

Preparation of a New Sorbent, Cetyltrimethylammonium Bromide (CTAB)-Modified Obsidian, for the Separation and Preconcentration of Pb(II) and Cd(II) Ions in Food and Water Samples

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INTRODUCTION

As a result of various industrial activities such as electroplating, metal finishing, battery manufacture, metallurgical and fertilizer industries, pollution of the environment with toxic heavy metals has increased and causes extremely serious human health problems. Pb(II) is in a class of elements that is described as totally toxic. Pb(II) ions block a variety of organs in the human body by damaging the nervous, reproductive, and immune systems (1). Cd(II) is also a potentially toxic and non-essential heavy metal. It does not have any functions in the human metabolism, but accumulates in the body and causes injury to organs such as the kidneys, liver, and lungs (2).

During the determination of Pb(II) and Cd(II) ions (and also other trace metals) in environmental samples by different well-known instrumental techniques, i.e., inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), flame atomic absorption spectrometry (FAAS), and electrothermal atomic absorption spectrometry (ET-AAS), generally a separation and preconcentration technique is required such as coprecipitation (3), cloud point extraction (4,5), ion exchange (6), solvent extraction

ABSTRACT

Cetyltrimethylammonium bromide (CTAB)-modified obsidian (CTAB-OB) was utilized as a new sorbent for the separation and preconcentration of Pb(II) and Cd(II) ions by solid phase extraction in some environmental samples prior to their flame atomic absorption spectrophotometric determination. The characterization of CTAB-OB was performed by BET surface area, FTIR and SEM techniques. The effects of significant analytical parameters, including pH of the aqueous solution, eluent type, concentration and volume, CTAB-OB amount, sample volume, adsorption and desorption contact time, were evaluated in detail on the recovery of the analyte ions. The adsorption capacity of CTAB-OB was found to be 48.8 and 43.4 mg g⁻¹ for the Pb(II) and Cd(II) ions, respectively. The detection limits for the analyte ions were 0.89 µg L⁻¹ for Pb(II) and 0.37 µg L⁻¹ for Cd(II), while the relative standard deviations were lower than 3.5% for both of them. In order to ensure the accuracy of the method, certified reference material (CRM-SA-C Sandy Soil C) analyses and spike tests were performed. Then the proposed method was applied to sea and stream water, black tea, and Turkish and import coffee samples to determine their Pb(II) and Cd(II) contents.

(7), and solid phase extraction (8,9) in order to increase the analyte signal and overcome the interferences of the matrix components. In this sense, solid phase extraction (SPE) is a unique technique because its application is very simple and rapid. High preconcentration factors can be obtained in SPE which results in easy and sensitive detection of the analyte ions. More importantly, it is an environmentally friendly method because of its low consumption of chemical reagents (8,9).

Up to the present, researchers have used a variety of natural and synthetic sorbents such as activated carbon (10), Amberlite XAD resins (11), cellulose (12), and zeolite (13), which has a high specific surface area and adsorption capacity, and is durable in high acidic and basic media. According to our literature survey, no investigation has been performed to evaluate the potential use of obsidian (OB) or modified obsidian as a solid phase extractor in the separation and preconcentration of metal ions. However, in this paper our aim was to develop a new adsorbent for the determination of Pb(II) and Cd(II) levels in water samples and more frequently consumed foods after the SPE procedure. Firstly, the obsidian was modified with cetyltrimethylammonium bromide (CTAB) to increase the adsorption capacity. The CTAB, a cationic surfactant, has a molecular formula of (C₁₆H₃₃)N(CH₃)₃Br. It is an effective antiseptic agent against bacteria and fungi (14). Thus, it is considered to be a harmless reagent to

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humans. After characterizing the CTAB-modified obsidian (CTAB-OB) procedure with several techniques, it was considered an efficient and low-cost adsorbent for the separation and preconcentration of Pb(II) and Cd(II).

In order to obtain the quantitative recovery values for Pb(II) and Cd(II), the experimental parameters were examined in detail and optimized. The adsorption mechanism of the analyte ions were elucidated by examining different kinetic models. Method validation was performed and applied for the determination of Pb(II) and Cd(II) in food and water samples.

