Article

Synthesis and Application of Magnetic Nanoparticle Supported Ephedrine as a New Sorbent for Preconcentration of Trace Amounts of Pb and Cu in Water Samples

Somayeh Mohammadi, Gholamreza Khayatian,* Bahareh Atashkar and Amin Rostami

Department of Chemistry, Faculty of Science, University of Kurdistan, P.O. Box 416, 66177-15175 Sanandaj, Iran

Um novo adsorbente para a determinação de Pb e Cu por espectrometria de absorção atômica de chama (FAAS) foi sintetizado e caracterizado por diferentes técnicas. O efeito de vários parâmetros como pH, tipo e volume do eluente, quantidade de adsorbente, volume da amostra e íons interferentes foram otimizados. Nas condições otimizadas, um gráfico de calibração linear foi obtido para a determinação de Pb(II) e Cu(II). As faixas lineares foram 15-500 µg L^{-1} e 18-500 µg L^{-1} para chumbo e cobre, respectivamente. Os limites de detecção e quantificação foram 4,3 e 14,5 µg L^{-1} para chumbo e 5,0 e 16,7 µg L^{-1} para cobre, respectivamente. O desvio padrão relativo para determinações de oito replicatas de 80 e 200 µg L^{-1} de Pb(II) foram 2,9 e 1,4% e para Cu(II) foram 3,5 e 1,9%, respectivamente. A aplicabilidade do método foi avaliada ao analisar traços de chumbo e cobre em diferentes amostras de água.

A new adsorbent for determination of Pb and Cu by flame atomic absorption spectrometry (FAAS) was synthesized and characterized with different techniques. The effect of various parameters such as the pH, the type and volume of eluent, amount of adsorbent, sample volume and interfering ions were optimized. Under the optimized conditions, a linear calibration graph was obtained for determination of Pb(II) and Cu(II). The linear ranges were found to be 15-500 µg L^{-1} and 18-500 µg L^{-1} for lead and copper, respectively. The limit of detection and limit of quantification were 4.3 and 14.5 µg L^{-1} for lead and 5.0 and 16.7 µg L^{-1} for copper, respectively. The relative standard deviation for eight replicate determinations of 80 and 200 µg L^{-1} of Pb(II) were 2.9 and 1.4% and for Cu(II) were 3.5 and 1.9%, respectively. Applicability of the method was evaluated by analyzing trace amounts of lead and copper in different water samples.

Keywords: magnetic solid phase extraction, lead(II), copper(II), MNPs-ephedrine, preconcentration

Introduction

In the past decade, the entry of pollutants of heavy metals has increased in the global ecosystem.[1] The amount of entering of heavy metals into the environment is far beyond the amount that is removed by natural processes. Their accumulations in water, air and soil and their non-metabolized is an important environmental problem. Moreover, they have deposited and accumulated in tissues such as fat, muscle, bones and joints. This causes several diseases and complications in the body. Most heavy metals in aquatic systems are Cu, Zn, Cd, Hg, Pb and Ni. It has long been found that, in the appropriate concentrations, many metals including Fe (hemoglobin), Cu (respiratory pigments), Zn (enzymes), Co (vitamin B$_{12}$),

Cr (carbohydrate metabolism), Se (antioxidant role), Mo and Mn (enzyme) are essential to living organisms but may be toxic at high concentrations. Metals such as Hg, Pb, Sn, Ni and As are generally not required for metabolic activity and are toxic at quite low concentrations.[2] Therefore, the measurement of trace amounts of heavy metals in environmental samples is very important for analytical chemists. Several techniques for measuring these elements have been employed such as flame atomic absorption spectrometry (FAAS),[3,4] electrothermal atomic absorption spectrometry (ETAAS),[5] inductively coupled plasma mass spectrometry (ICP-MS),[6] inductively coupled plasma optical emission spectrometry (ICP-OES)[7-10] and spectrophotometry.[11] Among these, FAAS, due to its simplicity and its lower price is more common than other instruments. But this technique has no sufficient sensitivity in direct determination of metals, therefore, separation and

*e-mail: gkhayatian@uok.ac.ir, gkhayatian@yahoo.com

preconcentration methods including: coprecipitation,[12-14] liquid-liquid extraction,[15] cloud point extraction,[16] solid phase extraction[17,18] can solve this problem. Solid phase extraction (SPE) is widely used due to its simplicity, consumption of small volumes of organic solvent, high preconcentration factor, high recovery, rapid phase separation and the ability to combine with different modern detection techniques.[19] SPE sorbent selection is critical to obtaining efficient SPE recovery. Until now, various adsorbents such as chelating resin,[20] activated carbon,[8] modified or bonded silica gel,[21] polyurethane foam,[22] naphthalene[23] and cellulose[24] have been used for metal ion sorption. Recently, nanomaterials have applied as one of the most promising adsorbents in SPE. A new method of solid phase extraction, based on the use of magnetic adsorbents has been developed.[25,26] Magnetic nanoparticles offer many advantages due to the unique size, easy separation from the solution using a magnet and high surface area.[3,7] The suitable surface coatings and effective protection strategies have developed to prevent the accumulation of nanoparticles, chemical analysis in specific environments as well as changes of the magnetic properties in complex environmental samples and biological systems.[10]

