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Removal of heavy-metal ions from wastewater samples using magnetic nanoparticles modified with ethylenediaminetetraacetic acid

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ABSTRACT

A study on the application of magnetic nanoparticles (MNPs) prepared from Fe_3O_4 and functionalized with ethylenediaminetetraacetic acid (FF-NH_2/EDTA) is reported. Based on the formation of the metal–EDTA complex, EDTA immobilized nanoparticles were used to extract Cd(II) and Pb(II) ions from aqueous solutions at pH 4. The magnetic nanomaterial can be readily separated from an aqueous solution by applying an external magnetic field. The extraction of Cd(II) and Pb(II) ions by these MNPs was studied and the effect of different parameters (amount of magnetic material, solution pH value and contact time) on the extraction of Cd(II) and Pb(II) ions was investigated. The concentration of Cd(II) and Pb(II) ions was determined using a bismuth film microelectrode by square wave anodic stripping voltammetry before and after the removal process. The results revealed that the magnetic nanomaterial has greater extraction capacity for Pb(II) ions than Cd(II) ions and indicated that 98.8% of Pb(II) could be removed from aqueous solutions at pH 4. FF-NH_2/EDTA loaded with heavy-metal ions can be reused as a magnetic nanomaterial after being treated with HNO_3 or Na_2EDTA solutions.

Keywords: Magnetic nanoparticles; Magnetic nanomaterial; Functionalization; Heavy metal; Removal; Extraction

1. Introduction

In recent years, increased industrial activity has caused environmental pollution and damage to ecosystems, such as the accumulation of heavy metals [1]. Heavy metals pollution is becoming one of the most serious environment problems globally [2–5]. Mining is an activity of great economic importance in Chile, but it has caused great impacts on the environment mainly by the dispersion of heavy metals into watersheds and leakage to the groundwater. Low concentrations of heavy metals in various water resources could be harmful to human health.

Different techniques are used for the separation and preconcentration of metals in solution. These include liquid–liquid extraction, precipitation, cation-exchange resins, cloud point extraction and solid phase extraction [6–10]. However, the application of these methods has been restrained by some inherent limitations, involving high capital and maintenance cost, expensive equipment, high sensitivity to operational conditions and significant energy consumption [11].

Many research groups have dedicated efforts to the development of new methods to remove heavy-metal ions in order to improve traditional approaches [12–21]. With the advancement of nanoscience and nanotechnology, magnetic nanoparticles (MNPs) have found numerous applications. Among MNPs, iron oxides (Fe_3O_4 and Fe_2O_3) have

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distinguished themselves by their unique properties, such as high surface area-to-volume ratio that promises a much greater extraction capacity and efficiency compared with other adsorbents. In addition, the surface functionality of MNPs can be easily modified to achieve selective sample extraction [22–24].

MNPs are also superparamagnetic, hence they can be attracted by a magnetic field and retain no residual magnetism after the field is removed. Especially in industries, magnetic separation is desirable because it can overcome many drawbacks occurring in the membrane filtration, centrifugation or gravitational separation and it is easy to achieve a given level of separation just via external magnetic field. Therefore, these superparamagnetic nanoparticles adhered to analytes in aqueous solution or complicated matrices can be removed by simply applying an external magnetic field, that is, no filtration or centrifugation is needed. However, the adsorption capacity and selectivity of MNPs are unsatisfactory, and they show poor stability under acidic conditions [25].

The functionalization of the surface of nanoparticles by promoting specific chemical reactions can give them greater stability in solution and selectivity to separate desired analyte targets [26]. To this end, metal chelators can be used to functionalize the surface of the nanoparticles and camouflage the action of toxic heavy metals. Hence, the main goal of this study was to investigate the efficiency of a procedure based on the use of MNPs functionalized with ethylenediaminetetraacetic acid (EDTA) and a magnetic field for the remediation of industrial wastewater samples containing Cd(II) and Pb(II).

2. Materials and methods

2.1. Chemicals, materials and samples

All reagents were of analytical grade and were used without further purification. The solutions were prepared by dissolving the reagents in deionized water processed through a water purification system (Nanopure Infinity, Barnstead). The reagents used were iron(II) chloride hydrate, iron(III) chloride hydrate, oleic acid, ethylenediaminetetraacetic dianhydride (98%) and (3-aminopropyl)triethoxysilane (APTES), obtained from Sigma-Aldrich Chem. Co., USA. Acetone, toluene, APTES, lead(II) nitrate and cadmium(II) nitrate were purchased from Merck, Darmstadt, Germany. Industrial wastewater samples were collected from a mining company, filtered (0.45 nm), stabilized by acidifying with HNO_3 (pH 2.0) and maintained at 4°C.