EXPERIMENTAL

Instrumentation

For this study, a Model Autosorb-1-C/MS specific surface area analyzer (Quantachrome Corporation, USA), a Model 1600 FTIR spectrometer (PerkinElmer Corporation, Shelton, CT USA), and a Model JEOL/JSM-6335F scanning electron microscope (JEOL Ltd., USA) were used to determine the surface area of CTAB-OB, to estimate the surface functional groups, and to disclose the surface morphology of CTAB-OB, respectively. Analyte ion determinations were performed using a PerkinElmer® AAnalyst™ 400 flame atomic absorption spectrometer with an air/acetylene flame. The instrumental operating conditions are listed in Table I. A mechanical shaker (Edmund Bühler GmbH, Tübingen, Germany) was used for the batch adsorption studies. The pH of the solutions was adjusted

with a Hanna pH-211 digital pH meter (HANNA Instruments, Romania) with a glass electrode. A Model Sigma 3-16P centrifuge (Sigma Laborzentrifugen GmbH, Germany) was employed for separation of the adsorbent from the aqueous solution. For digestion of the solid samples, a Milestone Ethos D closed vessel microwave system (Milestone Inc., Italy) was used.

Preparation of Adsorbent

For the separation and preconcentration of Pb(II) and Cd(II), an obsidian was used as the sorbent after modification with cetyltrimethylammonium bromide (CTAB). For the modification process, 200 mL of 4% (w/v) CTAB solution was mixed with 20 g obsidian and stirred on a mechanical shaker for 24 hours. Then the solution was filtered and the obtained solid phase washed twice with deionized water, then dried at 70 °C (15). This sorbent was denominated as CTAB-OB (modified obsidian). In the SPE experiments, a <150 μm particle size of CTAB-OB was used.

Reagents and Standard Solutions

All of the chemical reagents used in the present method were procured from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). 1000 mg L⁻¹ stock solutions of Pb(II) and Cd(II) ions were diluted to obtain the standard and working solutions.

Model Solutions

The model solutions were used for optimization of the developed

batch adsorption method for separation and preconcentration of Pb(II) and Cd(II) in environmental real samples. For that purpose, 50 mL of an aqueous solution containing 20 μg of Pb(II), 5 μg of Cd(II), and 5.0 g L⁻¹ of CTAB-OB suspension were placed in a centrifuge tube. The pH of the solutions was adjusted to 8.0 by the addition of dilute HNO₃ or NaOH solution. The mixture was agitated on a mechanical shaker at 400 rpm for 15 minutes. Then the suspension was centrifuged at 2000 rpm for 5 minutes. The aqueous solution was removed and the analyte ions were eluted from the sorbent with 5.0 mL of 1.0 M HNO₃ solution by agitating for 15 minutes. Then the suspension was centrifuged at 2000 rpm for 5 minutes, and the concentration of Pb(II) and Cd(II) measured in the dilute phase by FAAS.

Preparation of Real Samples

One of the primary objectives of the study was to base the developed separation and preconcentration procedure on the batch adsorption technique for the determination of analyte ion levels in real samples. Hence, after optimizing the experimental parameters by using model solutions, the method was applied to determine Pb(II) and Cd(II) levels in seawater, stream water, black tea, Turkish coffee, and import coffee.

Before the experiments, 500 mL of seawater (Blacksea, Trabzon, Turkey) and stream water (Sana, Trabzon, Turkey) samples were filtered by using a cellulose nitrate membrane. After adjusting the pH of the water samples to 8.0, an appropriate amount of CTAB-OB was added and the developed SPE procedure performed.

For the solid samples, microwave digestion was primarily carried out after separately weighing 0.750 g each of black tea, Turkish coffee, and import coffee, and 0.100 g of

TABLE I
Instrumental Operating Conditions

Element	Wavelength (nm)	Spectral Resolution (nm)	Lamp Current (mA)	Acetylene Flow Rate (L min ⁻¹)	Air Flow Rate (L min ⁻¹)
Pb(II)	283.31	2.7/0.8	450	7.5	6
Cd(II)	228.80	2.7/1.35	4	7.5	6

CRM-SA-C Sandy Soil C certified reference material (obtained from High-Purity Standard, Inc., Charleston, SC, USA) into Teflon® vessels. Then, 6 mL of HNO₃ and 2 mL of H₂O₂ were added to black tea, Turkish coffee, and import coffee samples; while 2 mL of H₂O₂ and 1 mL of HF were added to the CRM SA-C Sandy Soil C standard. The conditions were set according to the literature (16). The digested samples were brought to 50-mL volume with distilled water and then the SPE procedure was applied.

RESULTS AND DISCUSSION

Characterization of Adsorbent

The CTAB-OB sorbent has a relatively small specific surface area since the BET surface area of CTAB-OB was found to be lower than 5.0 m² g⁻¹. By evaluating the scanning electron micrographs (SEM) of OB [Figure 1(a)] and CTAB-OB [Figure 1(b)], it can easily be seen that the OB surface is coated substantially with CTAB molecules. The modification of the OB with CTAB molecules was also supported by the FTIR (Fourier transform infrared) spectra of OB [Figure 2(a)] and CTAB-OB [Figure 2(b)]. In the FTIR spectrum of CTAB-OB, two sharp peaks appear at 2920–2850 cm⁻¹ due to the

stretching vibration of -CH₃ and -CH₂, respectively, and the band near 1460 cm⁻¹ is related to the -CH₂ deformation peak (17). In addition, the broad band near 1000 cm⁻¹, which is seen in both spectra, is related to the stretch vibrations of the Si-O groups.

