Simultaneous Preconcentration of Cd(II) and Pb(II) with N,N′-bis(4-methoxysalicylidene) Ethylenediamine Coated Silica Gel Prior to Determination by Flame Atomic Absorption Spectrometry

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Abstract In this paper, a silica gel-based new sorbent was prepared with a Schiff base, called as N,N′-bis(4-methoxysalicylidene) ethylenediamine (MSE). The modified silica gel (Si-MSE) was used for simultaneous separation and preconcentration of Cd(II) and Pb(II) from aqueous solutions. Determination of analyte concentrations in eluates were achieved by flame atomic absorption spectrometry (FAAS). The analytical variables including pH, flow rate, and sample volume for sorption and flow rate, eluent concentration, and eluent volume for elution, were optimized by central composite design (CCD). HNO_3 was used as eluent and maximum preconcentration factor was found to be 200. Limit of detections (LODs) were found to be 49.6 ng L^{-1} and 1.3 µg L^{-1} for Cd(II) and Pb(II), respectively. Validation of the developed method was performed by using certified reference material (TMDA-53.3) and mixed metal standard. The methodology was applied for determination of Cd(II) and Pb(II) in natural water samples and satisfactory results were obtained.

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1 Introduction

Industrial effluents and wastewater disposal raises natural water pollution. Determination of trace metal levels in natural waters is very important due to contamination monitoring. Beside environmental pollution, Pb(II) and Cd(II) heavy metals affect living organisms owing to their cumulative toxicity. Long-term exposure to these metals can cause serious health problems such as damage in organs, especially in liver and kidneys; anemia; and cancer (Eklund et al. 2003; Lara et al. 2001; Yebra et al. 2002; Li et al. 2005; Tian et al. 2011). Therefore, accurate and sensitive methods for determination of Cd(II) and Pb(II) are required. Flame atomic absorption spectrometry (FAAS) is preferred for metal analysis depending on easy operation, selectivity, and cheapness. On the other hand, low sensitivity is the main problem for direct determination of metal concentrations at ppb level. In order to overcome this limitation, preconcentration techniques are frequently used (Ozcelik et al. 2012; Sabermahani et al. 2013; Shemirani et al. 2004). According to the reports, inorganics were preconcentrated/separated by various techniques such as liquid-liquid extraction (Baran and Yaşar 2010; Soylak and Yilmaz 2011), precipitation (Yuan-Zhen et al. 2012; Komjarova and Blust 2006), cloud point extraction (Silva et al. 2009), and solid-phase extraction (SPE) (Sabermahani et al. 2013; Shemirani et al. 2004) prior to FAAS determination.

Solid-phase extraction of trace metals is preferred to other preconcentration techniques according to

simplicity and minimal waste of organic solvent generation. Moreover, high preconcentration factor can be obtained at optimal conditions and the technique is able to combine with analytical instruments. Organic- and inorganic-based solid-phase materials such as XAD-2 and XAD-4 resins (Guo et al. 2004), polyurethane foam (Ferreira et al. 2003), alumina (Ahmed 2008), magnesia (Yu et al. 2006), zirconia (Li et al. 2012), and silica gel (Ozcelik et al. 2012; Sabermahani et al. 2013; Shemirani et al. 2004) have been widely used for separation and preconcentration. Besides thermal, chemical, and mechanical stability, and cheapness of silica gel, increases the usage as solid support, as compared to other organic and inorganic solid materials. The presence of silanol groups allows modification of silica surface with selective chelating agents such as N-(2-aminoethyl)-salicylaldimine (Ozcelik et al. 2012), N,N′-bis-(α-methylsalicylidene)-2,2-dimethyl-1,3-propanediamine (Bartyzel and Cukrowska 2011), and N,N′-bis(salicylidene) phenylene-1,3-diamine (Shemirani et al. 2004). Experimental conditions of SPE procedures are optimized by various chemometric techniques that are widely used. Beside rapidity, practicality, and economical benefits, optimization procedures make it possible to understand interactions between the factors that influence the analytical response, consequently recoveries (Zarei and Shemirani 2012; Shah et al. 2013; Ferreira et al. 2002; Lemos et al. 2009).

