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ARTICLES

MnO_2/3MgO Nanocomposite for Preconcentration and Determination of Trace Copper and Lead in Food and Water by Flame Atomic Absorption Spectrometry[1]

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Abstract—The presented study investigates the application of MnO_2/3MgO nanocomposite, as a new sorbent for solid phase extraction and determination of trace amounts of Pb^{2+} and Cu^{2+} from various samples using flame atomic absorption spectrometry. After extraction, the analytes were desorbed using 0.01 M ethylenediaminetetraacetic acid. The effects of various parameters were studied and optimized. Under optimized experimental conditions the linear dynamic ranges for Cu^{2+} and Pb^{2+} were 10–900 and 30–900 μg/L, respectively, with a preconcentration factor of 20. The detection limits of Cu^{2+} and Pb^{2+} were 4 and 11 μg/L, respectively, and relative standard deviations for eight determinations of 100 μg/L were 3.6 and 3.8% for Cu^{2+} and Pb^{2+}, respectively. The method was successfully applied for determination of copper and lead in mushrooms, rice, tap water and refinery wastewater with good spike recoveries ranging between 95–106%.

Keywords: solid phase extraction, nanocomposite, copper, lead

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The water and food pollution by heavy metal ions is one of the worldwide environmental problems due to the bioaccumulation tendency of these toxic materials [1]. Among the heavy metals, lead is extremely toxic even at very low concentration levels. It is well known that lead can cause blood enzyme changes, hyperactivity and neurological disorders in humans and animals [2]. Copper is considered an essential trace element for plants and animals. However, high amounts of copper can be harmful, causing irritation of nose and throat, nausea, vomiting, and diarrhea. Very high doses of copper can cause damage to liver and kidneys [3]. Therefore, it is important to develop sensitive, rapid, simple and reliable analytical methods to determine ultratrace heavy metals in various kinds of samples. Due to matrix effect and low concentration of metal ions, efficient separation and preconcentration steps are essential prior to analytical measurements [4]. Therefore, a variety of techniques have been developed for separation and preconcentration of heavy metal ions, including liquid–liquid extraction (**LLE**) [5], solid phase extraction (**SPE**) [6, 7], microwave-assisted subcritical water extraction [8], cloud point extraction (**CPE**) [9], solid phase microextraction [10] and liquid–liquid microextraction (**LLME**) [11, 12]. The solid phase extraction is one of the most effective preconcentration techniques that reduce solvent usage and exposure, disposal cost and extraction time for sample preparation [13]. Various materials such as amberlite XAD-4 [14], octadecyl-bonded silica disk [15], activated carbon [16], microcrystalline naphthalene [17], sulfur powder [18], modified aluminum oxide nanoparticles [19], ZrO_2/B_2O_3 nanocomposite [20] and graphene nanosheets [21] have been used in the solid-phase extraction as sorbent.

Nanosized manganese oxides exhibit an adsorptive performance superior to its bulk counterpart because of its polymorphic structure and higher specific surface area [22]. Magnesium oxide nanoparticles is an interesting basic oxide that has many applications in catalysis, adsorption and synthesis of refractory ceramics. It is a unique solid of high ionic character, simple stoichiometry and crystal structure that can be prepared with variable particle sizes and shapes [23]. Recently, hybrid nanostructured materials with high surface area, good conductivity and permeability have been considered to be of the most significant functional materials for various emerging research fields, such as sensors, energy conversion, and environmental remediation [24]. To the best of our knowledge, there are no reports on the MnO_2/3MgO nanocom-

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[1] The article is published in the original.

posite for separation of heavy metals from real samples.

In the present study, a $MnO_2/3MgO$ nanocomposite was successfully applied for determination of heavy metals in different samples. Because of high adsorption area in the new synthetic sorbent, the determination of trace heavy metals can be easily achieved from real samples. After elution of sorbent with 5.0 mL of 0.01 M EDTA, final measurements were performed by flame atomic absorption spectrometry (**FAAS**).

