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Ultralayered Co_3O_4 as a new adsorbent for preconcentration of Pb(II) from water, food, sediment and tobacco samples

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A B S T R A C T

In this study, ultralayered Co_3O_4 adsorbent was synthesized and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The surface area of the solid material was found to be 75.5 $m^2\ g^{-1}$ by BET method. The ultralayered Co_3O_4 was used for the first time as an effective adsorbent for the preconcentration of the Pb(II) ions in various samples prior to flame atomic absorption detection. Analytical parameters affecting the solid phase extraction of Pb(II) such as pH, adsorption and elution contact time, eluent volume and concentration, sample volume and common matrix ions were investigated. The recovery values for Pb(II) were found to be ≥92% even in the presence of 75,000 mg L^{-1} Na(I), 75,000 mg L^{-1} K(I), and 75,000 mg L^{-1} Ca(II) ions. 10 s vortexing time was enough for both adsorption and elution contact times. The elution was easily made with 2 mL of 2.0 mol L^{-1} HNO_3. The reusability (170 cycles) and adsorption capacity (35.5 mg g^{-1}) of ultralayered Co_3O_4 were excellent. The preconcentration factor of the method and detection limit were found to be 175 and 0.72 μg L^{-1}, respectively. The described method was validated with certified reference material (RM 8704 Buffalo River Sediment, BCR-482 Licken and SPS-WW1 Batch 111-Wastewater) and spiked real samples. It was also applied for the preconcentration of Pb(II) ions in various water (well water, mineral water, waste water and sea water), food (cauliflower and barley), street sediment and tobacco samples.

1. Introduction

The release of various harmful heavy metal ions into the environment has attracted great attention worldwide because of their toxicity and widespread use [1]. Lead is a highly toxic element to nervous, immune, reproductive and gastrointestinal systems of both humans and animals. Lead causes acute and chronic poisoning, and adverse effects on the kidney, liver, heart, and vascular [2,3]. Lead and its compounds have been used in a wide variety of products, including paint, ceramics, pipes and plumbing materials, solders, gasoline, batteries, ammunition and cosmetics [4]. The maximum tolerable concentration limit of lead in drinking water is 10 μg L^{-1} [5]. The main lead sources for humans are food, water and road dusts. Hence, the development of a rapid, simple, accurate method with high sensitivity for determination of lead at trace levels in natural water, food and road dust samples is of particular significance.

Several methods have been developed for the separation and preconcentration of trace lead from environmental matrices, such as solvent extraction [6], dispersive liquid–liquid microextraction [7], ion-exchange [8], coprecipitation [9], cloud point extraction [10] and solid phase extraction [11–14]. Among these methods, the most commonly used method is solid phase extraction, which provides advantages such as simplicity, high preconcentration factor, reduction or elimination of matrix interferences with high concentration, combination with different detection techniques and the availability of a wide variety of adsorbent. The main properties with respect to adsorbents to be used as solid-phase extractants are as follows: possibility of extracting of elements over a wide pH range, fast and quantitative adsorption, and elution, high capacity and accessibility [12,15,16].

The size range of nanoparticles is from 1 nm to almost 100 nm, which falls between the classical fields of chemistry and solid-state physics. One of the most interesting properties is that most atoms are on the surface of the nanoparticle. The unsaturated surface atoms can bind with other atoms possessing strong chemical activities which produce a high sorption capacity and it can adsorb metal ions selectively [12,17]. Nanoparticles exhibit intrinsic surface reactivity and high surface areas and can strongly chemisorb many substances such as acidic gases and polar organics. The size, surface structure and interparticle interaction of nanomaterials determine their unique properties and make their potential application in many areas [18–21].

In recent years, these materials have been proposed and used in the preconcentration of trace metals due to their high surface area, high adsorption capacity and high chemical activity. Moreover, the

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preparation of these adsorbents is very simple and low cost when compared with other commercially available solid-phase materials [21]. Nano materials such as carbon nanotubes [1,13], ZrO_2 [17], TiO_2 [15,19,22–24], SiO_2 [25], CeO_2 [26], alumina [27,28] and hybrid ZrO_2/B_2O_3 [16] have been used as adsorbent.

Among the transition metal oxides, Co_3O_4 is found to be one of the better alternate materials in electrochemical technology due to its higher surface area, good redox property, controllable size and shape, and structural identities [29]. In this work, ultralayered Co_3O_4 with high porosity have been synthesized and it was used for the preconcentration/separation of Pb(II) ions in various samples (water, food, street dust and tobacco). The effect of experimental parameters such as pH, contact time, eluent type and volume, sample volume, adsorption capacity and matrix effect was investigated. To our literature knowledge, there is no report yet about the use of ultralayered Co_3O_4 as an adsorbent for the solid phase extraction of lead ions.