Optimization of Experimental Parameters

The pH of the aqueous solution is an extremely effective factor on the sorption of the analyte ions onto the CTAB-OB surface since the surface charge of the sorbent may be altered by the pH of the aqueous solutions. Based on this, the effect of pH on the quantitative recoveries of the analyte ions was investigated in the pH range of 2.0–10.0

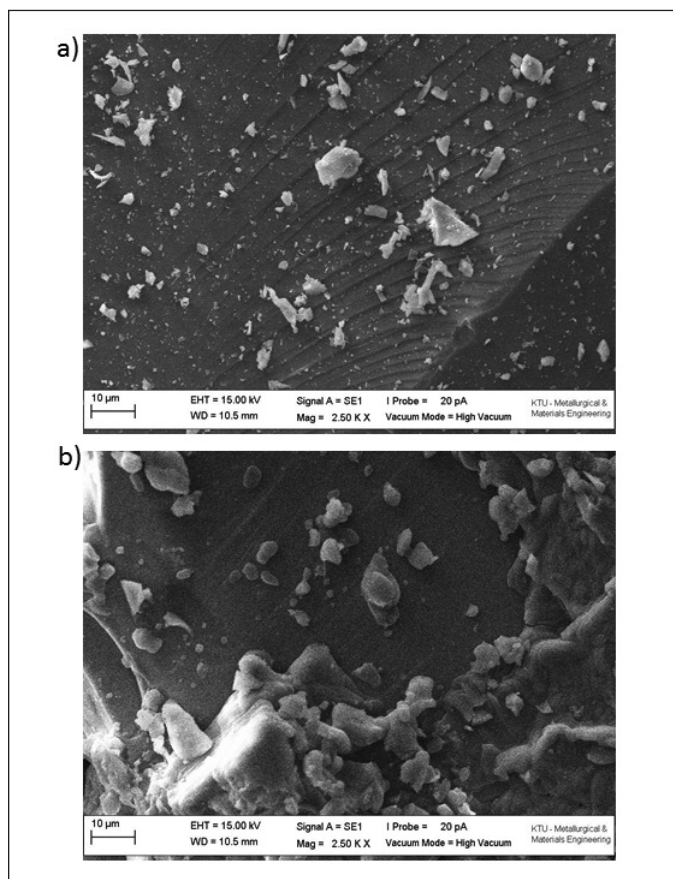


Fig. 1. SEM micrographs of (a) OB, (b) CTAB-OB.

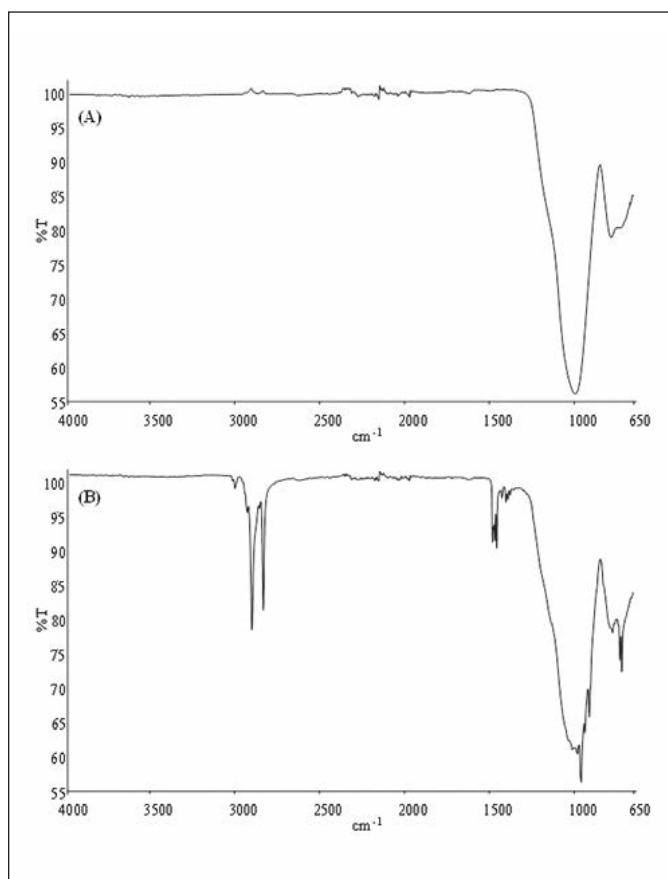


Fig. 2. FTIR spectrum of (a) OB, (b) CTAB-OB.

by keeping other parameters constant (Figure 3). The recovery values were quantitative after pH 8.0; hence, for the simultaneous separation and preconcentration of Pb(II) and Cd(II), all other experiments were carried out at pH 8.0.