EXPERIMENTAL

Instrumentation. Determination of copper and lead was performed on a Shimadzu AA-670 atomic absorption spectrometer (Kyoto, Japan) under the recommended condition for each metal ion. The instrumental parameters were as follows: wavelengths 324.8 and 217.0 nm, and bandwidths 0.5 and 0.3 nm for copper and lead, respectively. All measurements were carried out in an air/acetylene flame. All pH measurements were made using a Metrohm E-691 digital pH meter with a combined glass electrode. Stirring of the sample solutions was carried out by a magnetic stirrer (Rodwell, Monostir, England). A model Parasonic 7500S, 28 kHz, 100 W ultrasonic bath with temperature control was used to assist the dispersion process. A model Labofuge 400 (Heraeus, Germany) centrifuge was used in extraction process. Transmission electron microscopy (**TEM**) image was obtained by using Philips CM200 instrument. Fourier transform infrared spectra (**FTIR**) were performed using KBr disc on an infrared spectrometer Bruker-Vector 22.

Reagents and solutions. $Mg(NO_3)_2 \cdot 6H_2O$, $MnSO_4$, polyvinylpyrrolidone (**PVP**), HNO_3, NaOH, $HClO_4$ and EDTA from Merck were used as received. The stock solutions of Cu(II) and Pb(II) (1000 mg/L) were purchased from Merck (Darmstadt, Germany). The working standard solutions were prepared by appropriate dilution of the stock standard solutions with doubly distilled water. Other metal salts and solvents were of analytical grade and were also purchased from Merck.

Synthesis of $MnO_2/3MgO$ nanocomposites. $MnO_2/3MgO$ nanocomposites was synthesized with uses of PVP by sonochemical sol–gel method. In a typical procedure, 0.5 g PVP, 0.768 g (3.0 mmol) magnesium nitrate and 0.169 g (1.0 mmol) manganese sulfate were added into 50 mL of deionized water. The reaction mixture was transferred into an ultrasound bath at 60°C for 60 min to reach a colorless solution. Then 0.2 M NaOH solution was added dropwise to the vigorously stirred mixture. To prevent the agglomeration of nanocomposite, the obtained brown mixture was sonicated for 60 min, after which the mixture was centrifuged and twice washed with a 1 : 1 double-distilled water/ethanol solution. Then the brown precipitate was calcined at 550°C for 5 h to yield tan powder.

Preparation of water samples. The petroleum refinery input and output wastewater (Kermanshah, IRAN) and tap water (Sanandaj, Kurdistan, IRAN) were collected in 1.5 L polyethylene bottles. The samples were acidified to the $pH < 2$ using 5.0 mL of concentrated HNO_3. Petroleum refinery water samples were filtered across a filter paper to remove probable suspended solids. All samples were stored at about ~4°C in the refrigerator. In order to determine the heavy metals, 50.0 mL of water sample was transferred to a beaker and analysis was done according to general procedure.

Preparation of food samples. Mushroom and rice samples were purchased from the local supermarkets in Sanandaj, IRAN. The samples were dried at 105°C for 24 h. A portion of 0.25 g of sample was digested with 8.0 mL of concentrated HNO_3, 4.0 mL of concentrated $HClO_4$, and dried at 190°C for 2.5 h. The residue was diluted to 250 mL in a calibrated flask and 50.0 mL of this solution was taken through the general procedure [25].

General procedure. A 50.0 mL aliquot of 100 μg/L Cu(II) and Pb(II) or real sample solution (25.0–100.0 mL) was placed in a 100 mL beaker. The pH of solution was adjusted to 4.0 by adding 5.0 mL of 0.05 M acetate buffer. Then 10.0 mg of sorbent were added. The beaker was placed on the magnetic stirrer for 30 min. Afterwards, the nanocomposites were collected using centrifugation at 3500 rpm for 10 min. Then, the clear solution was decanted. For the desorption of adsorbed cations from the sorbent, the residual nanocomposits were rinsed with 5.0 mL of 0.01 M EDTA solution for 6 min in the ultrasonic bath. After centrifugation, the mixture was decanted and the concentration of metal cations was measured by FAAS.

RESULTS AND DISCUSSION

Characterization of sorbent. The sorbent was characterized by TEM, FT-IR, and elemental analysis by FAAS. Figure 1 shows the FTIR spectra of $MnO_2/3MgO$ nanocomposites. The peaks at 475 and 628 cm^{-1} are attributed to the Mg–O and Mn–O stretching vibrations. The peak at 1114 cm^{-1} was due to Mn–OH bending stretching and the peak at 1387 cm^{-1} resulted from the residual carbonate ions coordinated to the magnesium. The peak at 1632 cm^{-1} resulted from the bending vibration of OH from a water molecule combined with nanocimposite. The broad band at 2926 cm^{-1} was due to CH stretching vibration from residual PVP on the surface of nanocomposite. The broad band at 3419 cm^{-1} was due to OH stretching, which corresponds to hydroxyl groups attached to the magnesium oxide surface, and also the water molecules chemically adsorbed onto the magnesium oxide surface [26–30].