2.2. Instrumentation

A Model 620E Series Electrochemical Analyzer/Workstation (CH Instruments) was used for electrochemical measurements. A homemade Ag/AgCl (saturated KCl) and a platinum wire were used as reference and counter electrodes, respectively. A carbon fiber microelectrode was used as working electrode. The morphology and size of the FF-NH_2/EDTA nanoparticles were examined using transmission electron microscopy (TEM) with a Philips Tecnai 12 Biotwin transmission electron microscope at an accelerating voltage of 80 kV.

2.3. Determination of Cd(II) and Pb(II) using a bismuth film microelectrode

The fabrication of carbon fiber microelectrodes was already reported in previous studies by our research group [27]. Owing to special features such as excellent preconcentration capability and low toxicity, bismuth was used to coat the surface of the carbon fiber microelectrode. Accordingly, the determination of Cd(II) and Pb(II) before and after the removal process in water samples was carried out by square wave anodic stripping voltammetry (SWASV) using a bismuth film microelectrode (BiFME). In situ bismuth films were prepared by spiking the samples with a 1 mmol L^{-1} Bi(III) solution (final concentration of 6 μmol L^{-1}). Then, Bi and the metals were simultaneously electrodeposited on the surface of the microelectrode at –1.3 V for a period of 360 s. Voltammograms were recorded between –1.3 and 0.2 V by applying a square waveform. SWASV measurements were performed in quiescent solutions at an optimized pH of 4.0. Bi films were electrodeposited in situ on the surface of carbon fiber microelectrodes by taking into account the results of previous studies [27,28], according to which excellent analytical response to Cd(II) and Pb(II) and better repeatability were noticed in comparison with such parameters obtained with Bi microelectrodes prepared by using an ex situ procedure.

2.4. Synthesis of oleic acid-coated magnetic nanoparticles (FF)

The magnetite nanoparticles were prepared by the conventional coprecipitation method [29,30]: 15 mL of an aqueous solution of $FeCl_3$ (1.6 mol L^{-1}) were mixed with 7.5 mL of $FeCl_2$ (1.5 mol L^{-1}) dissolved in 2 mol L^{-1} HCl. Both solutions were freshly prepared with deoxygenated water before use. Immediately after mixed under nitrogen, the solution containing the iron chlorides was added to 250 mL of 0.7 mol L^{-1} ammonium hydroxide solution prepared with deoxygenated water under vigorous mechanical stirring (10,000 rpm, Ultra-Turrax T18 Homogenizer, IKA Works) under nitrogen atmosphere. After 30 min, the black precipitate formed was separated magnetically and redispersed in a new portion of water. Oleic acid (8 mmol) dissolved in 5 mL of acetone was added dropwise. The solution was heated at 80°C for 30 min under stirring. The resulting precipitate was separated magnetically, washed with acetone and redissolved in 45 mL of toluene. The resulting solution was centrifuged at 2,000 rpm for 30 min to separate any precipitates and the supernatant was collected.

2.5. Synthesis of the amino-modified oleic acid-coated magnetic nanoparticles (FF-NH_2)

Amino-modified nanoparticles were prepared as follows: 250 mg of FF was dissolved in 10 mL of toluene and 14 μL of APTES was added dropwise. The obtained solution was stirred magnetically for 30 min at room temperature. After the reaction time, the solid was isolated magnetically and washed twice with acetone (about 100 mL). The material was dried at 100°C for 20 h and identified as FF-NH_2.

2.6. Synthesis of EDTA-functionalized magnetic nanoparticles ($FF\text{-}NH_2/EDTA$)

The functionalization of FF-NH_2 MNPs was carried out as follows: 30 mL of anhydrous DMF, 1.0 mL triethylamine and 80 mg ethylenediaminetetraacetic dianhydride were added to the above prepared FF-NH_2 nanoparticles. The suspension was heated to 80°C for 30 min and then stirred overnight. Thereafter, MNPs were separated from the solution with a magnet and washed three times with DMF, ultrapure water and finally with acetone. The materials obtained are referred to as FF-NH_2/EDTA nanoparticles.