2. Experimental

2.1. Instrument

A BRUKER AXS D8 Advance model X-ray diffractometer using Cu K_α radiation ($\lambda = 0.15406$ nm) in the range of $2\theta = 10–90°$, a LEO 440 model scanning electron microscopy (SEM) with an accelerating voltage of 20 kV were used for the characterization of the synthesized ultralayered Co_3O_4. The surface area and porosity of the ultralayered Co_3O_4 were determined by the BET-N_2 method using a Micromeritics Gemini VII analyzer. The ultralayered Co_3O_4 was degassed at 100 °C for 12 h. A Clifton NES 280 model shaker, Wiggen Hauser VM model vortex and a WTW pH315i model pH meter equipped with a combined pH electrode were used in experiments. A PerkinElmer AAnalyst 800 flame atomic absorption spectrometry (Waltham, MA, USA) equipped with lead hollow cathode lamp, a deuterium lamp background corrector, and air/acetylene flame as an atomizer was used for the determination of lead. The instrument was set at a wavelength of 283.3 nm and slit width of 0.7 nm. Acetylene/air flow rate was 2.0/17 L min^{-1}.

2.2. Reagents and solutions

All solutions were prepared using ultra-high purity water from a Milli-Q system (18.2 MΩ cm, Millipore). All chemicals were of analytical grade and used without further purification. Pb(II) stock solution of 1000 mg L^{-1} was prepared by dissolving appropriate amount of its nitrate salt in 1 mol L^{-1} HNO_3. Working standard solutions of Pb(II) were prepared daily by dilution of its stock solution. H_3PO_4/NaH_2PO_4 buffer for pH 3, CH_3COOH/CH_3COONa for pH 4–6, CH_3COONH_4 for pH 7 and NH_3/NH_4Cl buffer for pH 8 and 9 were used in experiments. Diluted HNO_3 (Merck, 65%) and HCl (Merck, 37%) were tested as eluent.

2.3. Synthesis of ultralayered Co_3O_4

The composition and synthesis of ultralayered Co_3O_4 were fixed by Meher and Rao in earlier studies [29]. Ultralayered Co_3O_4 with high porosity was synthesized by a facile homogeneous precipitation process under hydrothermal conditions (see Supplementary material).

2.4. General procedure

The pH of model solution of 20 mL including 100 mg of Co_3O_4 and 8 μg of Pb(II) was adjusted to pH 5 by corresponding solution. After vortexing for 10 s, the solution was centrifuged at 4000 rpm for 5 min and the supernatant was removed. 2 mL of 2 mol L^{-1} HNO_3 was added on the adsorbent for elution of Pb(II) ions. After again vortexing for 10 s and centrifuging for 5 min, the Pb(II) concentration in eluate was determined by FAAS. The blank analyses were run without analyte.

The column method was used only for the optimization of sample volume. For this purpose 100 mg of Co_3O_4 was filled into a glass column (100 mm in length and 10 mm in diameter) plugged with a small portion of glass wool at both ends. The column was preconditioned by using the related buffer solution. An aliquot of 20 mL of the model solution including 8 μg Pb(II) at pH 5 was passed through the column at a flow rate of 2 mL min^{-1}. The retained Pb(II) ions were eluted with 2 mL of 2 mol L^{-1} HNO_3. The eluent was analyzed for the determination of Pb(II) by FAAS.

2.5. Sample preparation

The mineral water sample was purchased from a local market. The waste water sample from Kayseri city Organized Industrial Region and well water sample from Kayseri city, Turkey were collected. Before starting the preconcentration method, the waste water and well water samples were filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter. Aliquots of 40 mL of water samples and 20 mL of SPS-WW1 Batch 111-Wastewater reference material were used for analysis of Pb(II).

The food samples (cauliflower and barley) were purchased from a local market in Kayseri city, Turkey. They were dried at 100 °C and grounded. Five hundred milligrams of each food sample were taken into 100 mL beaker and 10 mL of concentrated HNO_3 (65% w/w) was added. The contents of the beaker were evaporated near to dryness on a hot plate at about 120 °C for 3 h. After cooling, 3 mL of concentrated H_2O_2 (30%, w/w) was added. The mixture was again evaporated near to dryness to obtain clear solution [11]. The solution was diluted to a volume of 20 mL by ultra-high purity water and preconcentration/separation procedure described above was applied to the sample solutions.