The structure and morphology of nanocomposite were characterized by TEM analysis. As displayed in

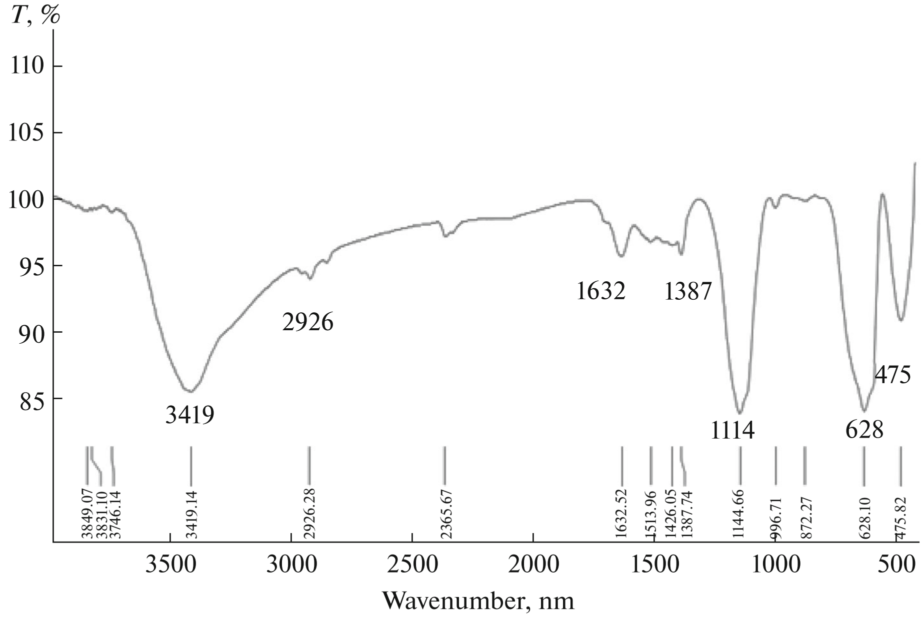

Fig. 1. FT-IR spectra of MnO_2/3MgO nanocomposites.

Fig. 2, the obtained sorbent is composed of spherical nanoparticles. In addition, AAS elemental analysis for the same material gives 25.7, 35.1 and 39.2% for weight percent of Mn, Mg and O (by difference from total), respectively. Based on these data, the empirical formula is Mg_3MnO_5. These results prove the successful synthesis of new MnO_2/3MgO nanocomposite.

Effect of extraction time. Extraction is an equilibrium process, and the maximum extraction efficiency is obtained when the system is at equilibrium. Therefore, optimum time is required to reach equilibrium. Thus, the effect of time on extraction efficiency of metallic cations from 50.0 mL of 100 μg/L sample solution containing copper and lead ions with 10.0 mg of sorbent was examined in the range of 15–60 min, while 5.0 mL 0.01 M EDTA was used as desorbing reagent. As can be seen from Fig. 3, the recoveries increase with increasing the extraction time up to 30 min and then slowly level off. Thus, the extraction time of 30 min was selected for further experiments.

Effect of desorption time. The effect of desorption time in ultrasonic bath on extraction efficiency of metal cations from 50.0 mL of 100 μg/L sample solution containing copper and lead ions with 10.0 mg of sorbent was examined in the range of 2–14 min, while 5.0 mL 0.01 M EDTA was used as desorbing reagent. It was found that maximum recovery could be obtained after 6 min. Hence, a time of 6 min was chosen for further experiments as the extraction time.

Selection of desorbing condition. In order to choose a proper desorbing reagent for recovery of metal cations, after extraction of the cations from 50.0 mL of 100 μg/L sample solution containing copper and lead ions, the sorbent was rinsed using sonication for 6.0 min with various types and volumes of reagents. The concentrations of metal ions were determined according to recommended procedure. Among different reagents, 5.0 mL of 0.01 M EDTA provides the best recovery and preconcentration factor. Therefore, this solution was chosen as an eluent for further study. The results for 5.0 mL of various desorbing reagents are shown in Fig. 4. Then, the volume of desorbing reagent was studied in the range of 2.0–6.0 mL. The results show that the maximum recovery could be obtained with 5.0 mL of desorbing reagent. Thus this volume was selected for further experiments.