In this paper, a new adsorbent, magnetic nanoparticle Fe_3O_4-immobilized ephedrine (MNPs-ephedrine) for the determination of Pb and Cu by FAAS is synthesized and characterized with different techniques. In the best of our knowledge, this adsorbent has not been used to the separation and preconcentration of trace amount of metal ions. Applicability of the method was evaluated by analyzing trace amounts of lead and copper in different water samples.

Experimental

Instrumentation

A Shimadzu model AA-670 atomic absorption spectrometer (Kyoto, Japan) equipped with lead and copper hollow cathode lamps and air-acetylene flame was used for determination of the metal ions. All pH settings were carried out by a Metrohm E-691 digital pH meter (Switzerland) with a combined glass electrode. The infrared spectra were recorded using an infrared spectrometer (Bruker-Vector 22, Germany) with KBr disks in the range of 4000-400 cm^{-1}. The scanning electron microscopy (SEM) image was obtained by VEGA TESCAN (Czech Republic). The XRD data were collected on an X'PertMPD Philips diffractometer (Netherland) with Cu Ka radiation source (λ = 1.54050 Å) at 40 kV voltage and 40 mA current. The TGA was carried out on a Bähr STA 503

instrument (Germany) under air atmosphere, heating rate 10 °C min^{-1}. The magnetic measurements were carried out in an Alternating Gradient Force Magnetometer (AGFM, Meghnatis Daghigh Kavir Co., Made in Iran) at room temperature. A magnet (Nd-Fe-B, 1.2 T, $50 \times 40 \times 20$ mm) was used for magnetic separation.

Reagents and solutions

All materials used in this work were of analytical grade from Merck Co. (Darmstadt, Germany). Stock standard solutions of Pb(II), Cu(II) (1000 mg L^{-1} each one) were purchased from Merck. Solutions with lower concentrations were prepared daily by suitable dilution of the stock solution with deionized water. (3-chloropropyl)-trimethoxysilane (CPTMS) and ephedrine hydrochloride were utilized for the synthesis of sorbent. The pH 4.5 of the sample solution was adjusted using acetate buffer. The HCl, H_2SO_4 and HNO_3 solutions, using as eluents were prepared by dilution of the concentrated solutions with deionized water.

Preparation of large-scale the magnetic Fe_3O_4 nanoparticles (MNPs)

Masses of 4.865 g $FeCl_3 \cdot 6H_2O$ and 1.789 g $FeCl_2 \cdot 4H_2O$ were added to 100 mL deionized water and sonicated until the salts dissolved completely. Then, 10 mL of 25% aqueous ammonia was added quickly into the reaction mixture in one portion under N_2 atmosphere at room temperature followed by stirring about 30 min with mechanical stirrer. The black precipitate was washed five times with doubly distilled water.[27]

Preparation of MNPs coated by (3-chloropropyl)-trimethoxysilane (MNPs-CPTMS)

Mass of 1.500 g MNPs powder was dispersed in 250 mL ethanol/water solution with volume ratio, 1:1 by sonication for 30 min, and then 2.5 mL CPTMS (99%) was added to the mixture. After mechanical stirring under N_2 atmosphere at 33-38 °C for 8 h, the suspended substance was separated with centrifugation (for 30 min). The settled product was re-dispersed in ethanol by sonication. The final sample was separated by an external magnet and washed five times with ethanol. The product was stored in a refrigerator to use.[27]

Preparation of MNPs-ephedrine ligand

To prepare the MNPs-ephedrine ligand, 1.00 g MNPs-CPTMS was dispersed in 6-8 mL dry toluene by ultrasonication for 10 min. Subsequently, 0.403 g ephedrine

hydrochloride and 0.672 g sodium bicarbonate were added and the mixture was refluxed for 28 h. Then, the final product was separated by magnetic decantation and washed twice by dry CH_2Cl_2 and ethanol respectively to remove the unattached substrates. The product was stored in a refrigerator until use.

Preparation of environmental waters

The water samples, such as tap water (Sanandaj, Iran), sea water from Caspian Sea (Rudsar, Iran), wastewater of oil refinery (Kermanshah, Iran) were stored in pre-cleaned polyethylene bottles for use. The pH water samples were adjusted to 1 with concentrated HNO_3. Before the analysis, the sea water and wastewater of oil refinery samples were filtered through a filter paper to remove suspended particular solids. Then, all samples were placed in refrigerator at approximately 4 °C.