For the dissolving of BCR-482 Licken certified reference material, 100 mg sample were used. The samples were digested in mixture of concentrated HNO_3: $HClO_4$; (v/v 9:1) on a hot plate at about 130 °C for 3 h [30]. The obtained clear solution was diluted to 20 mL by ultra-high purity water and the method described above was applied.

0.10 g tobacco sample was treated with a mixture of concentrated HNO_3 and HCl in a ratio of 1:1.5 (v:v), heated at a temperature of about 150 °C for 2 h [31]. After that, the samples were diluted and the method was applied.

0.10 g street dust sample and 0.10 g Reference Material 8704, Buffalo River Sediment were digested using 10 mL of aqua regia twice. The interior surface of the beaker was washed by ultra-high purity water and filtered through a blue band filter paper [11]. The pH was adjusted to pH 5 and the solution was diluted to 20 mL with ultra-high purity water. The preconcentration procedure was used to separate and preconcentrate of Pb(II).

3. Results and discussion

3.1. Characterization of synthesized ultralayered Co_3O_4

The structures of the prepared products are characterized using X-ray diffraction (XRD). Fig. S1 shows the XRD pattern of the product. All the diffraction peaks can be indexed as cubic Co_3O_4, which match well with literature results (JCPDS No. 43-1003). No peaks from other phases were detected, indicating the phase pure product. The average size of the nanocrystallites was also estimated by using the Debye–Scherrer formula [32]; $D = 0.9\lambda/(\beta \cos \theta)$, where λ,

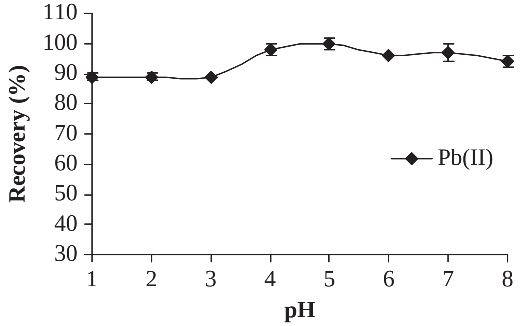

Fig. 1. Effect of pH on the recovery of Pb(II).

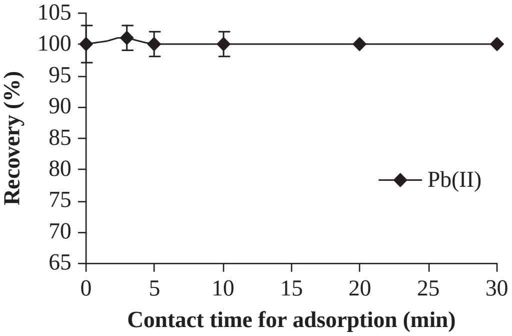

Fig. 2. Effect of contact time on the recovery of Pb(II).

β and θ are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak and the Bragg diffraction angle, respectively. The estimated crystallite size was found to 16.8 nm from XRD data.

The morphology of the product was investigated by SEM. Fig. S2 shows low and high magnification SEM micrographs of the product after heating process. Fig. S2 clearly shows that the product has highly layered morphology consisting of well arranged rectangular 2D microsheets.

The BET surface area and pore volume of the ultralayered Co_3O_4 was determined to be 75.5 $m^2\ g^{-1}$ and 0.16 $cm^3\ g^{-1}$, respectively. The BET isotherm of Co_3O_4 sample in Fig. S3 shows that the contribution of mesopores to the total surface area and pore volume is significantly higher than that of macropores.

3.2. Effect of pH

The pH value plays an important role with respect to the adsorption of ions on oxide surfaces. The pH of the solution affects the distribution of active sites on the surface of ultralayered Co_3O_4. The effect of solution pH on the adsorption of Pb(II) ions was examined in the pH range of 1–8 by using the model solutions of 20 mL containing 0.10 g of adsorbent and 8 μg Pb(II). For the both adsorption and elution, 30 min contacting time at a shaking rate of 200 rpm was used. As can be seen in Fig. 1, the recovery values for Pb(II) were found to be ≥94% in the range of pH 4–8. The decrease in recovery value at ≤pH 3 may be due to competition of hydronium ion and Pb(II) ion for the active sites of the Co_3O_4. The optimum pH was selected as 5 for Pb(II) adsorption in further tests. At pH 5, the recovery values for Cr(III), Mn(II), Fe(III), Ni(II), Cu(II), Co(II), Cd(II) and Zn(II) changed from 12 to 58%.