Effect of the amount of sorbent. The optimum amount of sorbent was obtained by investigating dif-

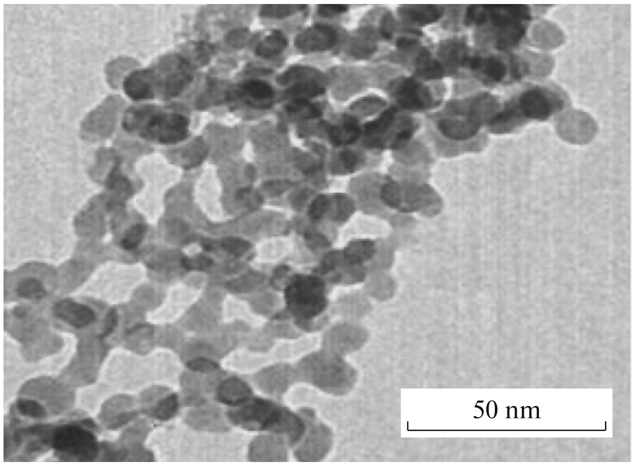

Fig. 2. TEM images of 3MgO/MnO_2 nanocomposites.

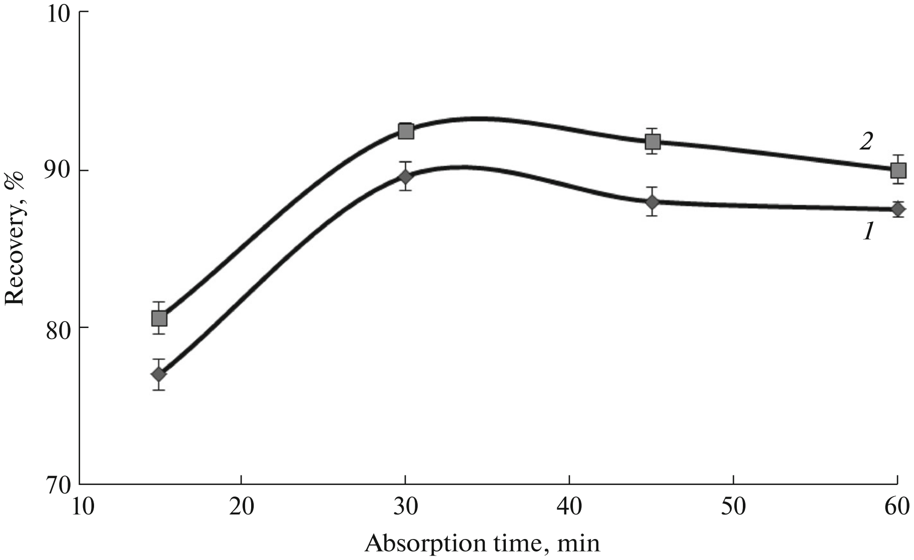

Fig. 3. Effect of extraction time on the recovery of copper (*1*) and lead (*2*).