General procedure

A 100 mL aqueous solution containing 10.0 µg Pb(II), Cu(II) was prepared and pH was adjusted at 4.5 with 10.0 mL acetate buffer solution (0.01 mol L^{-1}). The solution was added to 10.0 mg adsorbent in 100 mL beaker. The sample solution was sonicated for 10 min to simplify sorption of lead and copper ions. Then, a strong magnet was used and the magnetic adsorbent separated after a few minutes and the supernatants were decanted. For elution adsorbed analyte ions from nanoparticles, 2.0 mL H_2SO_4 and HCl mixtures (0.5 mol L^{-1} each one) with 2:1 volumetric ratio were added and the solution was again sonicated for 6 min and exposed on the magnet to deposit the magnetic nanoparticles. Afterwards, the eluate containing metal ions was determined by FAAS, using the conditions recommended by the manufacturer with a flow rate of 2.0 mL min^{-1}.

Results and Discussion

Preparation and characterization of MNPs-ephedrine

The process of the preparation of MNPs-ephedrine is shown in Scheme 1.
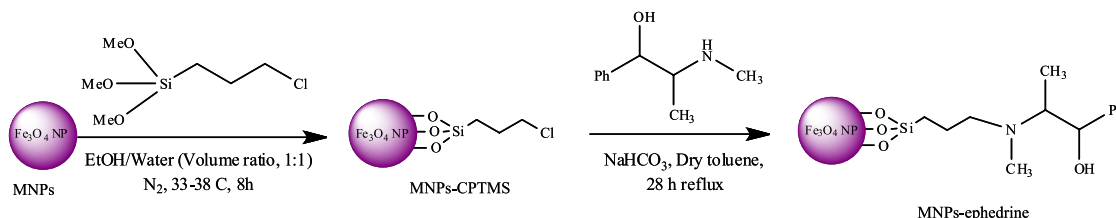
The metal ions are easily adsorbed on MNPs-ephedrine because ephedrine possesses a hydroxyl group and a nitrogen atom, which can complex with Cu (II) and Pb(II).[28] The MNPs-ephedrine has been characterized by SEM, X-ray diffraction (XRD), thermo gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and alternating gradient force magnetometer (AGFM).

The XRD pattern of MNPs-ephedrine is shown in Figure 1. According to the XRD analysis, the peaks with 2θ at 30.4°, 35.6°, 43.3°, 57.3° and 62.8° indicated the characteristic peaks of Fe_3O_4. Weak broad bands (2θ = 11.5-23°) appeared in XDR pattern which could be attributed to the amorphous silane shell formed around the magnetic cores.

The SEM image of MNPs-ephedrine is shown in Figure 2. It was confirmed that MNPs-ephedrine were made up of uniform nanometer-sized particles 20-32 nm.

Figure 3 shows FTIR spectra for MNPs, MNPs-CPTMS, and MNPs-ephedrine. The bands at low wavenumbers ≤ 700 cm^{-1} come from vibrations of Fe–O bonds of iron oxide, which for the bulk Fe_3O_4 samples appear at 570 and 375 cm^{-1} but for Fe_3O_4 nanoparticles appear at 624 and 572 cm^{-1} as a blue shift, due to the size reduction. The FTIR spectra of MNPs-CPTMS and MNPs-ephedrine show Fe–O vibrations in the same vicinity. The introduction of CPTMS to the surface of MNPs is confirmed by the bands at 1005 and 1128 cm^{-1} assigned to the Fe–O–Si and C–Cl stretching vibrations, respectively.[27] Reaction of MNPs-CPTMS with ephedrine produces MNPs-ephedrine, in which the presence of ephedrine is demonstrated with stretching vibrations at 3341 and 3380 cm^{-1}, which incorporates the N–H and O–H bonds and vibrations in the range of 1428-1652 cm^{-1} are attributed to the phenyl ring.