Several inorganic acids including HCl, H₂SO₄, and HNO₃ were tested at different concentrations for the elution of Pb(II) and Cd(II) since in an acidic medium the sorbent surface is positively charged and hence the desorption of positively charged metal ions from the sorbent surface becomes easier (18). In general, the recovery values of the analyte ions increased with an increase in acid concentration, except for H₂SO₄ (Table II). The decrease in the recovery of the analyte ions while increasing the H₂SO₄ concentration maybe due to the high interference effects of the SO₄²⁻ ions. As a result, for elution of Pb(II) and Cd(II), a 1.0 M HNO₃ solution was preferred. The eluent volume was also evaluated in the 1.0 M HNO₃ solution volume range of 2.5–10.0 mL. After 5.0 mL of eluent volume, the recovery values for both analyte ions were quantitative. For further studies, 5.0 mL of 1.0 M HNO₃ solution was used as the eluent.

The effect of the amount of CTAB-OB was investigated in the concentration range of 1.0–20.0 g L⁻¹ (Figure 4). Quantitative recoveries were obtained in the CTAB-OB range of 1.0–7.5 g L⁻¹. Above 7.5 g L⁻¹ of CTAB-OB, when 5.0 mL of eluent volume was used, the recovery decreased as the CTAB-OB concentration decreased. In the proposed procedure, use of 5.0 g L⁻¹ of CTAB-OB is recommended.

High preconcentration factors are necessary for the determination of lower analyte levels in real environmental samples. Hence, the effect of sample volume on the recovery of Pb(II) and Cd(II) ions was examined in the sample volume range of 50–1000 mL and by using model solutions containing 20 µg of Pb(II) and 5 µg of Cd(II). The sorption and recovery of the analyte ions were not affected in the 50–500 mL sample volume (Figure 5). At sample volumes higher than 500 mL, the recovery values decreased sharply. The preconcentration factor was calculated as 100 by the ratio of highest sample volume (500 mL) and the lowest final volume (5.0 mL).

TABLE II
Effect of Eluent Type and Concentration on Recoveries of the Analyte Ions
(n=3, pH: 8.0, CTAB-OB: 5.0 g L⁻¹, adsorption and desorption contact time: 15 min)

Eluent Type	Pb(II)	Cd(II)
1 M HCl	87.6±3.5	91.6±0.5
2 M HCl	95.6±2.1	92.8±2.1
3 M HCl	96.7±1.4	94.3±3.6
1 M H ₂ SO ₄	84.7±2.4	74.1±2.3
2 M H ₂ SO ₄	70.8±1.9	71.5±3.0
3 M H ₂ SO ₄	37.3±1.9	61.6±2.6
0.05 M HNO ₃	89.8±1.1	65.0±2.9
0.1 M HNO ₃	97.3±2.2	76.2±1.5
0.5 M HNO ₃	96.7±3.4	91.1±3.1
1 M HNO ₃	98.8±2.7	98.0±2.8
2 M HNO ₃	96.0±2.1	97.1±1.4
3 M HNO ₃	96.5±3.0	97.4±1.2

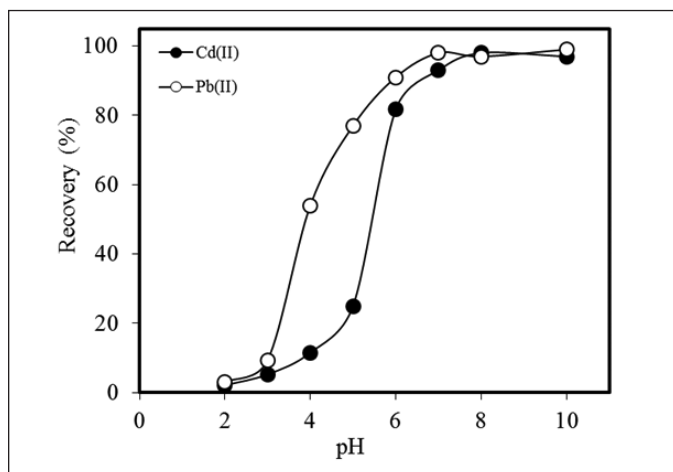


Fig. 3. Effect of pH on the recoveries of analyte ions. n=3, CTAB-OB: 5.0 g L⁻¹, eluent type and volume: 5.0 mL of 1.0 M HNO₃, adsorption and desorption contact time: 15 min.

