. Z.-Y. performed the elemental analysis, cadmium measurements and chemical principle analysis. L.-H.F. helped with the structure characterization and performance study. L.-H.W. provided the soil samples and explored the application requirements.

Additional Information
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