2.7. Removal efficiency of Cd(II) and Pb(II) from aqueous solutions

The extraction of Cd(II) and Pb(II) ions from aqueous media was tested by weighing about 5 mg of FF-NH_2/EDTA into glass tubes that were filled with 10 mL of the heavy metals solution with different concentrations at pH 4. The mixture was sonicated for 10 min and shaken for 5 min. Then, the MNPs were removed from the mixture with the help of an external magnetic force. The supernatant concentration of Cd(II) and Pb(II) was measured using a BiFME by SWASV. The pH of heavy-metal ions solution was adjusted with 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl solutions. All experiments were run in triplicate and the average values were reported here. The removal efficiency (RE%) and adsorption capacity (q, mg g^{-1}) of Cd(II) and Pb(II) were calculated using Eqs. (1) and (2), respectively:

$$\text{RE\%} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

$$q = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

where C_0 and C_e correspond to the concentration of Cd(II) and Pb(II) (mg L^{-1}) in the solutions before and after adsorption, respectively; V is the volume of the solution (L) and m is the weight of the adsorbent (g).

3. Results and discussion

3.1. Functionalized magnetic nanoparticles

Fe_3O_4 nanoparticles can be synthesized by coprecipitation of Fe^{2+} and Fe^{3+} in aqueous salt solution by adding a base solution. The precipitated magnetite, black color, is given by the chemical reaction (3). The control size, shape and composition of the nanoparticle are dependent on the type of salt used (chloride, sulfate, nitrate, etc.) and the concentration of Fe^{2+} and Fe^{3+} [31].

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \qquad (3)$$

In a first step, the synthesized MNPs were stabilized in toluene by subsequent treatment with oleic acid. The resulting solution has the properties of a ferrofluid. A solid sample of magnetite stabilized with oleic acid (FF) has a mass percentage concentration of hydrogen and carbon of 1.5% and 8.7%, respectively, assuming that any source of carbon and hydrogen present in the iron oxide is derived exclusively from oleic acid on the surface of the material [30]. In a second step, APTES was adsorbed and provided a high amount of free amine groups on the surface of the nanomagnet. In a third step, the reactive amine groups were used to attach heavy-metal chelating agents. In this case, diethylenetriamine pentaacetic acid dianhydride ($DTPA_{da}$) was used, which reacted with primary amines forming an amide secondary linker resulting in an EDTA like ligand after hydrolysis of the second anhydride group [32] (Fig. 1).

The morphology and structural feature of FF-NH_2/EDTA were examined by using TEM. The TEM image shown in Fig. 2 was taken from particles dispersed in ethanol and dried on a Cu grid covered with formvar/carbon. Although a good dispersion of the MNPs was not obtained, the analysis of the agglomerate reveals that the MNP has size and structure in the nanometer scale. The mean diameter and standard deviation of the particles were determined from TEM micrographs from the average of about 30 particles and the average diameter of the MNP was found to be 11.1 nm (±0.9 nm).

After the synthesis of new functionalized magnetic nanoparticles (FF-NH_2/EDTA), different studies were carried out to evaluate the removal efficiency for Cd(II) and Pb(II). The extraction of Cd(II) and Pb(II) from aqueous solutions was performed as described in section 2.7.

3.2. Variables optimization for the removal of Cd(II) and Pb(II) with ($FF\text{-}NH_2/EDTA$) aqueous solution

3.2.1. Effect of the amount of $FF\text{-}NH_2/EDTA$ on the removal of Cd(II) and Pb(II)

The efficiency of the synthesized material toward the removal of Cd(II) and Pb(II) was examined using the BiFME as the detection method of remaining metallic ions. Fig. 3 shows typical stripping voltammograms recorded with a BiFME in 10 mL solutions containing 10 mg L^{-1} Cd(II) and Pb(II) before (___) and after (_ _ _) the removal process. Experiments were performed in solutions containing different amounts