3.3. Effect of contact time for adsorption and elution

The effect of the contact time between ultralayered Co_3O_4 nanomaterial and Pb(II) ions was investigated to determine the adsorption and elution equilibrium time. The pH of the solutions including 8 μg Pb(II) was adjusted to 5. The equilibrium contact time for Pb(II) adsorption was changed in the range of 0–30 min at a shaking rate of 200 rpm. The contact time for elution was 30 min. Fig. 2 indicates that it is possible to reach equilibrium without shaking. For elution, the contact time of 0–30 min was also studied. The recovery values for Pb(II) were found to be quantitative for all the times. So 10 s vortexing time was considered as both adsorption and elution contact time in further studies. The adsorption and elution kinetic for Pb(II) is very fast. This can be attributed to the large surface area and high surface reactivity of adsorbent [33].

Table 1
Effect of concentration of eluents on the recovery of Pb(II), eluent volume: 2 mL.

Conc. of HNO_3 (mol L^{-1})	R (%) ± s	Conc. of HCl (mol L^{-1})	R (%) ± s
0.5	46 ± 0	0.5	73 ± 2
0.75	45 ± 2	0.75	77 ± 2
1.0	83 ± 2	1.0	90 ± 2
2.0	100 ± 0	2.0	97 ± 3

Table 2
Effect of some interfering ions on the recovery of Pb(II) by ultralayered Co_3O_4 (n=3).

Interfering ion	Salt	Concentration (mg L^{-1})	R ± s (%)
Na(I)	NaCl	25,000	93 ± 2
		50,000	89 ± 0
		75,000	85 ± 4
	$NaNO_3$	5,000	99 ± 2
		10,000	100 ± 2
		20,000	95 ± 0
		50,000	100 ± 3
		75,000	97 ± 1
K(I)	KNO_3	5,000	100 ± 2
		10,000	100 ± 0
		20,000	92 ± 3
		50,000	99 ± 2
		75,000	92 ± 1
Ca(II)	$Ca(NO_3)_2.6H_2O$	5,000	101 ± 2
		7,500	99 ± 2
		10,000	99 ± 2
		20,000	99 ± 3
		75,000	100 ± 1
Mg(II)	$Mg(NO_3)_2.6H_2O$	5,000	101 ± 0
		6,000	100 ± 0
		7,500	82 ± 2
Mn(II)	$Mn(NO_3)_2 \cdot 4H_2O$	50	95 ± 4
Co(II)	$Co(NO_3)_2 \cdot 6H_2O$	50	95 ± 2
Cu(II)	$Cu(NO_3)_2 \cdot 5H_2O$	50	100 ± 2
Cd(II)	$Cd(NO_3)_2 \cdot 4H_2O$	50	97 ± 3
Ni(II)	$NiCl_2 \cdot 6H_2O$	50	99 ± 0
Cr(III)	$Cr(NO_3)_3 \cdot 9H_2O$	50	100 ± 0
Al(III)	$Al(NO_3)_3 \cdot 9H_2O$	50	102 ± 0
Zn(II)	$Zn(NO_3)_2 \cdot 6H_2O$	50	93 ± 0
Fe(III)	$Fe(NO_3)_3 \cdot 9H_2O$	50	100 ± 0
SO_4^{2-}	Na_2SO_4	50	95 ± 2
		100	87 ± 3
		250	71 ± 0
PO_4^{3-}		25	94 ± 4
Cl^-	NaCl	35,000	93 ± 2
		75,000	89 ± 0
CO_3^{2-}	Na_2CO_3	100	94 ± 1
		150	89 ± 3
		250	82 ± 4

3.4. Effect of eluent type, concentration and volume

Various concentrations of 2 mL of hydrochloric acid and 2 mL of nitric acid (0.5, 0.75, 1.0, 1.5, and 2.0 mol L^{-1}) were used for elution of Pb(II) adsorbed on the ultralayered Co_3O_4. The results are shown in Table 1. When used 2 mol L^{-1} HCl and 2 mol L^{-1} HNO_3, the recovery values for Pb(II) were quantitative. 2 mol L^{-1} HNO_3 was selected as eluent. In the volume scanning of 2, 4, 6, 8, and 10 mL of 2 mol L^{-1} HNO_3, the quantitative recovery values (from 100 to 102%) for Pb(II) were obtained for all the studied volumes of eluent. In subsequent experiments, 2 mL of 2 mol L^{-1} HNO_3 was used for elution.