One indication of bond formation between the nanoparticles and the ligand can be inferred from TGA. The TGA curve of the MNPs-ephedrine shows the mass loss of the organic functional group as it decomposes upon heating (Figure 4). The weight loss at temperatures below 200 °C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. Organic spacers have been reported to desorb at temperatures above 260 °C.[27] The curve shows a weight loss about 19% from 260 to 600 °C. The loading of the ligand in MNPs-ephedrine can
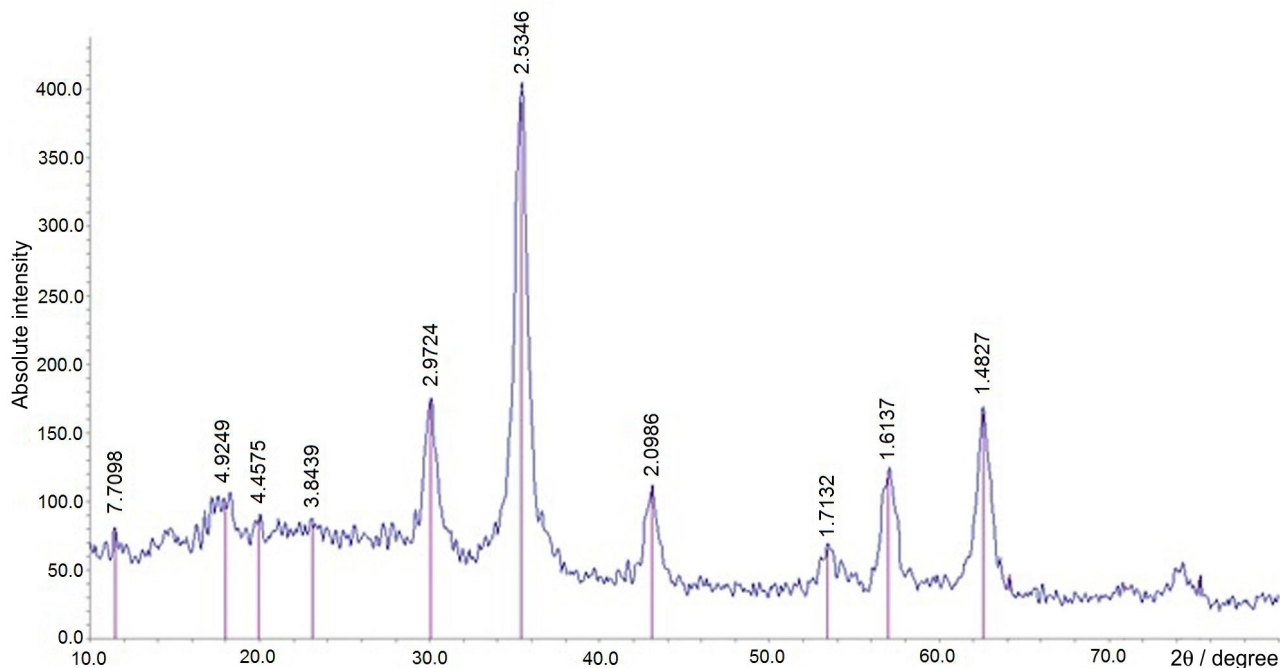

Scheme 1. The synthesis of ephedrine-functionalized magnetic Fe_3O_4 nanoparticles.

Figure 1. XRD pattern of MNPs-ephedrine.

Figure 2. SEM image of MNPs-ephedrine.

Figure 3. (a) FTIR spectra of MNPs (blue), (b) MNPs-CPTMS (black) and (c) MNPs-ephedrine (red).
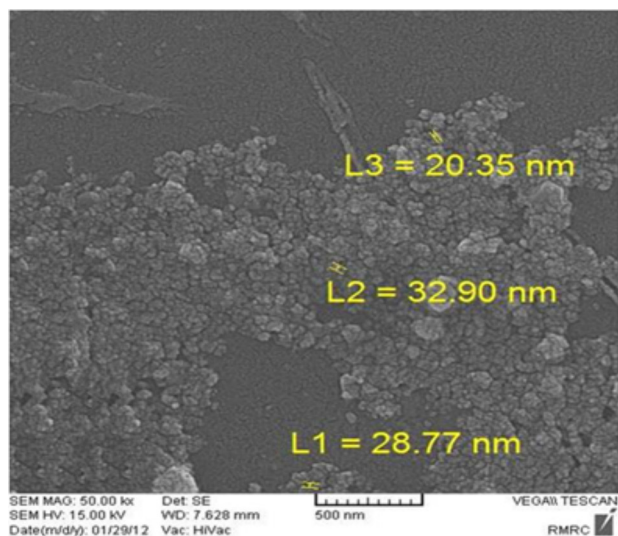
be calculated from TGA, which confirmed a loading of approximately 0.35 mmol g^{-1}.

Superparamagnetic particles are beneficial for magnetic separation; the magnetic property of MNPs and MNPs-ephedrine were characterized by AGFM. The room temperature magnetization curves of MNPs and MNPs-ephedrineare are shown in Figures 5a and 5b. As expected, the bare MNPs, showed the higher magnetic value (saturation magnetization, Ms) of 74.3 emug^{-1}, the Ms value of MNPs-ephedrine is decreased due to the silica coating and the layer of the grafted ligand (30.4 emug^{-1}). As a result, the
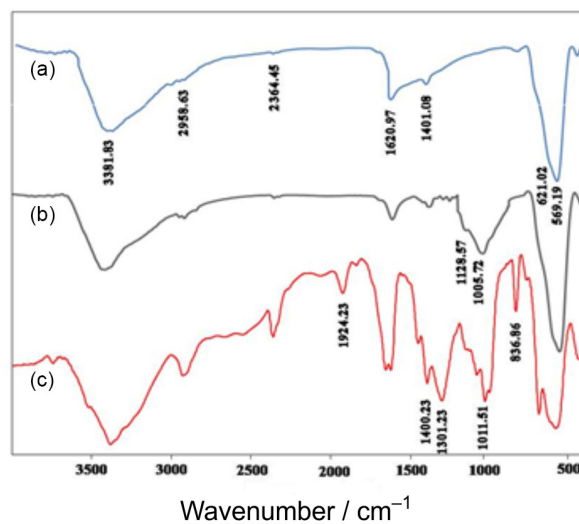
MNPs-ephedrine has a typical superparamagnetic behaviour, and can be efficiently attracted with a small magnet.