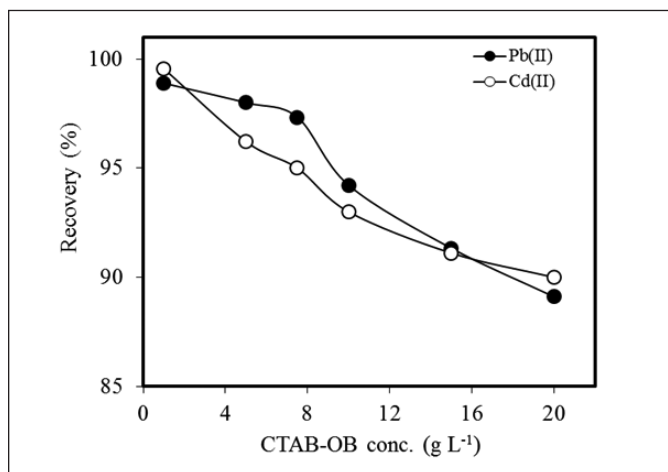


Fig. 4. Effect of CTAB-OB amount on the recoveries of analyte ions. n=3, pH: 8.0, eluent type and volume: 5.0 mL of 1.0 M HNO₃, adsorption and desorption contact time: 15 min.

In order to estimate sufficient contact time to reach equilibrium, the adsorption of Pb(II) and Cd(II) onto CTAB-OB was evaluated in the contact time range of 1–120 minutes by contacting 100 μg of Pb(II) and 20 μg of Cd(II) with 5.0 g L^{-1} of CTAB-OB suspensions. The samples were taken at different periods of time and analyzed for their Pb(II) and Cd(II) concentrations. The adsorption of the analyte ions onto CTAB-OB occurred in a very short time [Figure 6(a)]. Although equilibrium was reached after approximately 5 minutes of contact time and to ensure that sufficient contact time is provided for adsorption, further experiments were carried out using 15 minutes.

The effect of contact time for the desorption of Pb(II) and Cd(II) from CTAB-OB was also investigated in the range of 1–60 minutes. For that purpose, 5.0 g L^{-1} of CTAB-OB was equilibrated with a series of aqueous solutions containing 20 μg of Pb(II) and 5 μg of Cd(II)

at pH 8.0. After reaching equilibrium, CTAB-OB was separated by centrifugation at 2000 rpm for 5 minutes. Then, the Pb(II)- and Cd(II)-loaded CTAB-OB was eluted with 5.0 mL of 1.0 M HNO_3 solution during different time periods. Quantitative recovery was observed above the elution contact time of 15 minutes [Figure 6(b)]. For further studies, the elution contact time of 15 minutes was selected.

In order to determine the adsorption capacity of CTAB-OB, 20 mg of CTAB-OB was added to 250 mL of aqueous solution containing 1000 μg of Pb(II) and Cd(II) at pH 8.0. The mixture was stirred for 15 minutes with a magnetic stirrer, then filtered, and the levels of the analyte ions were determined in the dilute phase by FAAS. The adsorption capacity of CTAB-OB was calculated as 48.8 and 43.4 mg g^{-1} for Pb(II) and Cd(II), respectively.

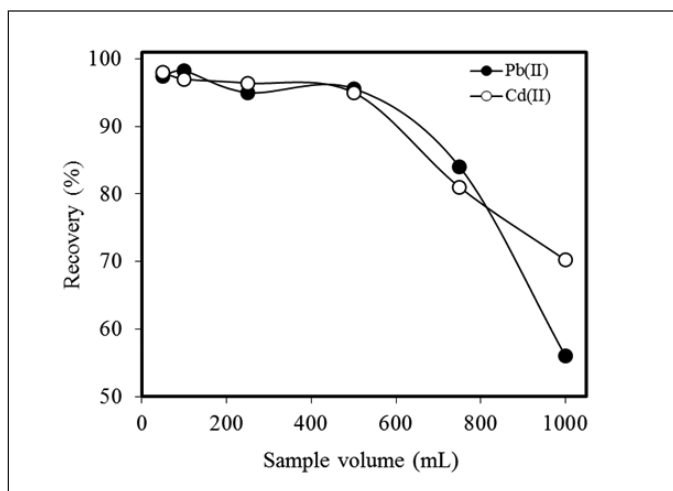


Fig. 5. Effect of sample volume on the recoveries of analyte ions. $n=3$, pH: 8.0, eluent type and volume: 5.0 mL of 1.0 M HNO_3 .