3.5. Effect of sample volume

The sample volume is important to obtain high preconcentration factor. For this purpose the model solutions of 20, 50, 100, 250, 350, 400 and 500 mL including 8 μg Pb(II) at pH 5 were prepared and the column method was applied. The elution was made by 2 mL of 2 mol L^{-1} HNO_3. The Pb(II) concentrations in these solutions corresponded to 0.4, 0.16, 0.08, 0.032, 0.023 and 0.016 mg L^{-1}, respectively. The recoveries of Pb(II) were between 95 and 100% for the sample volumes up to 350 mL. The preconcentration factor was obtained as 175 due to the elution volume of 2 mL.

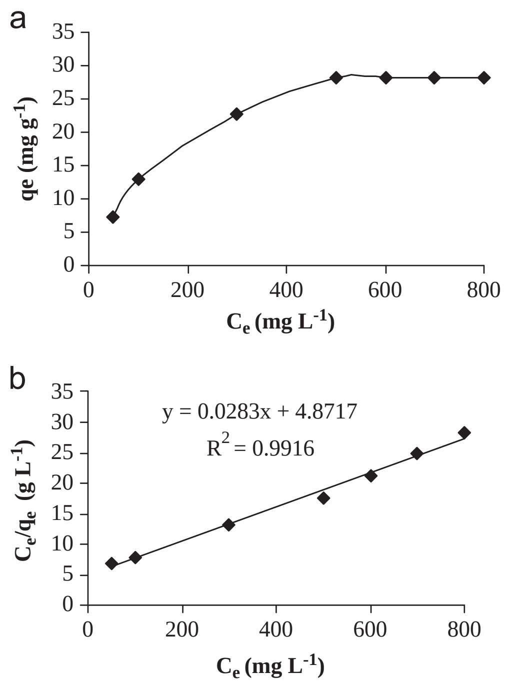

Fig. 3. (a) Adsorption isotherm of Pb(II) on ultralayered Co_3O_4. (b) Linearized Langmuir adsorption of Pb(II) on ultralayered Co_3O_4.

3.6. Reusability of the adsorbent

The stability and regeneration of ultralayered Co_3O_4 is the key factor for considering the performance of the adsorbent. In this work, the recovery values of Pb(II) after several adsorption and elution cycles were calculated. The adsorbent of 100 mg was reused after regenerated with 2 mL of 2 mol L^{-1} HNO_3 and then 5 mL of ultra pure water, respectively. The adsorbent was stored in ultra pure water when it was not in use. The cycle results show that the adsorbent is stable up to 170 runs without decrease in the recoveries of Pb(II) and it can be reused. The average ± standard deviation of Pb (II) recovery from 170 runs were found to be 99% ± 1.

3.7. Effect of interferences

The concentrations of trace metal ions may be affected by the other constituents in the samples. So, the effect of some interfering ions on the preconcentration and determination of Pb(II) was investigated. In the experiments, the described preconcentration method was applied for the model solutions of 20 mL containing 0.4 mg L^{-1} Pb(II) and interfering ions added at different concentrations. The tolerance limit is considered as the concentration of interfering ions that reduce the extraction efficiency of Pb(II) ions to ≥90% recovery value. The results (Table 2) show that the recovery values for Pb(II) were obtained as ≥90% even in the presence of the following ions: 25,000 mg L^{-1} for Na(I) as chloride salt, 75,000 mg L^{-1} for Na(I), K(I) and Ca(II) as nitrate salt, 6000 mg L^{-1} for Mg(II), 50 mg L^{-1} for Mn(II), Co(II), Cu(II), Cd(II), Ni(II), Cr(III), Al(III), Zn(II) and Fe(III), 100 mg L^{-1} for CO_3^{2-}, 50 mg L^{-1} for SO_4^{2-}, 25 mg L^{-1} for PO_4^{3-} and 35,000 mg L^{-1} for Cl^-. Especially, tolerance limits of 75,000 mg L^{-1} for Na(I), K(I) and Ca(II) from major constituents were fairly high. The results show that the ultralayered Co_3O_4 sorbent is quite selective to Pb(II) when considered commonly found interferences in the various water, food, sediment and tobacco samples used in this work.

3.8. Adsorption capacity of the ultralayered Co_3O_4

The adsorption isotherms and adsorption capacity of the ultralayered Co_3O_4 for Pb(II) were studied under optimal experimental conditions. The pH of model solutions of 20 mL containing 50–800 mg $L^{-1}$of Pb(II) was adjusted to 5 and the described method was applied. The eluent was diluted 100 or 200 fold. The adsorption equilibrium isotherm obtained for Pb(II) is given in Fig. 3(a).