Unfortunately, due to the magnetic properties of MNPs-ephedrine, it is actually impossible to further characterize this material by using solid-state nuclear magnetic resonance (NMR) spectroscopy.

The initial experiments indicated that the lead and copper ions are effectively adsorbed on MNPs-ephedrine. In order to use the present method for preconcentration and determination of trace amounts of metal ions, various parameters including, the pH of the sample solution, the
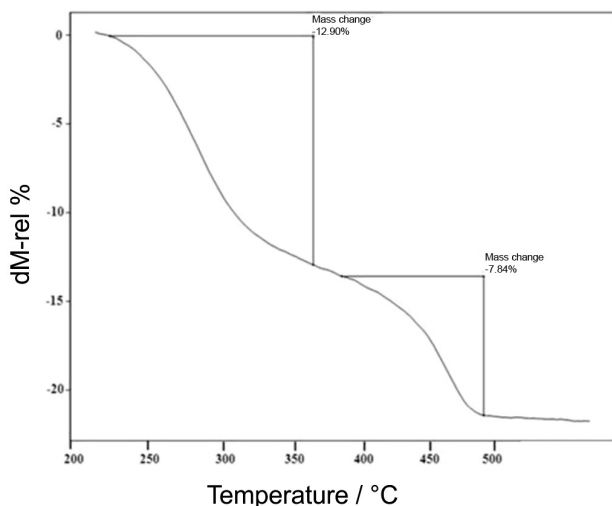
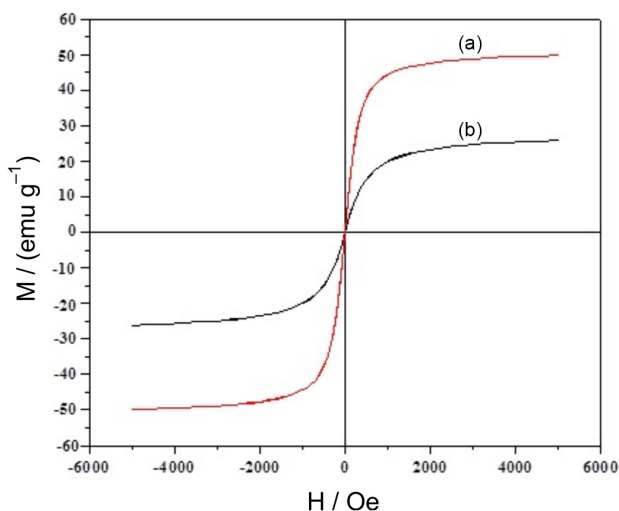**Figure 4.** TGA profile of MNPs-ephedrine.

Figure 5. AGFM curve of (a) MNPs, (b) MNPs-ephedrine.

type, concentration and volume of eluent, the amount of adsorbent, the sorption and desorption time, the volume of sample solution and the effect of different coexisting ions were optimized. The optimization of each of these parameters for determination Pb(II) and Cu(II) is described in the next sections.

Effect of pH

Due to the surface charge of the adsorbent and the solution chemistry of the metal ions, the pH of the aqueous solution is an important controlling factor in the uptake process of metal ions on adsorbents. Thus, the effect of pH, on the preconcentration of solutions containing 100 µg L^{-1} Pb(II) and Cu(II) in the pH range of 3.0-10.0 was evaluated. The pH of solutions was adjusted using either hydrochloric acid or sodium hydroxide solutions (0.1-1.0 mol L^{-1}) and the

result is shown in Figure 6. As can be seen, low extractions of Pb(II) and Cu(II) at pH < 4.0 may be due to the competition of proton with analyte ions for sorption on the MNPs-ephedrine surface and in the higher pHs (pH > 5.0), may be due to formation of metal hydroxide species such as Pb(OH)$^+$, Pb(OH)$_2$, Pb(OH)$_3^-$ and Cu$_2$(OH)$_2^{2+}$, Cu(OH)$_2$, Cu(OH)$_3^-$, Cu(OH)$_4^{2-}$,[29-31] that leads to the decrease in the efficiency of extraction. As can be seen from Figure 6, lead and copper ions were quantitatively recovered (≥ 95%) in the pH range of 4.0-5.0. So, the pH 4.5 was selected as the optimum value for subsequent experiments. This optimum pH was adjusted with 10.0 mL of acetic acid-acetate buffer solution.
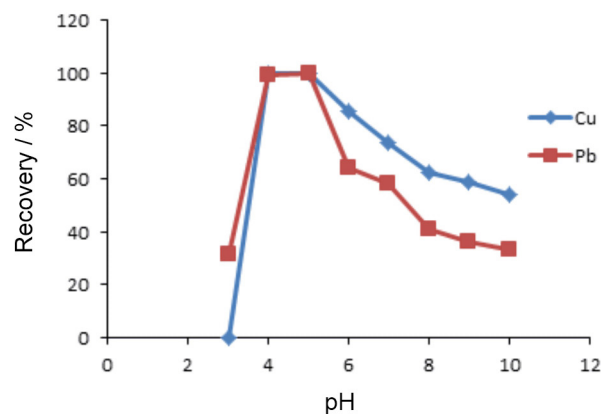