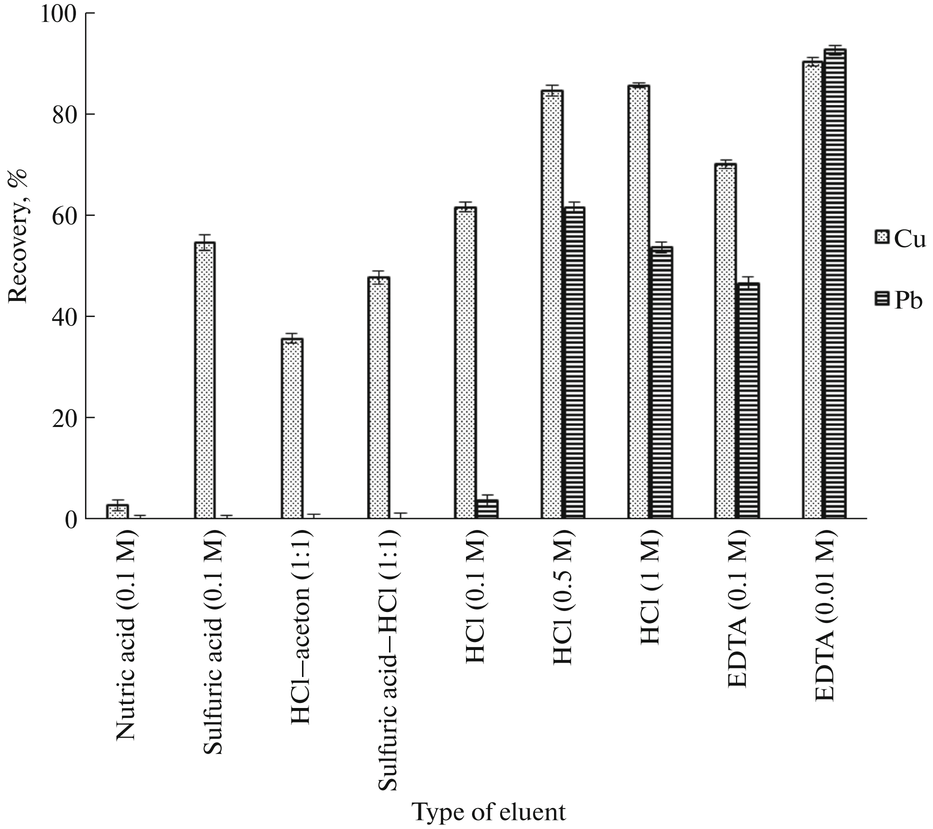

Fig. 4. Effect of 5.0 mL of desorbing reagent on the recovery of copper and lead.

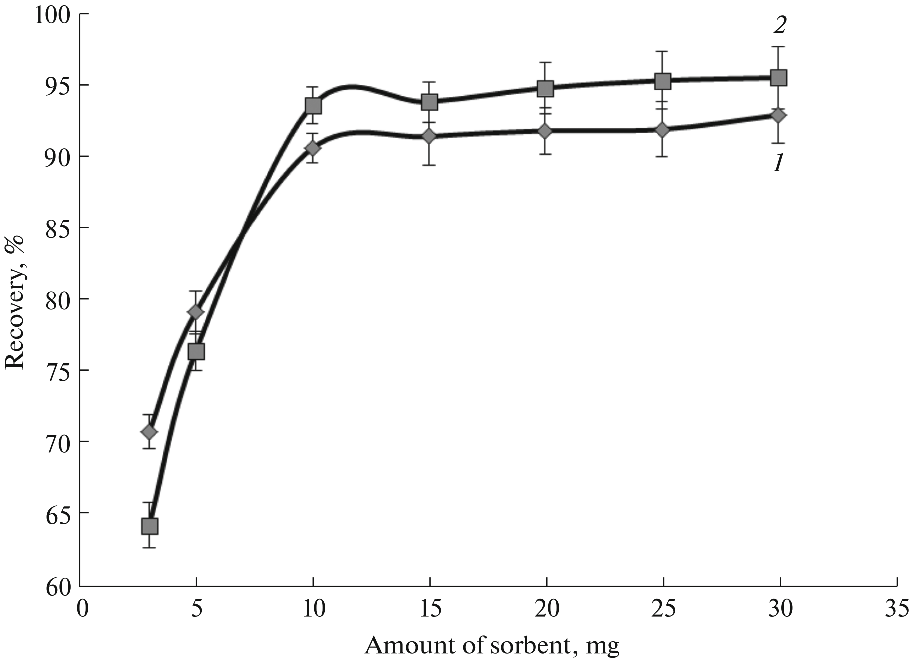

Fig. 5. Effect of the amount of sorbent on the recovery of copper (*1*) and lead (*2*).

ferent amounts of nanocomposite ranging from 3.0 to 30.0 mg for extraction of the heavy metal cations from 50 mL of 100 μg/L sample solution containing copper and lead ions. The results (Fig. 5) indicated that the extraction recovery increases with increasing the nanocomposite amount to 10.0 mg, and then remained constant when the sorbent amount was continuously increased. Hence, 10.0 mg were chosen for further experiments.

Effect of pH. In the SPE studies, pH is an important factor for the quantitative recoveries of analytes that plays a unique role on metal-chelate formation and subsequent extraction [31].