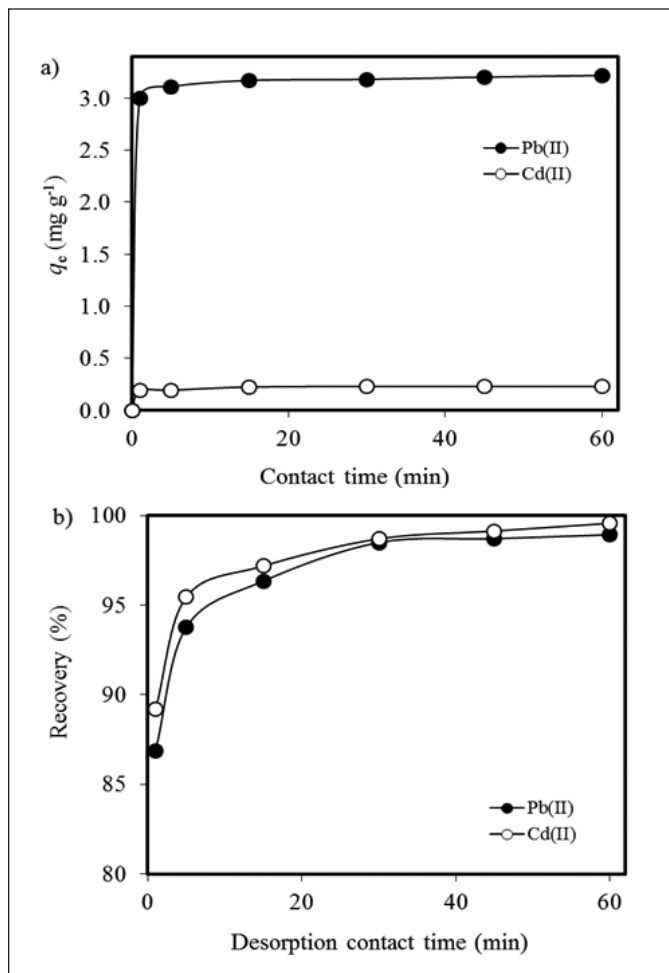


Fig. 6. (a) Effect of contact time on the adsorption. Pb(II): 100 μg , Cd(II): 20 μg , CTAB-OB: 5.0 g L^{-1} ; (b) Effect of contact time on the desorption. Pb(II): 20 μg , Cd(II): 5 μg , CTAB-O: 5.0 g L^{-1} .

TABLE III
Kinetics Parameters for Pb(II) and Cd(II) Adsorption Onto CTAB-OB

	Pseudo-first-order Model				Pseudo-second-order Model			Intra-particle Diffusion Model				
	$q_{e\ exp}$ (mg g ⁻¹)	k_1 (min ⁻¹)	$q_{e\ cal}$ (mg g ⁻¹)	R ²	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e\ cal}$ (mg g ⁻¹)	R ²	$k_{id,1}$ (g mg ⁻¹ min ^{-1/2})	R ²	$k_{id,2}$ (mg g ⁻¹ min ^{-1/2})	R ²	C
Pb(II)	3.22	-0.079	0.42	0.617	0.042	3.21	0.999	0.058	0.940	0.017	0.999	3.02
Cd(II)	0.23	-0.125	0.07	0.869	315.06	0.22	0.999	0.01	0.910	1.16	0.999	0.19

Adsorption Kinetics

The adsorption mechanism of Pb(II) and Cd(II) onto CTAB-OB was clarified by applying different kinetic models, including pseudo-first-order, pseudo-second-order, and intra-particle diffusion models.

The pseudo-first-order model can be expressed by the equation (19):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{Eq. 1})$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) shows the amounts of the metal ions adsorbed on the adsorbate at equilibrium and at any time t , respectively; and k_1 (min⁻¹) is the first order kinetics model rate constant. k_1 and q_e can be calculated from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ versus t , respectively.

The pseudo-second-order model is given in the following equation (20):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{Eq. 2})$$

where k_2 (g mg⁻¹ min⁻¹) is the second-order kinetic model rate constant. k_2 and q_e are determined from the intercept and slope of the plot of t/q_t versus t , respectively.

$\ln(q_e - q_t)$ versus t (for pseudo-first-order) and t/q_t versus t (for pseudo-second-order) graphs were plotted. The obtained data and constants with the correlation coefficients are given in Table III for both Pb(II) and Cd(II). By comparing the R² values, it can easily be seen that the pseudo-second-order was better

than the pseudo-first-order kinetic model. In addition, the calculated $q_{e\ cal}$ values were very close to the experimental values of $q_{e\ exp}$ obtained by the second-order kinetic model. Therefore, the pseudo-second-order adsorption mechanism is more suitable for describing the adsorption of Pb(II) and Cd(II) onto CTAB-OB.

