Solid-phase extraction method for preconcentration of cadmium and lead in environmental samples using multiwalled carbon nanotubes

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Abstract: A new sensitive and accurate solid-phase extraction method for preconcentration of trace amounts of cadmium and lead in various environmental samples prior to flame atomic absorption spectrometry determination has been developed. The proposed method is based on the utilization of multiwalled carbon nanotubes in combination with 5-benzyl-4-[-chlororbenzylidene amine]-4H-1,2,4-triazole-3-thiol (BCBATT) as a solid-phase sorbent with the aid of ultrasonication. The effect of the preconcentration parameters was investigated. Good recoveries ranging from 95% to 102% with relative standard deviations of 3.2% and 2.8% for Cd^{2+} and Pb^{2+}, respectively, were obtained, indicating high accuracy and precision. The limits of detection were 0.2 and 0.5 $\mu g/L$ for Cd^{2+} and Pb^{2+}, respectively. The preconcentration factor was 100. The validation of the proposed preconcentration procedure was performed using certified reference materials with satisfactory and compatible results. The proposed method was applied to various real environmental samples for determination of Cd^{2+} and Pb^{2+} concentrations and satisfactory results were obtained.

Key words: Solid-phase extraction, multiwalled carbon nanotubes, cadmium, lead, food and water samples

1. Introduction

In environmental samples, heavy metals are considered to be hazardous materials due to their toxicity for animals and humans even at low concentration levels.[1] Trace levels of cadmium and lead metals have acute and chronic effects on humans and other living organisms when accumulated in various tissues and can cause harmful gastrointestinal, cardiovascular, hematological, renal, kidney, and reproductive effects. Therefore, the determination of trace levels of Cd^{2+} and Pb^{2+} ions as important heavy metals in environmental samples is a very significant goal for chemists working in the fields of analytical chemistry and environmental analytical chemistry.[2−4] Flame atomic absorption spectrometry (FAAS) has been widely used for estimation of heavy metals in environmental samples.[5,6] However, trace quantities of analytes lower than the limit of detection of FAAS and the coexisting ions' interference are two limitations in FAAS estimations. A separation/enrichment step is necessary prior to the measurements to resolve these limitations by increasing the sensitivity and enhancing the accuracy of estimation.[5]

Recently, the development of various methods for the separation and enrichment of trace levels of Cd^{2+} and Pb^{2+} was reported in the literature, such as solid-phase,[7−9] dispersive liquid-liquid,[10−13] and single-drop[14−16] microextractions and cloud point[17−19] extraction and coprecipitation.[20−23]

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Solid-phase extraction (SPE) is an important and widespread method for the separation and preconcentration of trace quantities of metal ions in environmental samples with complex matrices because of its notable advantages, such as speed, simplicity, low cost, reusability of the adsorbent, and environmentally friendly and high enrichment factors. In SPE, the sorbent choice is very important for obtaining high enrichment factors and good recovery values and for increasing the precision and accuracy of the SPE method.[24] Because it follows the principles of green chemistry, the use of the SPE technique without and with ultrasound assistance for separation and enrichment of heavy metals has recently attracted much attention.[25]

Since their discovery in 1991, due to their large surface area; excellent mechanical, electrical, chemical, thermal, or conducting properties; low density; and high adsorption capacity, carbon nanotubes have attracted intense attention as novel sorbents for the separation and preconcentration of several types of species and compounds in trace quantities.[26,27]

The use of multiwalled carbon nanotubes (MWCNTs) as SPE sorbents to preconcentrate trace levels of metal ions is a relatively significant field of environmental analytical chemistry.[27,28] MWCNT surfaces may be filled with a number of ligands to promote adsorption capability and functionality, and a suitable chelating agent is generally necessary.[28−40] The elution of the analytes and the choice of the eluting solvent is the final stage of SPE for obtaining a significant enrichment factor and high recovery of adsorbed metal ions on MWCNTs.

Based on our survey of the literature, a newly synthesized Schiff base, 5-benzyl-4-[-chlororbenzylidene amine]-4H-1,2,4-triazole-3-thiol (BCBATT) was used as a chelating agent in combination with MWCNTs for the first time in this work as an effective sorbent for the separation and enrichment of trace quantities of Cd^{2+} and Pb^{2+} in various food and water samples. Characterization of the synthesized reagent was performed using FT-IR and ^{1}H-NMR. The elution of Cd^{2+} and Pb^{2+} ions complexed with BCBATT adsorbed on MWCNTs was assisted by sonication before the FAAS determination. The effects of different experimental variables on both analyte ions' recoveries were estimated quantitatively.