As shown in Fig. 3(b), the adsorption data were fitted according to the linear form of the Langmuir isotherm model based on the following equation [34]:

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

where q_e and C_e are the amount adsorbed (mg g^{-1}) and the Pb(II) concentration in solution (mg L^{-1}), respectively, at equilibrium. K_L is the Langmuir constant (L mg^{-1}) and q_m is the maximum

Table 3
Determination of Pb in certified reference materials.

Element	RM 8704 Buffalo river sediment			BCR-482 Licken			SPS-WW1 Batch 111-wastewater		
	Certified[a] (μg g^{-1})	Found[b] (μg g^{-1})	R(%)	Certified[a](μg g^{-1})	Found[b](μg g^{-1})	R(%)	Certified[a] (μg L^{-1})	Found[b] (μg L^{-1})	R(%)
Pb	150 ± 17	148 ± 4	99	40.9 ± 1.4	41.0 ± 2.2	100	100 ± 0.5	105 ± 8	105

[a] At 95% confidence level.
[b] $\bar{x} \pm s$, $n=3$.

adsorption capacity of the adsorbent (mg g^{-1}). Langmuir isotherm was used to determine the q_m and K_L values from the linear coefficients obtained by plotting C_e/q_e as a function of C_e. The adsorption capacity was found to be 35.3 mg g^{-1}. The Langmuir constant was 0.006 L mg^{-1}.

Table 4
Determination of Pb(II) in various water samples (sample volume: 40 mL, final volume: 2 mL).

Sample	Added (μg L^{-1})	Found[a] (μg L^{-1})	R (%)
Well water	–	nd[b]	
	100	106 ± 2	106
	200	202 ± 2	101
Mineral water	–	nd[b]	
	100	101 ± 4	101
	200	190 ± 4	95
Wastewater	–	78 ± 4	
	100	175 ± 6	97
	200	267 ± 3	95
Sea water	–	nd[b]	
	25	24.1 ± 4.1	96
	50	48.6 ± 3.4	97

[a] $\bar{x} \pm s$, $n=3$.
[b] Not detected.

Table 5
Determination of Pb(II) in various food, street sediment and tobacco samples.

Sample	Added (μg g^{-1})	Found[a] (μg g^{1})	R (%)
Cauliflower		5.2 ± 0.3	
	8	13.2 ± 0.9	100
	16	21.3 ± 0.9	101
Barley		1.9 ± 0	
	2	3.8 ± 0.5	95
	4	6.0 ± 0	103
Street sediment		142 ± 2	
	100	241 ± 5	99
	200	332 ± 5	95
Tobacco	–	1.7 ± 0.5	
	2	3.7 ± 0.3	100
	4	5.6 ± 0.3	98

[a] $\bar{x} \pm s$, $n=3$.

3.9. Analytical figures of merits

The linear range of the calibration curve for Pb(II) was found to be 1.0–10 mg L^{-1} (Absorbance = 0.01 [Pb]+0.0002, r^2 = 0.9997). The calibration data were obtained without the preconcentration method. The detection limit (DL, 3 s/b) of the method for Pb(II) was determined with preconcentration factor of 175 by using blank solutions (n = 13) [35]. The DL calculated as three times the standard deviation of the blank solutions divided by the slope of the calibration curve of the method was found to be 0.72 μg L^{-1} for Pb(II). The limit of quantification (10 s/b) was 2.38 μg L^{-1}. The precision of the method assessed as relative standard deviation (RSD, %) and calculated from 10 independent cycles at 0.4 mg L^{-1} concentration for Pb(II) was 1.5%.

3.10. Validation of the method and analysis of real samples

The validation of the developed method by using ultralayered Co_3O_4 as an adsorbent for preconcentration of Pb(II) was evaluated by both the certified reference materials (RM 8704 Buffalo River Sediment, BCR-482 Lichen, SPS-WW1 Batch 111-Wastewater) and by the recovery studies. As can be seen from Table 3, the obtained results were in good agreement with the certified values. The method was applied for the determination of trace Pb(II) in water (well water, mineral water, waste water and sea water), food (cauliflower and barley), street sediment and tobacco samples. The analytical results with the recoveries for spiked samples are given in Tables 4 and 5. As can be seen, the recovery values for Pb(II) were changed from 95 to 106%. These results show that the developed method can be applied for various samples (water, food, street sediment and tobacco samples).

3.11. Comparison of the present method with others

Some of the other some preconcentration works using nano-sized metal oxides described in literature are given in Tables S1

Table 6
Comparison of the proposed method with some preconcentration methods reported in literature for Pb(II) preconcentration.