The intra-particle diffusion model equation is given as (21):

$$q_t = k_{id} t^{1/2} + c \quad (\text{Eq. 3})$$

where k_{id} (mg g⁻¹ min^{-1/2}) is the rate constant of the intra-particle diffusion model and c (mg g⁻¹) is a constant which gives an idea about the boundary layer thickness. In most cases, the plot of q_t versus $t^{1/2}$ exhibits a multilinear correlation. The first phase in the multilinear line is film diffusion, the second phase is intraparticle or pore diffusion, and the last phase shows the sorption onto interior sites. In the intraparticle mass transfer curves of Pb(II) and Cd(II), the first and second phases were observed. The rate constants for these phases ($k_{id,1}$ and $k_{id,2}$) and c parameters were obtained from the plot of q_t versus $t^{1/2}$ and the results are listed in Table III. Although the lower values of $k_{id,2}$ than $k_{id,1}$ may let us think that the rate limiting step for Pb(II) and Cd(II) adsorption is intra-particle diffusion, yet the line did not pass through the origin. It can, therefore, be concluded that the intra-particle diffusion is not the only rate limiting mechanism and a complex process involving surface

sorption and intraparticle diffusion is responsible for the adsorption of Pb(II) and Cd(II) onto CTAB-OB (22).

Effect of Diverse Ions

In order to assess the possible use of the recommended separation and preconcentration method for the determination of the analyte ions in environmental samples which have a very complicated matrix, the effects of some interfering ions, which may be present together with the analyte ions in real samples, were tested. The method was applied to model solutions containing a constant amount of analyte ions [20 µg of Pb(II) and 5 µg of Cd(II)] and different concentrations of the foreign ions under optimized experimental conditions. A wide variety of ions at high concentrations have no significant interfering effects on the determination of the analyte ions such that in all cases the recovery values were higher than 90% (Table IV). These results indicated the selectivity and applicability of the developed method for the determination of Pb(II) and Cd(II) in real samples containing different types of salts and some transition metal ions.

Analytical Performance of the Method

The detection limits based on three times the standard deviation of the blank samples were evaluated by applying the developed procedure to blank samples (n=10) under the optimum experimental

conditions and were found to be 0.89 and 0.37 $\mu\text{g L}^{-1}$ for Pb(II) and Cd(II) ions, respectively. The relative standard deviation (RSD), specifying the precision of the method, was 3.2% and 2.4% for Pb(II) and Cd(II), respectively, by repeating the optimized method 10 times and using 50 mL of aqueous solution containing 20 μg of Pb(II) and 5 μg of Cd(II).

Method Accuracy and Application to Real Samples

The accuracy and applicability of the method was tested firstly by spiking different amounts of Pb(II) and Cd(II) in seawater and stream water as liquid samples (Table V), and black tea, Turkish coffee, and import coffee as solid samples (Table VI). Then the added and measured amounts of the analytes were compared with each other after applying the developed separation and preconcentration procedure. In most cases, the recovery values were quantitative, which indicated the usability of the method for both water and solid samples. The certified reference material CRM SA-C Sandy Soil C was also analyzed as another method for validation of the method (Table VII). The certified and measured values were compatible with each other. Finally, to ensure the accuracy of the method, we applied it to determine the Pb(II) and Cd(II) levels in some environmental real samples (Table VIII).

CONCLUSION

The cetyltrimethylammonium bromide (CTAB)-modified obsidian (CTAB-OB) sorbent was produced for the first time in the present study and used as an effective sorbent for the separation and preconcentration of Pb(II) and Cd(II) ions in some real samples by using the

solid phase extraction (SPE) method. The optimum experimental parameters determined included pH 8.0, eluent type, concentration and volume; 5.0 mL of 1.0 M HNO_3 , 500 mL sample volume; 5.0 g L^{-1} of CTAB-OB; and adsorption and desorption contact time of 15 minutes for the quantitative recovery of the analyte ions. It was found that the

TABLE IV
Influence of Some Foreign Ions on the Recoveries of Analyte Ions
(n=3, pH: 8.0, sample volume: 50 mL, CTAB-OB amount: 5.0 g L^{-1} ,
eluent type and volume: 5.0 mL of 1.0 M HNO_3 ,
adsorption and desorption contact time: 15 min)