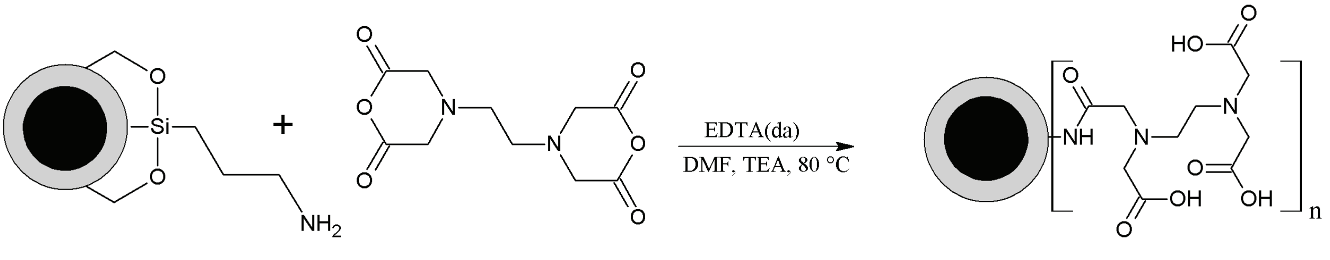

Fig. 1. Reaction of functionalization of FF-NH_2 with $EDTA_{(da)}$.

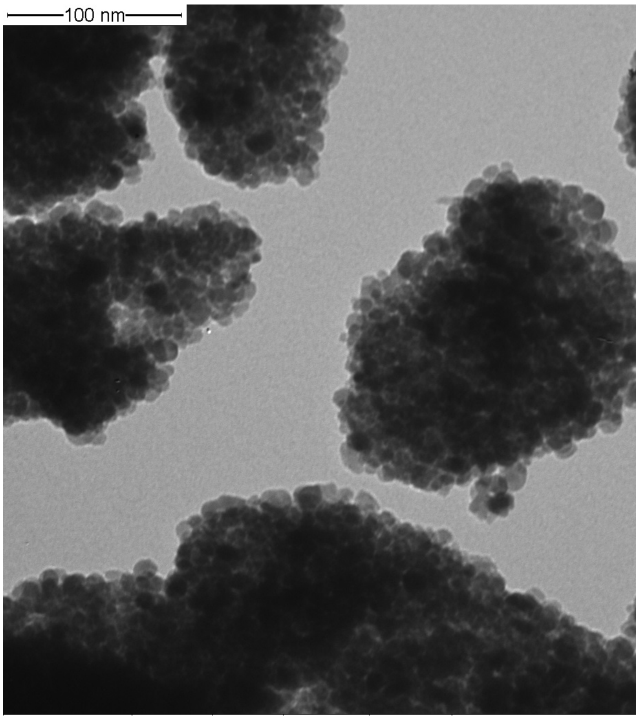

Fig. 2. TEM image of FF-NH_2/EDTA.

of MNPs: 2, 5, 10 and 20 mg (Figs. 3(A)–(D), respectively). By looking at the voltammograms recorded before the addition of FF-NH_2/EDTA, anodic peaks corresponding to the oxidation of Cd(II) and Pb(II) can be seen at about –0.73 and –0.53 V vs. Ag/AgCl (saturated KCl), respectively.

The addition of FF-NH_2/EDTA to the metallic ions solution was effective concerning the removal of Pb(II). The results showed that practically all Pb(II) was removed even after addition of a relatively low amount of FF-NH_2/EDTA, as the peak at –0.53 V completely disappeared. Increasing the amount of FF-NH_2/EDTA from 2 to 20 mg did not significantly affect the removal of Pb(II). On the other hand, a different situation was observed for Cd(II) ions, as the peak at –0.73 V decreased upon addition of FF-NH_2/EDTA, but not at the same extent as for Pb(II). For instance, the percentage removal for Cd(II) changed from 25% ± 4% to 58% ± 2% after addition of 2 and 20 mg of FF-NH_2/EDTA, respectively. This indicates that the interaction of Pb(II) ions with the solid phase is much more effective in comparison with Cd(II). Therefore, based on the above experiments, 10 mg was chosen as the optimal amount of FF-NH_2/EDTA.