In the present work, silica gel was employed for production of a new solid phase. Schiff base, shown in Fig. 1 and named N,N′-bis(4-methoxysalicylidene) ethylenediamine (MSE) was used for modification of silica gel. The synthesized and characterized new sorbent (Si-MSE) was utilized for preconcentration of Cd(II) and Pb(II) from natural water samples. Determination of metal concentrations was achieved by FAAS after preconcentration procedure. The experimental conditions were optimized by central composite design (CCD).
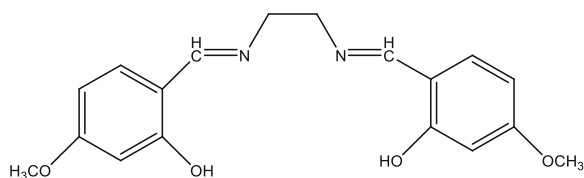
2 Experimental

2.1 Reagents and Chemicals

The analytical-grade deionized water was obtained by reverse osmosis system. All containers and glassware were kept overnight in 10 % nitric acid and rinsed three times with water prior to use. One thousand milligrams per liter stock metal standard solutions were prepared from $Cd(NO_3)_2.4H_2O$ and $Pb(NO_3)_2$ (Merck) and diluted as required to the micrograms per liter levels. In interference study, cations were added as nitrates and the anions were added as sodium salts. Silica gel (70–230 mesh) was purchased from Merck. N,N′-bis(4-methoxysalicylidene) ethylenediamine (MSE) was synthesized by condensation reaction of 4-methoxysalicylidene and diamino ethane (Merck). Feasibility of the suggested method was tested with Lake Ontario water certified reference material (TMDA-53.3, lot 0310) and multi element standard solution (1.11355, Merck).

2.2 Apparatus

A Philips X Pert-Pro diffractometer (Cu Kα $\lambda=$ 1.54060 A°, 30 mA, 40 kV), and PerkinElmer Spectrum 65 FTIR-ATR spectrometer were used to confirm the synthesized Si-MSE. Modification period of silica gel was monitored by PG Instrument T80+ UV–Vis spectrometer. Determination of metals in solutions was carried out by PerkinElmer AAnalyst 200 FAAS equipped with deuterium background correction. All measurements were performed in an air/acetylene flame. GFL 3005 orbital shaker having speed and time control was used for preparation of the sorbent. During the solid-phase extraction experiments, VELP Scientifica SP311 peristaltic pump with Tygon tubes was used. A Thermo Orion 5 Star model pH meter, Heidolph MR 3001K model magnetic stirrer, Sartorius TE214S electronic balance, and Eppendorf Research micro pipettes were used for the present work. Funnel-tipped glass tube (10×100 mm) equipped with stopcock was used as a column for the preconcentration experiments.

2.3 Preparation of Solid Phase

The commercially available silica gel was activated by refluxing with 0.5 mol L^{-1} HNO$_3$ for 1 h to remove any

Fig. 1 Scheme of [N,N′-bis(4-methoxysalicylidene)-ethylenediamine]

adsorbed metal ions. Then, it was filtered and washed with deionized water until the filtrate was neutral.

In order to synthesize physically bonded Si-MSE, 10.0 g of silica gel was added to 50.0 mL acetone containing 50 mg MSE and refluxed for 1 h. The product was filtered off and washed with deionized water and dried at room temperature.

2.4 General Enrichment Procedure

First, 1.0 g of Si-MSE was filled in the column and the effective factors on the preconcentration including pH, flow rate, and selection of eluent type, were investigated using 50-mL model solutions containing 5 μg Cd(II) and 10 μg Pb(II). Determination of metal ions in 5-mL eluates was achieved by FAAS. According to the precipitation of the metal hydroxides at alkaline environment, pH effect was evaluated within the range of 3.00–7.00. Experiments of flow rate for sorption and elution were performed at 3–20 mL min^{-1}. In order to choose a proper eluent for desorbing Cd(II) and Pb(II) from the Si-MSE surface, different mineral and organic acids were tested.