Figure 6. Effect of pH on the recovery of 100 µg L^{-1} of Pb(II) and Cu(II). Conditions: amount of adsorbent, 10.0 mg; sample volume, 50.0 mL; eluent, 5.0 mL of H$_2$SO$_4$ and HCl mixture (0.5 mol L^{-1} each one), sorption time, 14 min; desorption time, 6 min (n = 3).

Effect of type and volume of eluent

The desorption process of Pb(II) and Cu(II) from sorbent is influenced by the type and concentration of eluents. Various eluents such as EDTA, HNO$_3$, HCl, H$_2$SO$_4$ with different concentration and the mixture of HCl and H$_2$SO$_4$ (0.5 mol L^{-1}) were tested. As shown in Figure 7, a mixture of 2:1 v/v of H$_2$SO$_4$ and HCl (0.5 mol L^{-1} each one) provided higher efficiency compared to other eluents. Thus, a mixture of 2:1 v/v of H$_2$SO$_4$ and HCl was chosen for further studies.

The effect of the eluent volume on the extraction of metal ions was also studied. Different volumes of eluent in the range of 2.0 to 5.0 mL were examined. According to the results shown in Figure 8, 2.0 mL of the mixture of 2:1 v/v of H$_2$SO$_4$ and HCl (0.5 mol L^{-1} each one) was sufficient for quantitative recovery of analyte ions.

Effect of amount of adsorbent

In the sorption step, the selection of a proper amount of adsorbent is very important. In order to investigate the effect of the quantity of adsorbent on preconcentration of lead
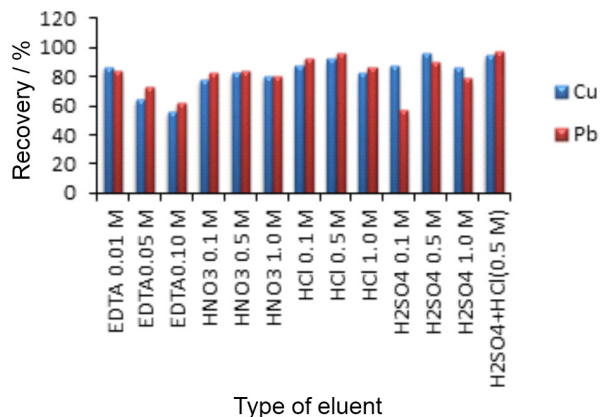
Figure 7. Effect of type of eluent on the recovery of 100 µg L^{-1} of Pb(II) and Cu(II). Conditions: pH, 4.5, 10.0 mL acetate buffer 0.01 mol L^{-1}; amount of adsorbent, 10.0 mg; sample volume, 50.0 mL; sorption time, 14 min; desorption time, 6 min; (n = 3).

Figure 8. Effect of volume of eluent on the recovery of 100 µg L^{-1} of Pb(II) and Cu(II). Conditions: pH, 4.5, 10.0 mL acetate buffer 0.01 mol L^{-1}; amount of adsorbent, 10.0 mg; sample volume, 50.0 mL; sorption time, 14 min; desorption time, 6 min; (n = 3).
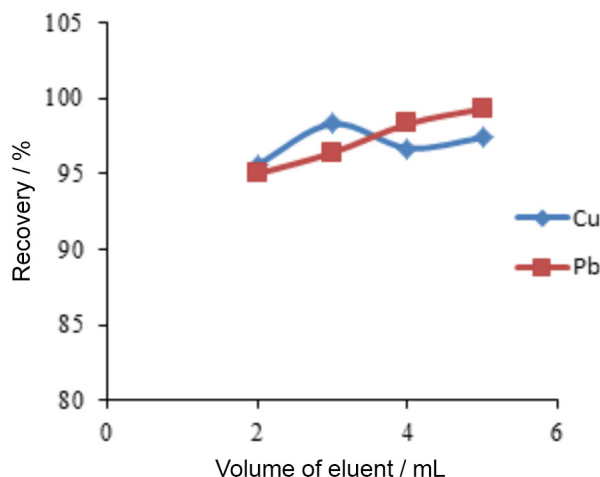
and copper ions, various amounts of modified MNPs from 5.0 to 15.0 mg were used. The results shown in Figure 9, indicate that the quantitative recovery (> 95%) for Pb(II) and Cu(II) was obtained when the amount of adsorbent was greater than 5.0 mg. Therefore, in the further experiments, 10.0 mg of adsorbent was applied because it showed higher values of recovery.