The removal efficiency of MNPs in a solution containing different metallic ions depends on the availability of chelating sites. Hence, when the metallic ions compete for the same sites of a support, those with greater affinity could displace others with weaker affinity. The extent to which a metallic ion will bind to a ligand depends strongly on the chemistry of the ion and its preference to form covalent or ionic bonding [33,34]. For instance, Badruddoza et al. [35] showed that the percentage removal of Cd(II) and Ni(II) was reduced significantly in the presence of Pb(II). This tendency of higher adsorption of Pb(II) ion on different adsorbents containing

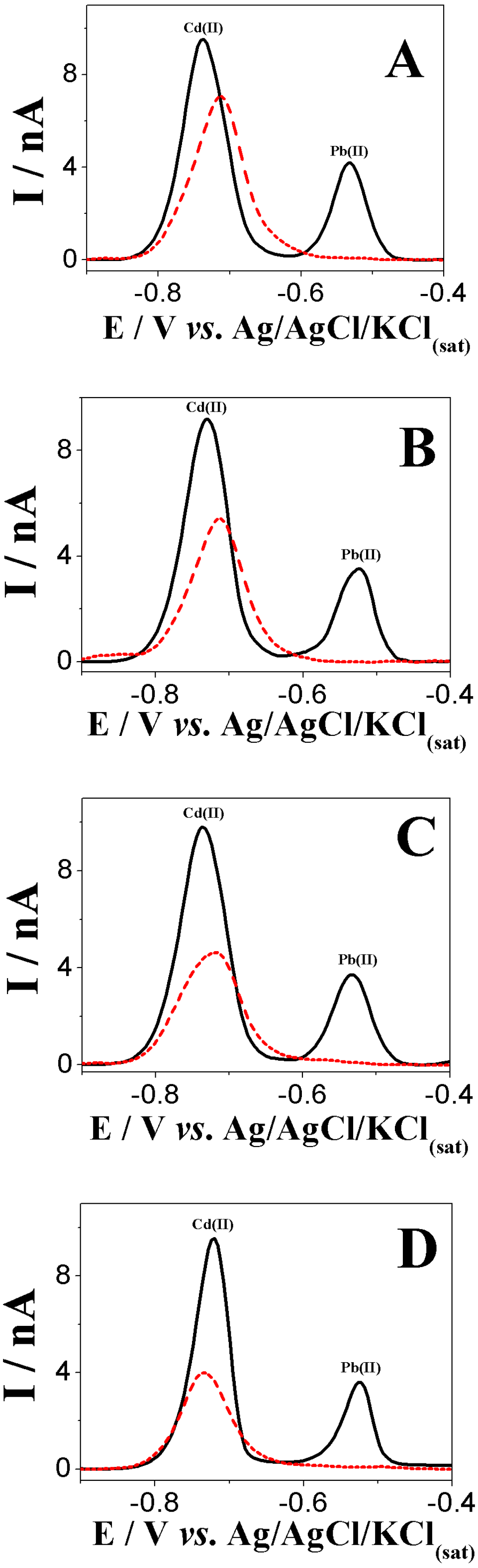

Fig. 3. Square-wave stripping voltammograms recorded with an in situ bismuth film-modified carbon fiber microelectrode in a solution containing 10 mg L^{-1} Cd(II) and 10 mg L^{-1} Pb(II) (pH 4.0) before (___) and after (_ _ _) removal with different amounts of FF-NH_2/EDTA: 2 mg (A), 5 mg (B), 10 mg (C) and 20 mg (D). Total volume of the solution: 10 mL.

–COOH and OH functional groups in multimetal solutions was also reported in other studies [35,36].

3.2.2. Effect of pH in the removal of Cd(II) and Pb(II)

It is well known that pH is an important parameter when chelation procedures are to be performed. Accordingly, experiments to optimize the solution pH in the removal process of Cd(II) and Pb(II) were carried out in the range from 2.0 to 6.0. pH values higher than 6.0 result in the hydrolysis of Cd(II) and Pb(II) and experiments were not performed at such acidity conditions as this would introduce uncertainty into the results [37]. The effect of the pH on the removal efficiency of Cd(II) and Pb(II) ions is shown in Fig. 4(A). As expected, the removal efficiency of Cd(II) and Pb(II) ions is clearly pH dependent and higher values are obtained at pH ≥ 4.0 owing to the deprotonation of magnetic nanomaterial surface [38,39]. At more acidic conditions, the removal of both metallic ions takes place at lower extents due to the competition between H^+ and Cd(II)/Pb(II) ions by the chelating agent.