2. Results and discussion

2.1. Characteristic IR and ^{1}H-NMR spectra of BCBATT

The IR spectra v (cm^{-1}) of the BCBATT Schiff base showed bands at 3050 (C-H, aromatic), 2040 (C-H, aliphatic), and 1697 cm^{-1} (N=CH, azomethine group); a weak broadband at $\sim$2561 cm^{-1} due to (SH) vibrations; and bands at 1620–1454 (C=C, benzene ring) and 1492, 1273, 1085, and 110 (N-C=S, amide bands) (Figure 1a). The band of the azomethine group at 1697 cm^{-1} shifted toward the new band at lower frequencies of about 507–514 cm^{-1} due to m (M–N) coordination.[41] The SH band at $\sim$2561 cm^{-1} in the metal complexes' spectra disappeared due to complexation with sulfur after deprotonation. Two new bands at 749–752 cm^{-1} and 340–346 cm^{-1} appeared in the metal complex spectra due to m (C–S) and m (M–S), respectively. A broadband in the region of 3304–3310 cm^{-1} appeared due to the coordinated water molecules in the metal complexes (Table 1).

Figure 1b shows the ^{1}H NMR spectra of the BCBATT Schiff base. The BCBATT Schiff base showed a single peak at 10.05 ppm due to the azomethine proton (s, 1H, N=CH). The coordination of the azomethine nitrogen atoms of the ligands with metal ion shows the deshielding of the signal at 10.05 ppm in the metal complex spectra.[41] Additionally, the signal at 13.89 ppm was ascribed to the SH proton (s, 1H, SH). Due to the deprotonation of the SH group, its signal disappeared in the metal complex spectra. Due to the coordination, a
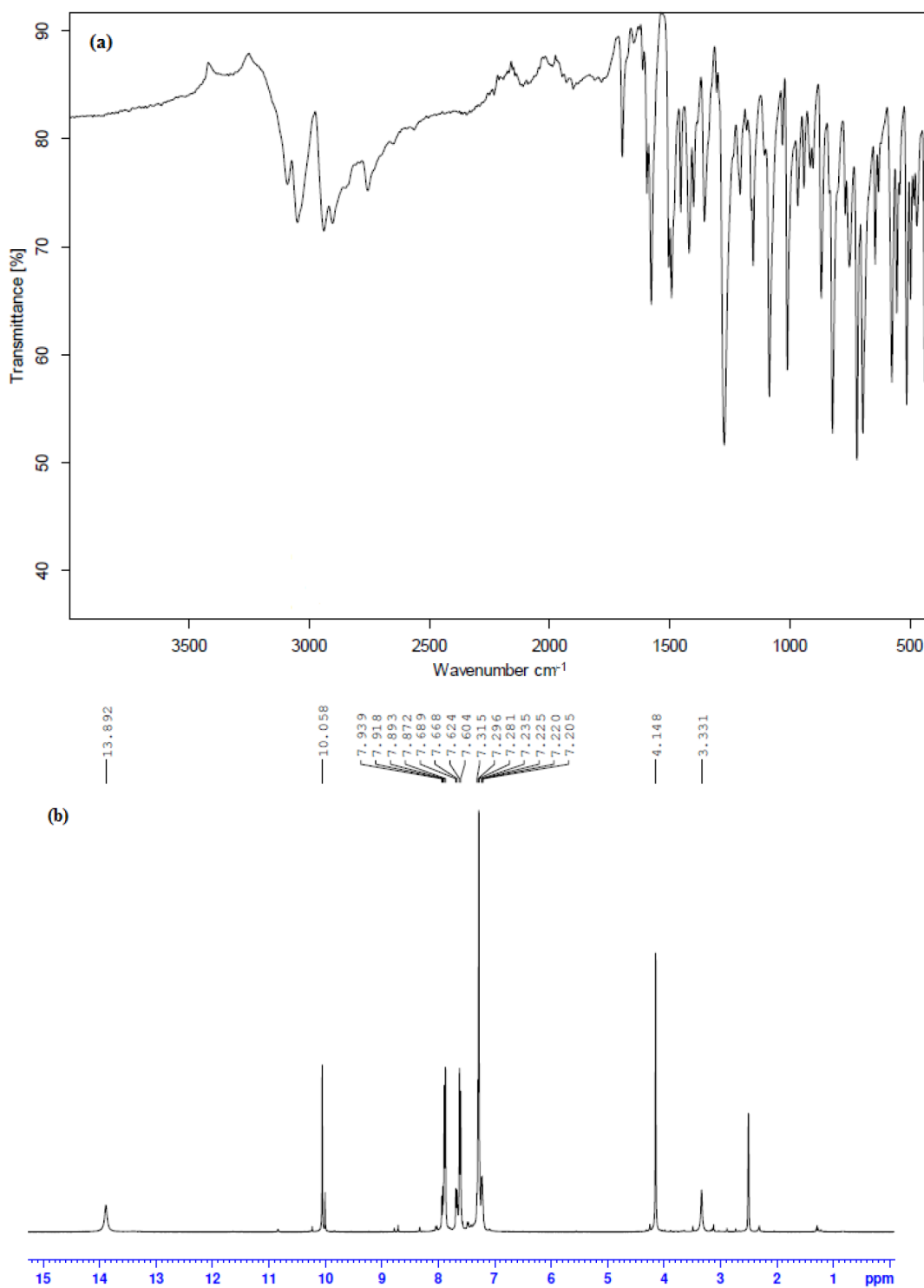
Figure 1. a) FT-IR and b) H-NMR spectra of BCBATT.