Effect of sorption and desorption time

The ultrasonic times of analytes sorption and desorption were evaluated. According to the experimental results, the quantitative recovery of lead and copper ions was obtained when ultrasonication time was greater than 10 min for sorption and greater than 6 min for desorption. Therefore, the optimum times of sorption and desorption were 10 min and 6 min, respectively.
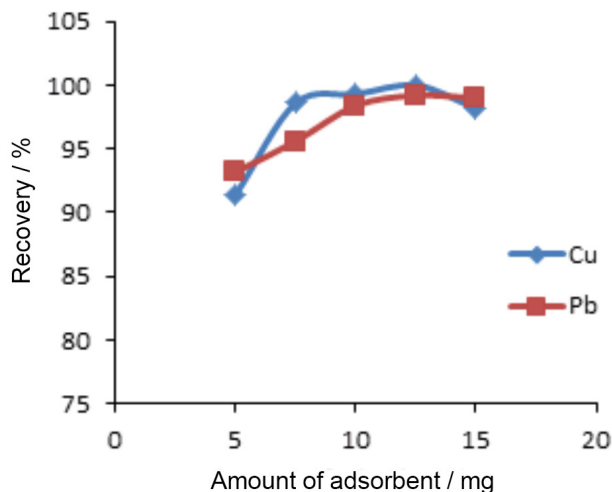

Figure 9. Effect of amount of adsorbent on the recovery of 100 µg L^{-1} of Pb(II) and Cu(II). Conditions: pH, 4.5, 10.0 mL acetate buffer 0.01 mol L^{-1}; sample volume, 50.0 mL; eluent, 2.0 mL of the mixture of 2:1 (v/v) of H$_2$SO$_4$ and HCl (0.5 mol L^{-1} each one); sorption time, 14 min; desorption time, 6 min; (n = 3).

Effect of sample volume

For the preconcentration of trace elements, it is important to have high preconcentration factors. In order to achieve, the preconcentration factors, maximum applicable sample volume must be examined. For this purpose, the sample volumes of 50, 75, 100, 150, 200, 300 and 500 mL containing 10.0 µg of Pb(II) and Cu(II) were studied according to the recommended procedure. The quantitative recoveries were achieved when the volume of solution was less than 200 mL. Hence, a sample volume of 200 mL was selected as the largest usable sample volume. Thus, in this work, by using 2.0 mL of elution solution, a preconcentration factor of 100 is obtained.

Effect of diverse ions

In order to investigate the selectivity of the method, the interference effect of different ions on the recovery of metal ions under the optimized conditions was evaluated. The concentration of diverse ions which resulted in an error ± 5% in determination 100 mL of 100 µg L^{-1} Pb(II) and Cu(II) was considered as the tolerance limit. The results summarized in Table 1 demonstrate that the method is relatively selective for determination Pb and Cu in real samples.

Sorption capacity

A batch method was used to calculate the sorption capacity. Langmuir isotherms were used to describe the sorption process at the solid-liquid interface which is represented by the following equation:

Table 1. Effect of diverse ions on the determination of 100 µg L^{-1} of Pb(II) and Cu(II)

Interference species	Tolerable concentration ratio X/Pb(II)	Tolerable concentration ratio X/Cu(II)
Na$^+$, Cl$^-$, Mg^{2+}, Ca^{2+}	10000	10000
F$^-$, I$^-$, K$^+$, SO$_4^{2-}$	10000	5000
Co^{2+}	100	100
Cd^{2+}	50	50
Ni^{2+}	20	100
Cr^{3+}	50	20
Fe^{3+}	10[a]	1

[a]The interference of Fe^{3+} up to 10-fold was overcome by the addition of 1.0 mL of 1000 mg L^{-1} of F$^-$ solution.

$$\frac{C}{q} = \frac{1}{kq_m} + \frac{C}{q_m} \tag{1}$$

where C (mg L^{-1}) is the equilibrium concentration, q (mg g^{-1}) is the amount of metal adsorbed *per* unit mass of adsorbent at equilibrium, q$_m$ (mg g^{-1}) is the maximum amount of sorption in monolayered sorption systems and k (L mg^{-1}) is the Langmuir constant, which can be considered as a measure of sorption energy.

A linear plot of C/q against C was applied to obtain the values of q$_m$ and k from the slope and intercept of the plot.

In order to calculate the sorption capacity, 3.0-10.0 mg L^{-1} of metal ions were added to 10.0 mg of adsorbent. The results indicated that the sorption capacity of MNPs-ephedrine for Pb(II) and Cu(II) are 9.4 and 0.6 mg g^{-1}, respectively.