3.2.3. Effect of extraction time in the removal of Cd(II) and Pb(II)

The removal of the analytes depends on the contact time of the liquid phase with the solid phase and short times are always desired. In this regard, replicate sets of analytes and MNPs were prepared by weighing about 5 mg of FF-NH_2/EDTA into glass tubes that were filled with 10 mL of the heavy metals solution and measurements of the concentration of free metallic ions were performed at different time intervals: 2, 5, 10, 15 and 20 min. Results showed that the removal efficiency of Pb(II) was almost 100% (Fig. 4(B)). Removal of Cd(II) and Pb(II) from the solution reached more than 53% ± 3% and 99% ± 2% respectively, after about 10 min. Therefore, ultrasonication time of 10 min was selected as the optimal for further works.

3.2.4. Adsorption capacity

In order to determine the adsorption capacity, 10 mg of FF-NH_2/EDTA were added to 10 mL of a solution containing 40 mg L^{-1} Cd(II) and Pb(II) and the resulting mixture was equilibrated for 30 min. The maximum adsorption capacity of FF-NH_2/EDTA was found to be 82.8 ± 0.7 and 44.8 ± 0.9 mg g^{-1} for Cd(II) and Pb(II), respectively. The performance of the proposed method for Cd(II) and Pb(II) adsorption was compared with that of other materials reported in the literature, as shows Table 1. Such comparison confirms that the developed method is significantly better than some of those

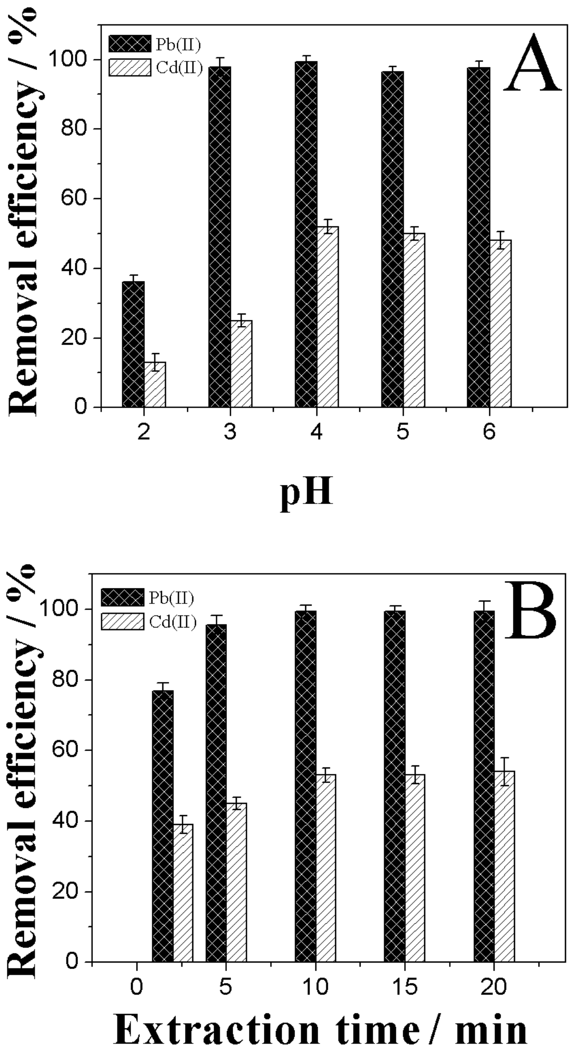

Fig. 4. Effect of pH (A) and extraction time (B) on Cd(II) and Pb(II) removal efficiency using FF-NH_2/EDTA. Initial concentration: 10 mg L^{-1} and magnetic nanomaterial amount: 10 mg.

Table 1
Comparison of adsorption capacity (mg g^{-1}) of various adsorbents

Sorbents	Pb(II)	Cd(II)	Time (min)	Reference
FF-NH_2/EDTA	82.8	44.8	7	This work
EDTA-modified chitosan/SiO_2/Fe_3O_4	123.5	63.3	360	[40]
Fe_3O_4 yeast treated with EDTA dianhydride	99.3	48.7	30	[41]
Silica-coated magnetic nanoparticles modified with γ-mercaptopropyltrimethoxysilane	70.4	45.2	2	[42]
Fe-modified sporopollenin (Fe-Sp) biomass	22.7	–	104	[43]
Magnetic activated carbon (MAC)	86.2	49.8	30	[44]
Amino-functionalized magnetic nanoadsorbent	40.1	–	5	[45]

already described with respect to the adsorption capacity and adsorption time. According to these results, one can conclude the synthesized MNP material is a good candidate for environmental remediation purpose and to reduce the hazardous impact of heavy metals.