The effect of pH on the complex formation and extraction of copper and lead from 50.0 mL of 100 μg/L sample solution containing Cu^{2+} and Pb^{2+} ions was studied over the range of 2.0–10.0. The pH values were adjusted by either nitric acid or 0.1 M sodium hydroxide solution. The experimental results are illustrated in Fig. 6 showing that the maximum recovery of copper and lead is obtained at pH 4.0. The decrease in recovery at a higher pH (>5) may be due to the competition of the hydroxyl ion with sorbent to react with the analyte [32, 33], while decrease at lower pH levels (<3.0) are due to protonation of the oxygen atoms of the sorbent at these pH values. Therefore, pH 4.0 was chosen for subsequent experiments. For adjustment of this pH, many buffers such as acetate, phosphate and citrate with various concentrations and volume (from 0.01 to 0.1 M) have been tested. Among these buffers, 5.0 mL 0.05 M acetate buffer gives the best results. Thus adjustment of pH was carried out with acetate buffer solution (pH 4.0) in further experiments.

Effect of salt. The effect of salt on extraction efficiency of copper and lead was studied by varying the concentration of $NaNO_3$ within the range of 0.0–4.0% (w/v). The results showed that the addition of salt had no significant effect on the extraction efficiency, perhaps because of the two opposite effects of salt addition in SPE of heavy metals. One involves the salting out effect which increases the extraction of heavy metals, and the other is aggregation of nanoparticles in high ionic strength which decreases extraction recovery. Hence, no salt was added in the subsequence experiments.

Effect of the sample volume. In order to investigate the effect of sample volume, 25.0, 50.0, 100.0, 150.0, 200.0, 250.0 and 300.0 mL of sample solutions containing 5.0 μg each of Cu^{2+} and Pb^{2+} ions were extracted with 10.0 mg of sorbent according to the recommended procedure. It was found that recovery of copper and lead was 96.6 and 98.35% for 50.0 mL of sample solution. The recoveries decreased when the volume of solution exceeded 100.0 mL. Therefore, a sample volume of 100.0 mL was selected as the largest usable sample volume. Thus, the preconcentration factor (**PF**) calculated by dividing the maximum aqueous phase volume (100 mL) by the final volume of extracted phase (5.0 mL) equalled 20 [34].

Reusability and loading capacity of the sorbent. The reusability of the sorbent in several successive adsorption and desorption processes was studied. The obtained results showed that the nanocomposite could

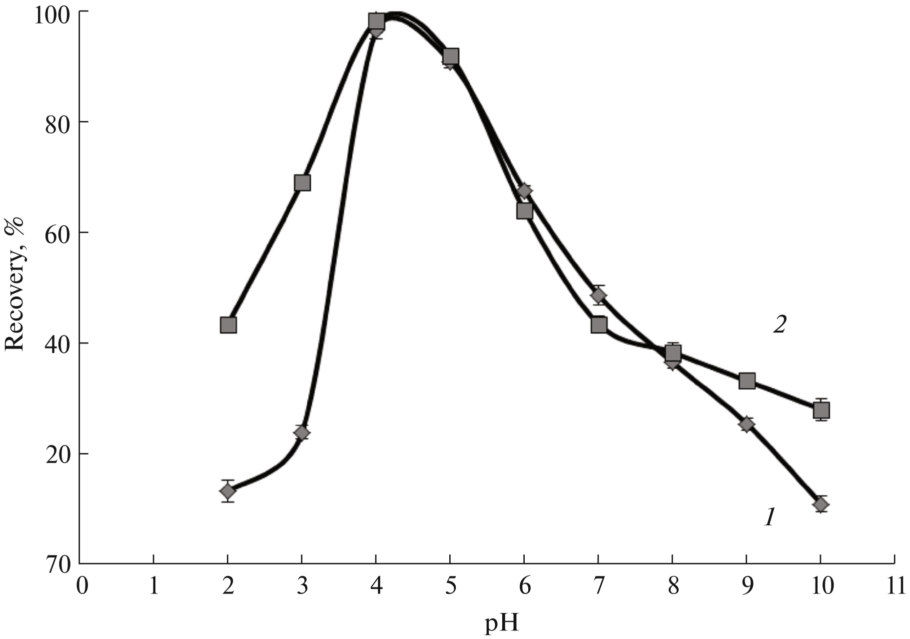

Fig. 6. Effect of pH on the recovery of copper (*1*) and lead (*2*).

be reused up to 4 times without any considerable loss in its adsorption efficiency. The extraction recoveries for both copper and lead were higher than 94% after 4 times use. The maximum loading capacity of the sorbent was obtained from addition of 10.0 mg of sorbent to 50.0 mL of sample solution with various concentration (0.01–1.2 mg/L) and metal cations were determined according to the recommended procedure. The loading capacities were 4.6 and 4.5 mg/g for copper and lead, respectively.