Adsorbent/technique	pH	AC[a] (mg g^{-1})	PF[b]	DL[c] (μg L^{-1})	RSD (%)	Contact time (min)	Reusability	Resin amount (mg)	Application	References
Modifed nanometer-sized alumina/FAAS	7–8	16.4	250	0.17	3.2			50	Tap, mineral water, and plant samples	[12]
Nanometer TiO_2 immobilized on silica gel/GFAAS	5	3.16	50	0.0095	3.2		20	50	Tap and lake water	[20]
Magnetic adsorbent (Shiff base-functionalized Fe_3O_4/SiO_2)/FAAS	7		87.5	0.14	1.4	10		130	Tap, waste water, food, tobacco and hair samples	[35]
Bismuthiol-II-immobilized magnetic nanoparticles/ICP-OES	7	9.4	87	0.085	3.7	10	3	100	River and lake water	[36]
Nanometer-sized alumina coated with chromotropic acid/ICP-AES	8	15.4	50	0.53		30	15	50	River water, green leaves	[37]
Nano TiO_2 modified with diethyldithiocarbamate/ICP-AES	5	19	33	1.7	5.6	30		20	Lake, river water, liver and pear leaves	[38]
Nano-sized manganese dioxide functionalized multi-wall carbon nanotubes/ETAAS	6	6.7	100	0.0044	3.2			50	River and reservoir water	[39]
Ultralayered Co_3O_4/FAAS	5	35.3	175	0.72	1.5	10 s	170	100	Well, mineral, waste water, food, street sediment and tobacco samples.	This work

[a] AC: Adsorption capacity.
[b] PF: Preconcentration factor.
[c] DL: Detection limit.

and 6. Table S1 shows the tolerance limits for common major constituents in samples, Na(I), K(I), Ca(II) and Mg(II), when compared to the other works used for the determination of Pb (II). The tolerance limits for the present work are higher than those of the other works. The time to attain equilibrium for several metal oxides was reported to be long (see Table 6). Compared to the other methods, the short contact time for both adsorption and elution suggests that the kinetic of the ultralayered Co_3O_4-metal interaction is rather rapid. The preconcentration factor of the method, adsorption capacity and reusability of adsorbent are much higher than those of the other methods. The method requires low eluent volume (2 mL) and it can also be successfully applied to various matrices.

4. Conclusions

In this work, utralayered Co_3O_4 was synthesized, characterized and used for the first time for the solid phase extraction of Pb(II) in various samples. The method is simple and selective. The used adsorbent has rather rapid adsorption and elution kinetic. The reusability (170 cycles) and adsorption capacity (35.5 mg g^{-1}) of ultralayered Co_3O_4 were excellent. The acidic working pH (5), good precision (1.5%) and high preconcentration factor (1 7 5) are the other advantages of the method. The analyses of certified reference materials and recovery tests show that the described method can be used for Pb(II) extraction selectively from various water, food, sediment and tobacco samples.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.06.042.