Analytical figures of merit

The analytical performance characteristics of the method are shown in Table 2. Under the optimized conditions, a linear calibration graph was obtained for determination Pb(II) and Cu(II). The linear ranges were

found to be 15.0-500 µg L^{-1} and 18.0-500 µg L^{-1} for lead and copper, respectively. The regression equations for the lines were A = 0.0017 C − 0.0003 with r = 0.9992 for lead, A = 0.0016 C + 0.0325 with r = 0.9982 for copper, where A is absorbance and C is concentration of lead and copper ions in µg L^{-1}. The limit of detection and limit of quantification were defined as 3S$_b$/m and 10S$_b$/m where m is the slope of calibration graph and S$_b$ is the standard deviation of ten blank determinations were 4.3 and 14.5 µg L^{-1} for lead and, 5.0 and 16.7 µg L^{-1} for copper, respectively. The relative standard deviations for eight replicate determinations of 80 and 200 µg L^{-1} of Pb(II) were 2.9 and 1.4% and for 80 and 200 µg L^{-1} of Cu(II) were 3.5 and 1.9%, respectively. The reusability of the sorbent in several successive sorption and desorption processes was studied. The obtained results showed that the sorbent could be reused two times without any considerable loss in its sorption efficiency.

Table 2. Analytical characteristics of proposed method at the optimum conditions

	Cu	Pb
Regression equation	A = 0.0016 C + 0.0325	A = 0.0017 C − 0.0003
Correlation coefficient (r)	0.9982	0.9992
Linear range / (µg L^{-1})	18.0-500	15.0-500
LOD / (µg L^{-1}) (n = 10)	5.0	4.3
LOQ / (µg L^{-1}) (n = 10)	16.7	14.5
RSD[a] / % (n = 8) (80 µg L^{-1})	3.5	2.9
RSD / % (n = 8) (200 µg L^{-1})	1.9	1.4

[a]Relative standard deviation.

Application

The present method was applied to determination of Pb and Cu in water samples. The results are shown in Table 3. To evaluate the accuracy of the results, different

Table 3. Determination of Pb and Cu in water samples

Real sample	Added / (µg L^{-1})	Pb(II) found / (µg L^{-1})	Recovery / %	Cu(II) found / (µg L^{-1})	Recovery / %
Caspian Sea	−	15.56 ± 0.033	−	15.40 ± 0.008	−
	100	113.71 ± 0.009	98.1	110.42 ± 0.003	95.0
	200	206.65 ± 0.013	95.5	209.70 ± 0.015	97.1
Waste water of oil refinery (Input)	−	21.00 ± 0.002	−	22.50 ± 0.004	−
	100	116.72 ± 0.028	95.7	118.70 ± 0.009	96.2
	200	220.26 ± 0.017	99.6	213.50 ± 0.023	95.5
Tap water (Sanandaj)	−	N. D.[a]	−	N. D.	−
	25	24.3 ± 0.009	97.2	24.8 ± 0.006	99.2
	200	192.5 ± 0.035	96.3	190.4 ± 0.051	95.5

[a]Not detected

Table 4. Comparison of the proposed method with some other methods to determination the metal ions

Metal ions	Adsorbent	Detection method	Preconcentration factor	R.S.D / %	Linear range / (μg L^{-1})	LODs / (μg L^{-1})	Reference
Cu	Modified silica gel	FAAS	30	4.3	–	1.1	32
Pb			30	4.7	–	6.1	
Cu	Modified	FAAS	> 100	0.62-1.40	5-40	0.54	17
Fe	naphthalene		For each one	1.9-3.4	10-100	3.1	
Pb				1.0-2.2	10-200	4.5	
Cu	Activated carbon	FAAS	50	1.4	40-1000	2.9	19
Ni			For each one	1.4	40-1100	3.5	
Co				1.3	40-1000	3.4	
Pb				1.2	40-1000	8.4	
Pb	Modified silica gel	FAAS	–	≤ 9	–	22.5	21
Cu				For each one		1.0	
Ni						2.9	
Co						0.95	
Cd						1.1	
Pb	IL-MNPs	FAAS	200	1.45	5.0-330	1.61	3
Cd				2.87	0.3-20	0.122	
Pb	Silicon carbide nanoparticles	FAAS	–	1.3	2-150	0.4	29
Pb	MNPs-ephedrine	FAAS	100	1.4	15-500	4.3	This work
Cu				1.9	18-500	5.0	

amounts of investigated metal ions were spiked to the real sample by standard addition. The recovery values for added concentration of analyte ions were quantitative.

Conclusions

In this study, magnetic Fe$_3$O$_4$ modified with ephedrine has been applied for the first time for preconcentration of lead and copper in water samples. It was found that this procedure was relatively selective, simple, fast, low cost and eco-friendly and with a good preconcentration factor, wide linear dynamic range. A comparison with some of the previously reported works is also given in Table 4.

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