Effect of potentially interfering ions. The effects of common potentially interfering ions on the recovery of copper and lead were studied. In these experiments, 50.0 mL of solutions containing metal cations (100 μg/L of Cu^{2+} and Pb^{2+}) and various amounts of diverse ions were treated according to the recommended procedure under optimum conditions. A given species was considered to interfere if it resulted in a ≥±5% variation of the absorbance signal. As shown in Table 1, most of the cations and anions had no obvious influence on the determination of copper and lead under selected conditions. The results show that, the method is selective in the presence of different species. The most interference was seen for Al^{3+} and Fe^{3+}, which might be due to “hard acid” (Al^{3+} and Fe^{3+}) and “hard base” (oxygen atoms of MgO and MnO_2) interaction [35]. These interferences were eliminated with application of F^- (0.5 mL of 1000 mg/L) as masking agent. For the other transition metals such as Mn, Co, Ni and Zn, the complexation of Cu with oxygen donor ligand may follow Irving–Williams series (Mn < Fe < Co < Ni < Cu > Zn), thus, Cu^{2+} had a higher stability constant due to the crystal field stabilization energy that makes the complexes of Cu^{2+} increasingly stable.

Analytical figures of merit. The analytical characteristics of the present method, including linear dynamic range, limit of detection (**LOD**), limit of quantification (**LOQ**), relative standard deviation (**RSD**), correlation coefficient (R^2), and preconcentration factor were obtained. Under optimum experimental conditions, calibration curves were achieved by analyzing 50.0 mL of Cu^{2+} and Pb^{2+} standard solution containing a known amount of target ions at pH of 4.0. The results are summarized in Table 2.

Applications. The present method was successfully applied for determination of copper and lead in various samples with different matrixes such as tap water, refinery wastewater and food samples. The results along with the recovery for the spiked samples are given in Tables 3, 4. The determination of heavy metals was performed by the standard addition method. The accuracy of the proposed method was evaluated by means of recovery experiments. As can be seen, the added ions were quantitatively recovered from all samples. These results indicate the validity of the proposed method for the determination of copper and lead in real samples.

Separation and determination of the heavy metal cations by the developed method were compared with the other preconcentration methods. The results are shown in Table 5. As can be seen, the present procedure shows a LOD comparable to or better than the others. Likewise, good precision and high adsorption capacity makes this method suitable for measuring concentrations of heavy metal in various samples.

Table 1. Effect of coexisting ions on the extraction of 100 µg/L copper and lead

Ion	Added as	Tolerance limit, µg/L ratio	
		$c_{\text{ion}}/c_{\text{Cu}}^{2+}$	$c_{\text{ion}}/c_{\text{Pb}}^{2+}$
Na^+	$NaNO_3$	2000	2000
K^+	KNO_3	2000	2000
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	1000	1000
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	1000	500
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	1000	1000
Ag^+	$AgNO_3$	1000	1000
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	500	500
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	500	500
Sn^{2+}	$SnCl_2$	200	200
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	200	200
Fe^{2+}	$NH_4Fe(SO_4)_2 \cdot 9H_2O$	100	100
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	1[a]	1[a]
		10[b]	10[b]
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	1[a]	1[a]
		10[b]	10[b]
NO_3^-	KNO_3	2000	2000
CO_3^{2-}	Na_2CO_3	2000	2000
F^-	NaF	2000	2000
Cl^-	NaCl	2000	2000
Br^-	KBr	2000	2000
I^-	NaI	1000	500

[a] Without F^- as masking agent; [b] with F^- as masking agent.