3.2.5. Effect of interfering cations

Generally, industrial wastewater samples contain more than one cation. Thus, the presence of other cations may interfere in the removal efficiency of Cd(II) and Pb(II). Accordingly, Cu(II) and Hg(II) were used as model interfering ions, and the influence of such cations on Cd(II) and Pb(II) adsorption was studied and the results are shown in Fig. 5. Surprisingly, the presence of these cations has no remarkable influence on Pb(II) removal efficiency. On the other hand, for Cd(II) the removal efficiency decreased from 55% ± 3% to 27% ± 4% in the absence and presence of the interfering cations, respectively. Similar observations have been reported by other researchers for the adsorption of Cd(II) and Pb(II) onto MNPs surfaces [36,46].

The performance of our functionalized nanoparticles (FF-NH_2/EDTA) in the removal of Cd(II) and Pb(II) ions from real industrial wastewater samples was also studied. These samples were analyzed with respect to the content of Cd(II) and Pb(II) before and after treatment by using the BiFME (section 2.3). The results presented in Table 2 clearly indicate that the magnetic support has potential applications for the removal of Pb(II) from industrial wastewater. As already mentioned, Cd(II) was not completely removed from the samples and removal efficiency values from 25% ± 5% to 69% ± 3% were obtained at some selected experimental conditions. Hence, it can be concluded that the functionalized MNPs respond effectively in a real matrix for Pb(II) removal.

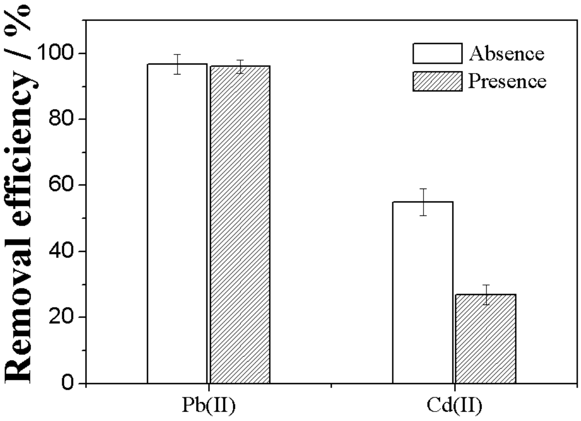

Fig. 5. Removal efficiency for Cd(II) and Pb(II) in the absence and presence of Cu(II) and Hg(II). Initial cations concentration: 5 mg L^{-1}, magnetic nanomaterial amount: 10 mg, contact time: 7 min and pH 4.0.

3.2.6. Desorption and regeneration studies

Desorption and regeneration performance of the MNPs is an important factor as it determines the cost of the adsorption system. With rising prices of raw materials and wastewater treatment processes, the attractiveness of product recovery processes has increased significantly. The possibility of desorption and regeneration of the FF-NH_2/EDTA was examined by batch desorption experiments conducted by dispersing Cd(II)/Pb(II)-loaded FF-NH_2/EDTA in HNO_3 and Na_2EDTA solutions of different concentrations (Fig. 6). The dependence of adsorption of Cd(II) and Pb(II) ions on the pH was confirmed, hence it seems quite clear that the desorption can be achieved by increasing the concentration of the HNO_3 solutions from 0.01 to 0.05 mol L^{-1}. The results indicated excellent desorption efficiency for Pb(II) (97% ± 3% recovery), but a less significant value was obtained for Cd(II) (55% ± 2%). More acidic conditions were not employed because of the possible dissolution of magnetite nanoparticles. This suggests that the adsorption of Pb(II) onto FF-NH_2/EDTA is reversible and the Pb(II)-loaded nanomagnet can be easily desorbed using 0.01 mol L^{-1} HNO_3. However, Na_2EDTA is able to desorb Cd(II) ions more efficiently from the surface of FF-NH_2/EDTA and it is clear that the desorption ratio of Cd(II) increases slightly as the concentration of Na_2EDTA increases from 0.05 (66% ± 3%) to 0.1 mol L^{-1} (73% ± 4%). Hence, Na_2EDTA was selected as a better eluent for regeneration, as it shows excellent desorption efficiency for both Cd(II) and Pb(II).

In order to investigate the reusability of the MNPs, the extraction–desorption process for Pb(II) was repeated five times using the same nanomagnet. The removal efficiency of FF-NH_2/EDTA remained almost constant during these cycles (Fig. 7) and these results are inspiring and indicate that the proposed FF-NH_2/EDTA adsorbent has good reusability and stability.