The proposed analytical procedure for Cd(II) and Pb(II) preconcentration was optimized using three-level full factorial CCD. The optimization procedure was performed separately for sorption and elution steps. Three variables; pH, sample volume, flow rate and eluent volume, eluent concentration, flow rate were regarded as factors for sorption and for elution, respectively. Based on the experimental data, simultaneous preconcentration of certain ions were carried at given conditions for sorption: pH = 5.2, flow rate = 4.0 mL min^{-1}, and sample volume = 50 mL, and for elution: flow rate = 4.0 mL min^{-1}, concentration of HNO$_3$ = 0.5 mol L^{-1}, and volume of eluent = 4.8 mL.

3 Results and Discussion

3.1 Modification and Characterization of Sorbent

Modification period of the solid-phase surface is a critical step in SPE procedures. Accordingly, during mechanical shaking of MSE solution and activated silica gel, 1–2 mL proportion was taken from the liquid phase and the absorbance was measured at 328 nm. This wavelength is specific for MSE in order to obtain maximum absorbance and the absorbance of the solution

was monitored with 1-h intervals for 6 h. The time-dependent changes in absorbance, shown in Fig. 2, indicate that 1 h is sufficient for modification of silica gel with MSE.

The modification of silica gel was confirmed by Fourier transform infra red (FTIR) and x-ray diffraction (XRD) analyses. In the comparison of the IR spectrum of bare silica gel with modified silica gel, new peaks were monitored and shown in Fig. 3. The silica gel showing the characteristic peak at 805 cm^{-1} is ascribed to the Si–O–Si bending vibration and at 1031 cm^{-1} Si–O stretching vibration. The IR spectrum of the modified silica gel has some different peaks that corresponding to ligand at 2932 and 2988 cm^{-1} (C–H) and 1667 cm^{-1} (C=N).

According to the literature data about XRD analysis, silica gel and its functionalized derivatives appeared at 24 °, which is the amorphous diffraction peak of silica gel. Also, it is reported that organic moieties decrease the intensity of the diffraction peak (Qu et al. 2008). The spectra of Si-MSE and silica gel obtained from XRD analyses depicted in Fig. 4 are in agreement with literature. According to experimental results, silica gel is successfully modified with MSE.

3.2 Effect of pH

The pH of the sample solution plays an important role in retention of metals on sorbent. The pH of the model solutions containing 5 μg Cd(II) and 10 μg Pb(II) were adjusted to certain value using diluted HNO$_3$ and NaOH. As shown in Fig. 5, the recovery results were not dramatically affected by the change in pH between 4.00 and 7.00 for Cd(II) and Pb(II). Accordingly, center value of pH was chosen as 5.00 for both of analytes for the optimization procedure.
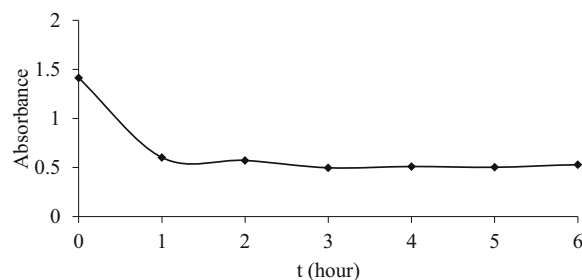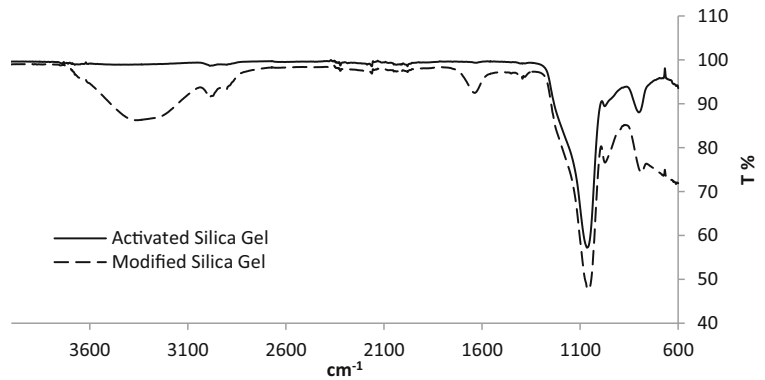