Ions	Added	Conc. (mg L^{-1})	Recovery (%)	
			Pb(II)	Cd(II)
Na^+	NaCl	5000	97.6 \pm 0.3	93.3 \pm 1.8
K^+	KCl	1000	99.2 \pm 1.4	98.3 \pm 2.4
Ca^{2+}	CaCl_2	1000	96.6 \pm 2.1	96.8 \pm 2.9
Mg^{2+}	$\text{Mg}(\text{NO}_3)_2$	1000	97.4 \pm 0.6	102.6 \pm 1.1
CO_3^{2-}	Na_2CO_3	1000	91.9 \pm 3.8	96.1 \pm 4.2
NO_3^-	NaNO_3	1000	98.5 \pm 1.5	104.0 \pm 0.8
PO_4^{3-}	Na_3PO_4	1000	97.0 \pm 0.9	96.7 \pm 2.4
NH_4^+	NH_4NO_3	250	93.9 \pm 1.7	94.9 \pm 0.8
F^-	NaF	250	94.3 \pm 2.9	94.7 \pm 1.8
Al(III), Cu(II), Fe(III), Zn(II), Ni(II), Cr(III), Co(II)	^a	25	99.4 \pm 0.6	99.8 \pm 3.2
Mixed ^b			94.8 \pm 0.8	95.1 \pm 2.7

^a Added as their nitrate salts.

^b 5770 mg L^{-1} Na^+ , 8389 mg L^{-1} Cl^- , 2621 mg L^{-1} NO_3^- , 250 mg L^{-1} K^+ , Ca^{2+} , Mg^{2+} , CO_3^{2-} , PO_4^{3-} , NH_4^+ , F^- , 10 mg L^{-1} Al(III), Cu(II), Fe(III), Zn(II), Ni(II), Cr(III), Co(II).

TABLE V
Spiked Recoveries of Analyte Ions From Water Samples
(n=3, pH: 8.0, sample volume: 50 mL,
eluent type and volume: 5.0 mL of 1.0 M HNO_3)

Element	Added (μg)	Stream Water		Seawater	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Pb(II)	0	ND ^a	-	ND ^a	-
	16.0	15.75 \pm 0.35	98.4	15.25 \pm 0.21	95.3
	32.0	30.55 \pm 0.92	95.5	32.85 \pm 1.34	102.6
Cd(II)	0	ND ^a	-	ND ^a	-
	2.0	1.84 \pm 0.08	92.0	1.91 \pm 0.03	95.5
	4.0	3.87 \pm 0.17	96.8	3.76 \pm 0.08	94.0

^aNot detected.

common foreign ions, which may be present in the samples together with the analyte ions, have no significant interfering effects on the recovery values. In addition to the advantages such as simplicity, rapidity and lower operating cost, the method has a very high preconcentration factor with low detection limits and relative standard deviations, thus providing the opportunity to detect lower levels of analyte ions in most of the samples with high sensitivity and accuracy.

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TABLE VI
Spiked Recoveries of Analyte Ions From Solid Samples
(n=3, pH: 8.0, sample volume: 50 mL, sample quantities: 0.750 g)

Element	Added (μg)	Black Tea		Turkish Coffee		Import Coffee	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Pb(II)	-	ND	-	0.49 ± 0.02	-	0.38 ± 0.02	-
	16.0	14.75 ± 0.78	92.2	16.05 ± 0.21	97.2	15.22 ± 0.57	92.8
	32.0	30.85 ± 1.06	96.4	30.90 ± 0.71	95.0	30.80 ± 0.99	95.1
Cd(II)	-	ND	-	ND	-	ND	-
	2.0	1.83 ± 0.06	91.5	1.89 ± 0.04	94.5	1.92 ± 0.06	96.0
	4.0	3.79 ± 0.04	94.8	3.70 ± 0.07	92.5	3.91 ± 0.05	97.8

ND = not determined.

TABLE VII
Application of Present Method to Certified Reference Materials (CRM-SA-C Sandy Soil amount: 0.100 g)

Pb(II)		Cd(II)	
Certified Value ($\mu\text{g g}^{-1}$)	Found Value ($\mu\text{g g}^{-1}$)	Certified Value ($\mu\text{g g}^{-1}$)	Found Value ($\mu\text{g g}^{-1}$)
120 ± 8	113 ± 5	109 ± 8	106 ± 3

TABLE VIII
Application to Real Samples
(Black Tea, Turkish and Import Coffee amount: 0.750 g,
Sea and Stream Water volume: 500 mL, Final Volume: 5.0 mL)

Element	Liquid Samples		Black Tea ($\mu\text{g g}^{-1}$)	Solid Samples Turkish Coffee ($\mu\text{g g}^{-1}$)	Import Coffee ($\mu\text{g g}^{-1}$)
	Seawater ($\mu\text{g L}^{-1}$)	Stream Water ($\mu\text{g L}^{-1}$)			
Pb(II)	4.01 ± 0.09	14.4 ± 0.35	ND	0.65 ± 0.03	0.51 ± 0.02
Cd(II)	3.14 ± 0.02	5.42 ± 0.11	ND	ND	ND

ND = not determined.

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