Table 2. Analytical figures of merit

Parameter	Analytical feature	
	Cu^{2+}	Pb^{2+}
Sample consumption, mL	50	50
Slope of calibration curve, L/mg	0.9840	0.4104
Intercept	–0.004	–0.006
Correlation coefficient, R^2	0.9989	0.9992
Preconcentration factor[a]	20	20
Enhancement factor[b]	10	10
Linear dynamic range, µg/L	10–900	30–900
Limit of detection, µg/L[c]	4	11
Limit of quantification, µg/L[d]	12.1	36.6
Precision (RSD, $n = 8$), %[e]	3.6	3.8
Recovery, %[f]	96.60	98.35

[a] The preconcentration factor was calculated by dividing the maximum aqueous phase volume (100 mL) to the final volume of extracted phase (5.0 mL).

[b] The enhancement factor as the ratio of calibration sensitivity after preconcentration to that before preconcentration.

[c] The limit of detection ($n = 8$, LOD $= 3s_{\text{blank}}/m$) where m is the slope of the analytical curve in accordance to IUPAC recommendation.

[d] The limit of quantification ($n = 8$, LOQ $= 10s_{\text{blank}}/m$).

[e] The RSD for eight replicate measurements of 100 µg/L solution each of Cu^{2+} and Pb^{2+} ions.

[f] The recovery of extraction calculated according to: $(c_eV_e)/(c_sV_s) \times 100$, where c_e and c_s are the concentrations of analyte in eluent and sample solutions, V_e and V_s are the volumes of the eluent and the sample solution, respectively.

Table 3. The application of present method for analysis of natural water samples ($n = 3$)

Sample	Added, µg/L	Found, µg/L		Recovery, %	
		Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}
Tap water (Sanandaj)	0	11.0 ± 0.8[a]	NF[b]	—	—
	40	50 ± 1	41 ± 1	97.5	102.5
	100	106 ± 1	105 ± 1	95.20	105.22
Refinery input water (Kermanshah)	0	38.0 ± 0.8	NF	—	—
	40	80 ± 1	42 ± 1	104.44	105.75
	100	137 ± 2	106 ± 2	98.68	105.70
Refinery output water (Kermanshah)	0	23.0 ± 0.9	NF	—	—
	40	63 ± 1	42 ± 1	98.75	103.75
	100	118 ± 1	104 ± 1	95.39	104.00

[a] Mean ± standard deviation, [b] not found.

Table 4. The application of proposed method for analysis of food samples (*n* = 3)

Sample	Added, µg/g	Found, µg/g		Recovery, %	
		Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}
Mushroom (Atlas)	0	12.5 ± 0.6[a]	BLDR[b]	–	–
	40	54 ± 1	41 ± 1	103.75	102.50
	100	111 ± 2	103 ± 1	98.58	103.45
Iranian Rice (Shahram)	0	4 ± 1	BLDR	–	–
	20	22.6 ± 0.8	21 ± 1	95.50	103.75
	50	55 ± 3	52 ± 1	103.00	104.56

[a] Mean ± standard deviation, [b] BLDR – below linear dynamic range.

Table 5. Performance characteristics of the present and other reported methods for copper and lead determination

Method	Detection technique	Adsorption capacity, mg/g		LOD, µg/L		PF	RSD, % Cu, Pb	Reference
		Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}			
SPE	FAAS	4.6	4.5	4	11	20	3.6, 3.8	This study
SPE	ICP-OES[a]	1.3	2.3	1.6	1.5	80	1.4, 2.1	[36]
SPE	ICP-OES	12	18	0.2	0.5	20	3.9, 4.6	[37]
SPE	FAAS	–	0.23	–	8	110	2.51	[2]
LLE	UV-Vis	–	–	27	–	10	–	[38]
Co-precipitation	ICP-OES	–	–	3	3	60	1.7, 2.3	[39]
LLME	FAAS	–	–	1.8	–	25	2.1	[40]
CPE	FAAS	–	–	1.6	–	30	–	[9]

[a] ICP-OES – inductively coupled plasma-optical emission spectroscopy.

CONCLUSIONS

In the present work, synthesis of a new selective sorbent was presented and described for the first time for simultaneous extraction of two heavy metals from environmental water, wastewater and food samples. The use of the nanocomposite offers several advantages including experimental convenience, safety, low cost and high stability of the sorbent. Furthermore, the described procedure gives a wide linear dynamic ranges, proper RSD values and high adsorption capacity. Desorption and reuse experiments indicated that the adsorbent could be regenerated and reused almost without any loss of adsorption capacity for 4 times. Likewise, wide linear dynamic range and good enrichment factor and good selectivity make this method suitable for measuring concentrations of copper and lead in various samples.

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