Fig. 2 Time-dependent changes in MSE absorbance (at 278 nm)

Fig. 3 FTIR spectra of bare and modified silica gel

3.3 Selection of Desorption Reagent

For desorption of Cd(II) and Pb(II) from Si-MSE, 0.5 mol L^{-1} of HNO_3, HCl, CH_3COOH, H_2SO_4, and H_2O_2 were tested. Except for HNO_3 elution experiments, the recovery percentages were varied between 5.7 and 87.9 % and 1.3 and 104.1 % for Cd(II) and Pb(II), respectively. The recovery percentages of HNO_3 elution experiments were 94.2±1.5 % for Cd(II) and 104.2±1.4 for Pb(II). It was observed that HNO_3 is the best eluent for Cd(II) and Pb(II) and suitable for simultaneous desorption of certain metal ions.

3.4 Effect of Flow Rate on Sorption and Elution

The retention of a metal ion on the sorbent also depends on the flow rate of the sample solution. Thus, the effect of flow rate on sorption and desorption of Cd(II) and Pb(II) ions were investigated between 3 and 20 mL min^{-1}. Results showed that sorption of Cd(II)

and Pb(II) ions are not quantitatively (>95 %) affected by flow rate up to 10.0 and 6.0 mL min^{-1}, respectively. Increased flow rate, decreases the retention times and sorption percentages of ions. Similarly, quantitative recoveries could be obtained with elution flow rate up to 8.0 mL min^{-1} for Cd(II) and 5.0 mL min^{-1} for Pb(II). In order to avoid an abrupt change in adsorption and increase the contact time of the sample solution with the sorbent, center value of flow rate was selected as 4 mL min^{-1} for optimization of sorption and elution steps.

3.5 Effect of Sample Volume

The preconcentration studies were applied to solutions within the range of 25.0–1000.0 mL and the possibility of enriching at low concentration with high enrichment factor was explored. Model solutions, containing 5 μg amount of Cd(II) and 10 μg Pb(II) were separately passed through the Si-MSE filled column. After eluting with suitable eluent, metal concentrations were deter-
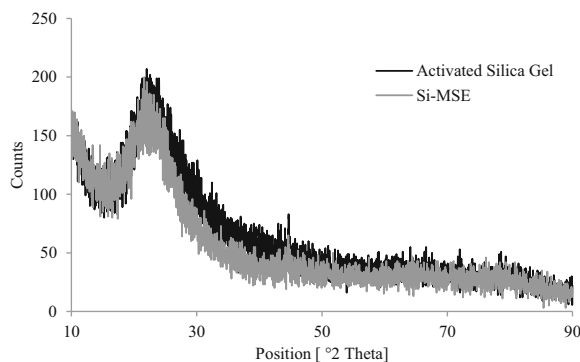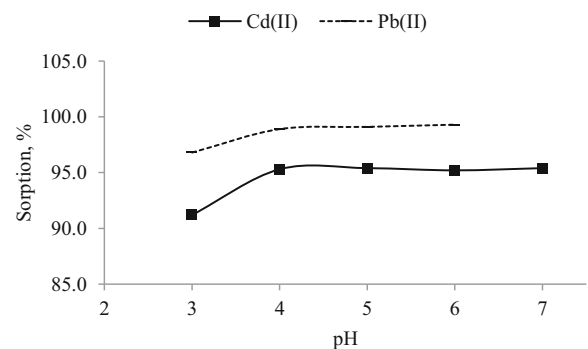

Fig. 4 XRD spectra of bare and modified silica gel

Fig. 5 Effect of pH on preconcentration of Cd(II) and Pb(II)