References

[1] A. Afkhami, H. Bagheri, H. Khoshsafar, M.S. Tehrani, M. Tabatabaee, A. Shirzadmehr, Anal. Chim. Acta 746 (2012) 98–106.
[2] A. Afkhami, H. Ghaedi, T. Madrakian, M. Rezaeivala, Electrochim. Acta 89 (2013) 377–386.
[3] A Baysal, M. Ozcan, S. Akman, Food Chem. Toxicol. 49 (2011) 1399–1403.
[4] 〈http://www.epa.gov/lead/pubs/leadinfo.htm#health〉 (accessed 02.02.13).
[5] 〈http://ec.europa.eu/health/scientific_committees/environmental_risks/docs/scher_o_128. pdf〉 (accessed 02.02.13).
[6] A R.K. Dapaah, N. Takano, A Ayame, Anal. Chim. Acta 386 (1999) 281–286.
[7] K. Kocot, B. Zawisza, R. Sitko, Spectrochim. Acta, Part B 73 (2012) 79–83.
[8] M.R. Jan, J. Shah, M. Sadia, Atta-ul-Haq, Solvent Extr. Ion Exch. 30 (2012) 306–319.
[9] M.S. Bispo, E.S. da, B. Morte, M das, G.A. Korn, L.S.G. Teixeira, M. Korn, A.C. S. Costa, Spectrochim. Acta, Part B 60 (2005) 653–658.
[10] F. dos, S. Depoi, T.C. de Oliveira, D.P. de Moraes, D. Pozebon, Anal. Methods 4 (2012) 89–95.
[11] Ş. Turan, Ş. Tokalioglu, A. Şahan, C. Soykan, React. Funct. Polym. 72 (2012) 722–728.
[12] M. Ezoddin, F. Shemirani, Kh. Abdi, M.K. Saghezchi, M.R. Jamali, J. Hazard. Mater. 178 (2010) 900–905.
[13] A.F. Barbosa, M.G. Segatelli, A.C. Pereira, A. de S. Santos, L.T. Kubota, P.O. Luccas, C.R.T. Tarley, Talanta 71 (2007) 1512–1519.
[14] L.N. Hu, Z.G. Ren, Chin. Chem. Lett. 20 (2009) 334–338.
[15] L. Zhang, Y. Wang, X. Guo, Z. Yuan, Z. Zhao, Hydrometallurgy 95 (2009) 92–95.
[16] O. Yalcınkaya, O.M. Kalfa, A.R. Turker, J. Hazard. Mater. 195 (2011) 332–339.
[17] J.S. Suleiman, B. Hu, X. Pu, C. Huang, Z. Jiang, Microchim. Acta 159 (2007) 379–385.
[18] A. Kaur, U. Gupta, Eurasian J. Anal. Chem. 4 (2009) 175–183.
[19] P. Liang, Y. Qin, B. Hu, T. Peng, Z. Jiang, Anal. Chim. Acta 440 (2001) 207–213.
[20] R. Liu, P. Liang, J. Hazard. Mater. 152 (2008) 166–171.
[21] V.A Lemos, L.S.G Teixeira, M. de A.Bezerra, A.C.S. Costa, J.T. Castro, L.A. M. Cardoso, D.S. de Jesus, E.S. Santos, P.X. Baliza, L.N. Santos, Appl. Spectrosc. Rev. 43 (2008) 303–334.
[22] F.-Y. Zheng, S.-H. Qian, S.-X. Li, X.-Q. Huang, L.-X. Lin, Anal. Sci. 22 (2006) 1319–1322.
[23] Y. Hang, Y. Qin, J. Shen, J. Sep. Sci 26 (2003) 957–960.
[24] S. Li, N. Deng, F. Zheng, Y. Huang, Talanta 60 (2003) 1097–1104.
[25] Y. Cui, X. Chang, X. Zhu, N. Jiang, Z. Hu, N. Lian, Microchem. J 86 (2007) 23–28.
[26] S. Recillas, J. Colón, E. Casals, E. González, V. Puntes, A. Sánchez, X. Font, J. Hazard. Mater. 184 (2010) 425–431.
[27] J.L. Manzoori, M. Amjadi, M. Darvishnejad, Microchim. Acta 176 (2012) 437–443.
[28] L. Zhang, T Huang, M. Zhang, X. Guo, Z. Yuan, J. Hazard. Mater. 157 (2008) 352–357.
[29] S.K. Meher, G.R. Rao, J. Phys. Chem. C 115 (2011) 15646–15654.
[30] R Bajpai, G.K Mishra, S Mohabe, D.K Upreti, S. Nayaka, J. Environ. Biol. 32 (2011) 195–199.
[31] B. Kaličanin, D. Velimirović, Int. J. Electrochem. Sci. 7 (2012) 313–323.
[32] L.V. Azarof, M.J. Buerger, The Powder Method in X-ray Crystallography, first ed., McGraw-Hill, New York, 1958.
[33] A Uheida, M. Iglesias, C. Fontás, M. Hidalgo, V. Salvadó, Y Zhang, M. Muhammed, J. Colloid Interface Sci. 301 (2006) 402–408.
[34] M.M. Bekheit, N. Nawar, A.W. Addison, D.A. Abdel-Latif, M. Monier, Int. J. Biol. Macromol. 48 (2011) 558–565.
[35] H. Bagheri, A. Afkhami, M.S. Tehrani, H. Khoshsafar, Talanta 97 (2012) 87–95.
[36] J.S. Suleiman, B. Hu, H Peng, C. Huang, Talanta 77 (2009) 1579–1583.
[37] A. Ramesh, B.A. Devi, H Hasegawa, T. Maki, K. Ueda, Microchem. J. 86 (2007) 124–130.
[38] H. Zheng, X. Chang, N. Lian, S. Wang, Y. Cui, Y. Zhai, Int. J. Environ. Anal. Chem. 86 (2006) 431–441.
[39] B Yang, Q. Gong, L. Zhao, H. Sun, N. Ren, J. Qin, J. Xu, H. Yang, Desalination 278 (2011) 65–69.