4. Conclusions

In this work, superparamagnetic nanoparticles were synthesized with a diameter of ~11 nm using a coprecipitation method. We have demonstrated that a simple and inexpensive compound (FF-NH_2/EDTA) can be successfully used

Table 2
Cd(II) and Pb(II) concentration in industrial wastewater samples (n = 3) and removal (%) after treating with FF-NH_2/EDTA (removal efficiency)

Samples	$Cd(II)_{initial}$/mg L^{-1}	$Cd(II)_{removal}$/%	$Pb(II)_{initial}$/mg L^{-1}	$Pb(II)_{removal}$/%
A1.1	0.89 ± 0.05	69	3.85 ± 0.09	97
A1.2	0.20 ± 0.03	53	1.93 ± 0.05	99
B2.1	0.46 ± 0.07	33	0.98 ± 0.06	98
B2.2	0.70 ± 0.05	25	5.56 ± 0.05	91

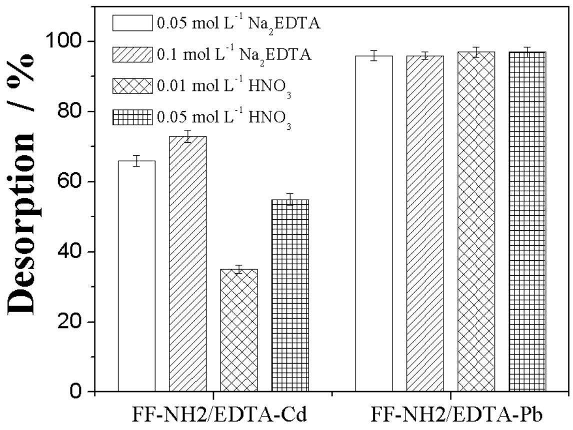

Fig. 6. Desorption of Cd(II) and Pb(II) from Cd(II)/Pb(II)-loaded FF-NH_2/EDTA supports in different eluents.

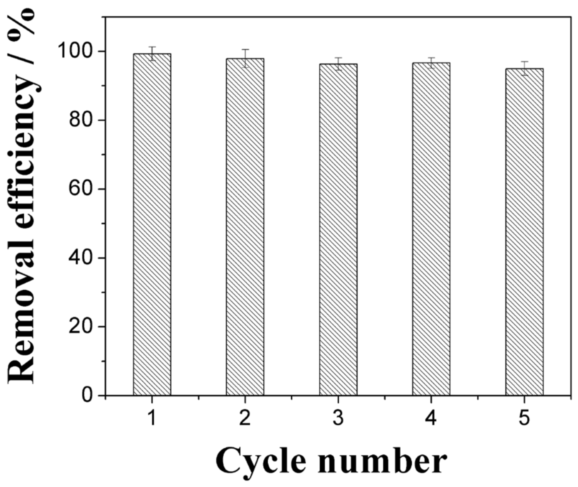

Fig. 7. Reusability of FF-NH_2/EDTA for removal/desorption of Pb(II) during five cycles. Initial concentration of Pb(II): 10 mg L^{-1}, magnetic nanomaterial amount: 10 mg, and extraction time: 15 min.

as an alternative material for the removal of heavy metals from wastewater in a short time with high removal efficiency and good adsorption capacity. Adsorption of Cd(II) and Pb(II) by FF-NH_2/EDTA reached equilibrium within 10 min and the removal efficiency was highly pH dependent. The adsorption capacity for Cd(II) and Pb(II) was 82.8 ± 0.7 and 44.8 ± 0.9 mg g^{-1}, respectively. In a multimetal solution, FF-NH_2/EDTA could selectively remove Pb(II) ions, without being affected its removal efficiency. Experiments performed with solutions containing Cd(II) and Pb(II) as typical metallic ions commonly present in wastewater, confirmed the usefulness of the proposed procedure for complete removal of Pb(II), whereas less remarkable results were found for Cd(II). Desorption and regeneration studies indicated that the synthesized magnetic nanomaterial can be used repeatedly, without impacting the removal efficiency. Therefore, FF-NH_2/EDTA is recommended as a fast, effective and inexpensive adsorbent for rapid removal of metallic ions from wastewater effluents.

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