Table 1 Levels and the real values of factors utilized in CCD

	Sorption						Elution					
	Factors	Levels					Factors	Levels				
		$-\alpha$	-1	0	$+1$	$+\alpha$		$-\alpha$	-1	0	$+1$	$+\alpha$
Cd(II), Pb(II)	pH	3.3	4.0	5.0	6.0	6.7	F	2.3	3	4	5	5.7
	F	2.3	3.0	4.0	5.0	5.7	C_E	0.08	0.25	0.50	0.75	0.92
	V_S	8.0	25.0	50.0	75.0	92.0	V_E	3.3	4	5	6	6.7

F flow rate (mL min^{-1}), V_S sample volume (mL), C_E eluent concentration (mol L^{-1}), V_E eluent volume (mL)

mined with FAAS. The recovery value was obtained as 98.7 % at 1000 mL sample volume by analyzing 5-mL eluate and the highest preconcentration factor was found to be 200 for Cd(II). Similarly, preconcentration of Pb(II) was quantitatively achieved up to 1000.0 mL with 98.7 % recovery and the preconcentration factor was calculated as 200. It was seen that, without damaging the structure of Si-MSE, enrichment process could be able to apply in a wide range of sample volumes. In optimization procedure, sample volume was considered as a factor and 50.0 mL was chosen as center value for both of metal ions.

Table 2 Experiments and recovery values for the sorption and elution of Cd(II) and Pb(II)

Run	Cd(II)				Pb(II)			
	Sorption		Elution		Sorption		Elution	
	Rec. %	y	Rec. %	y	Rec. %	y	Rec. %	y
1	99.91	11.636	100.56	1.786	96.19	0.265	94.57	0.184
2	104.58	0.218	95.60	0.227	53.51	0.022	85.81	0.070
3	112.41	0.081	105.68	0.176	94.70	0.189	90.35	0.104
4	82.40	0.057	96.88	0.320	27.98	0.014	93.57	0.156
5	113.56	0.074	107.40	0.135	100.13	7.760	101.06	0.942
6	13.10	0.012	108.36	0.120	58.30	0.024	100.08	12.225
7	113.47	0.074	104.28	0.234	33.10	0.015	102.90	0.3442
8	99.30	1.420	100.80	1.250	68.87	0.032	103.05	0.328
9	100.62	1.623	99.60	2.500	105.32	0.188	105.14	0.195
10	81.40	0.054	98.80	0.833	12.78	0.012	94.91	0.197
11	72.30	0.036	95.90	0.244	43.90	0.018	100.47	2.218
12	96.00	0.250	105.50	0.182	109.76	0.102	96.27	0.268
13	81.91	0.055	102.30	0.435	97.68	0.431	106.85	0.146
14	99.56	2.272	54.78	0.022	103.93	0.254	106.46	0.155
15	96.83	0.316	108.35	0.120	90.98	0.111	102.31	0.432
16	111.44	0.087	95.60	0.227	95.17	0.207	97.28	0.368
17	103.61	0.277	96.90	0.323	107.14	0.140	99.56	2.260
18	113.12	0.076	102.50	0.400	103.75	0.267	98.42	0.633
19	105.37	0.186	100.80	1.250	98.84	0.862	96.16	0.260
20	100.97	1.033	98.80	0.833	101.75	0.573	105.44	0.184

3.6 Optimization of Variables

Optimization of the preliminary studies was achieved by a three-level full factorial CCD with 20 runs. Table 1 lists the maximum, minimum, and center values of the variables for sorption and elution. The metal concentration in solutions was determined with external standard calibration method by FAAS. The results including recovery percentages and responses for sorption and elution are given in Table 2. The obtained experimental data were applied in the CCD and the quadratic equations (Eqs. (1) and (2)) show the relationship of pH (pH), retention flow rate (F), and sample volume (V_S) for sorption of Cd(II) and Pb(II), respectively. Also, Eqs. (3) and (4) show the relationship between flow rate (F), concentration (C_E), and volume (V_E) of eluting solution for desorption of Cd(II) and Pb(II), respectively.

$$y = 0.512149 - 0.72568(\text{pH}) - 0.70171(F) - 0.98307(V_s) \quad (1)$$
$$+ 0.51656(\text{pH})^2 + 0.171216(F)^2 + 0.493081(V_s)^2$$
$$+ 1.565725(\text{pH})(F) + 1.556098(\text{pH})(V_s)$$
$$+ 1.606256(F)(V_s)$$

$$y = 0.343881 - 0.59481(pH) - 0.53199(F)$$
$$+ 0.520031(V_s) + 0.0628896(\text{pH})^2$$
$$+ 0.151948(F)^2 + 0.122292(V_s)^2$$
$$+ 0.977413(\text{pH})(F) - 0.91287(\text{pH})(V_s) \quad (2)$$
$$- 0.95694(F)(V_s)$$

$$y = 0.683354 + 0.018073(F) + 1.220284(C_E) \quad (3)$$
$$+ 0.130563(V_E) - 0.57667(F)^2 + 1.235323(C_E)^2$$
$$- 0.33237(V_E)^2 + 0.071216(F)(C_E)$$
$$- 0.06881(F)(V_E) - 0.07954(C_E)(V_E)$$

$$y = 0.6098 + 1.058149(F) - 0.92959(C_E) + 1.009865(V_E) \quad (4)$$
$$+ 0.44385(F)^2 + 0.10629(C_E)^2 + 0.136802(V_E)^2$$
$$- 1.39162(F)(C_E) + 1.41604(F)(V_E)$$
$$- 1.562426(C_E)(V_E)$$

Table 3 Optimum preconcentration conditions for metal ions

		Cd(II)	Pb(II)
Sorption	pH	5.2	5.4
	F (mL min^{-1})	4.3	4.0
	V_S (mL)	55.0	35.1
Elution	F (mL min^{-1})	4.0	3.6
	C_E (mol L^{-1})	0.4	0.6
	V_E (mL)	4.8	4.8

pH, F, and V_S, and F, C_E, and V_E represents the first, second, and third factors for sorption and elution, respectively. Derivatives of the equations were equalized to zero and solved using Microsoft® Excel. The real values presented in Table 3 were obtained by CCD and used as optimal conditions for further experiments.

As can be seen in Table 3, the optimum values in pH and flow rate for both metals are so close. As mentioned before, the sample volume has no dramatic effect on sorption efficiencies between the range of 25.0 and 1000.0 mL. Therefore, Cd(II) and Pb(II) preconcentration experiments can be performed in the same conditions. The sorption of Cd(II) and Pb(II) were done together at following conditions: pH=5.2, flow

Table 4 Tolerance limits of matrix ions on the recovery of Cd(II) and Pb(II)

Interfering ions	Interfering ion/analyte (w/w)	
	Cd(II)	Pb(II)
Mn^{2+}	750	250
Fe^{3+}	750	50
Zn^{2+}	2000	250
Pb^{2+}	2000	–
Cd^{2+}	–	125
K^+, Cl^-	1000	500
Ca^{2+}	2500	375
Na^+	3000	500
SO_4^{2-}	5000	500
NO_3^-	10,000	500
Mg^{2+}	2500	250
Ni^{2+}	2500	250
Co^{2+}	2500	250
Cu^{2+}	2500	125
Cr^{3+}	2500	50

Table 5 Analysis of standard reference material

		Certified Value (μg L^{-1})	Found value (μg L^{-1})	Recovery (%)
CRM	Cd(II)	118.0±4.6	115.9±11.7	98.2
(TMDA-53.3)	Pb(II)	349.2±18.1	356.7±13.2	102.2
Multi element	Cd(II)	100.0±1.0	96.5±2.2	96.5
standard	Pb(II)	100.0±1.0	103.5±3.0	103.5

rate 4.0 mL min^{-1}, and sample volume 50.0 mL. In a similar approach, the simultaneous elution was done in these conditions: flow rate 4.0 mL min^{-1}, concentration of HNO$_3$ 0.5 mol L^{-1}, and volume of eluent 4.8 mL.

3.7 Interference Effects

The preconcentration procedures of trace metal ions can be strongly affected by other ions. The effects of matrix ions such as SO_4^{2-}, Cl^-, NO_3^-, Na^+, Ca^{2+}, Mg^{2+}, K^+, Fe^{3+}, Mn^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Cu^{2+} on preconcentration and on the selectivity of the developed method were investigated under optimal conditions. Model solutions, which includes 100 μg L^{-1} Cd(II) and 2 mg L^{-1} Pb(II) and different amounts of other ions were prepared and the suggested SPE procedure was applied. The tolerance limits were given in Table 4 and are defined as the interfering ion concentration causing a relative error smaller than ±5 % related to the preconcentration of analytes. The experiments indicated

that no further sample treatment or masking reagents are needed for preconcentration of Cd(II) and Pb(II).

3.8 Analytical Figures of Merit

The accuracy (recovery, %) and precision (RSD, %) of the proposed solid-phase extraction procedure under optimal conditions were investigated ($n=10$) as 102.0 ±4.0 and 3.9 % for Cd(II) and as 98.0±2.0 and 2.0 % for Pb(II), respectively. Limit of detection (LOD) was obtained by using a criterion signal-to-noise ratio of 3. LODs were calculated as 49.6 ng L^{-1} for Cd(II) and 1.3 μg L^{-1} for Pb(II).

3.9 Validation and Application of the Improved Method

The developed procedure was validated by Cd (II) and Pb(II) determination in certified reference material. The results given in Table 5 show good agreement with the certified values. The obtained recovery percentages were acceptable and it shows that the presented method can be applied for the preconcentration of Cd(II) and Pb(II) in natural water samples.

3.10 Real Sample Analysis

Applicability of the optimized preconcentration procedure was tested with various water samples such as tap water, Selimiye lake water, mineral water, snow water, and bottled drinking water. The suitability of the method was checked by spike recovery tests. The mean recovery

Table 6 Real sample analysis ($n=3$)

	Cd(II)			Pb(II)		
Sample	Spiked (μg L^{-1})	Found (μg L^{-1})	Recovery %	Spiked (μg L^{-1})	Found (μg L^{-1})	Recovery %
Tap water	–	ND	–	–	ND	–
	100.0	101.8±8.2	101.8	200.0	193.8±6.4	96.9
Selimiye Lake water	–	ND	–	–	ND	–
	100.0	103.0±4.6	103.0	200.0	197.6±4.2	98.8
Mineral water	–	ND	–	–	ND	–
	100.0	90.80±5.4	90.8	200.0	193.2±3.0	96.6
Snow water	–	ND	–	–	ND	–
	100.0	92.4±3.6	92.4	200.0	196.2±8.8	98.1
Bottled drinking water	–	ND	–	–	ND	–
	100.0	94.8±3.6	94.8	200.0	181.0±2.8	90.5

results for each sample are summarized in Table 6. The recovery percentages of the method were between 90.8 and 103.0 % for Cd(II) and 90.5 and 98.8 % for Pb(II). Taking into consideration these results, the improved method was suggested as practical, accurate, precise, effective, simple, and cheap determination method for Cd(II) and Pb(II) in natural water samples.

4 Conclusion

In the present study, a new silica gel-based sorbent has been reported. The work presented offers a useful and efficient simultaneous separation and preconcentration for Cd(II) and Pb(II) in various water samples. The modified silica gel was prepared easily and sorbed Cd(II) and Pb(II) rapidly. The optimized parameters are pH=5.2, flow rate 4.0 mL min^{-1}, and sample volume 50 mL for sorption and flow rate 4 mL min^{-1}, eluent concentration 0.5 mol L^{-1}, and eluent volume 4.8 mL in elution for simultaneous procedure. Preconcentration factor was found to be 200 for both metal ions. The mean recovery values for spiked water samples were acceptable and confirmed the validity of the method. Modified sorbent can be used for one cycle, but silica gel can be reused plenty of times and be modified again with MSE in a short period. Finally, the proposed method can be suggested as a simple, sensitive, accurate, and repeatable method for simultaneous preconcentration and determination of Cd(II) and Pb(II).

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