slight shift of the doublets of the aromatic protons was observed. In the BCBATT Schiff base spectrum, peaks at 7.20–7.31 (m, 5H, Ar-H), 7.62 (d, 2H, Ar-H), and 7.87 (d, 2H, Ar-H) and another band at 4.15 (s, 2H, CH_2) (Table 1) were observed.

Table 1. IR and ^{1}H-NMR spectral data of the BCBATT Schiff base and their metal complexes.

Compounds	BCBATT	Cd(BCBATT)$_2$.2H$_2$O	Pb(BCBATT)$_2$.2H$_2$O
IR			
υ (N=CH)	1697	1682	1672
υ (C-S)	-	752	749
υ (SH)	2561	-	-
υ (H$_2$O)	-	3304	3310
υ (M-S)	-	340	346
υ (M-N)	-	514	507
^{1}H-NMR (DMSO-d$_6$)δ (ppm)	4.15 (s, 2H, CH$_2$), 7.20–7.31 (m, 5H, Ar-H), 7.62 (d, 2H, Ar-H), 7.87 (d, 2H, Ar-H), 10.05 (s, 1H, N=CH), 13.89 (s, 1H, SH)	4.10 (s, 2H, CH$_2$), 7.10–7.40 (m, 5H, Ar-H), 7.60 (d, 2H, Ar-H), 7.90 (d, 2H, Ar-H), 10.15 (s, 1H, N=CH)	4.18 (s, 2H, CH$_2$), 7.15–7.36 (m, 5H, Ar-H), 7.60 (d, 2H, Ar-H), 7.80 (d, 2H, JAr-H), 10.20 (s, 1H, N=CH)

## 2.2. Optimization of analytical conditions

In the present work, the preconcentration of trace quantities of Cd^{2+} and Pb^{2+} ions after chelation with BCBATT using the MWCNT sorbent was developed. To achieve a high efficiency and recovery of both Cd^{2+} and Pb^{2+} ions, the following variables need to be optimized: pH; BCBATT amounts; sample volume; different elution conditions such as the eluent type, volume, and concentration; and the influence of temperature and sonication.
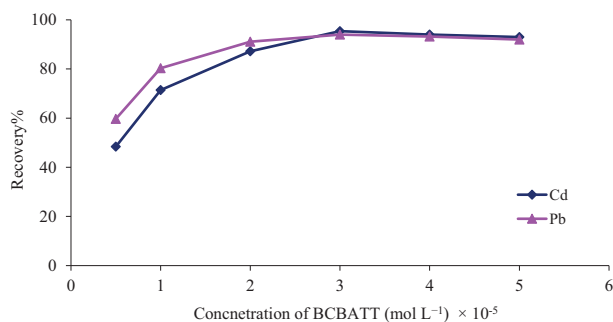
2.2.1. Influence of pH

The recovery of metal ions in the proposed SPE procedure is significantly influenced by the pH of the solution.[28−32] The hydrophobic complexes of BCBATT with Cd^{2+} and Pb^{2+} ions were formed and adsorbed on MWCNTs at a pH between 4.0 and 10. As illustrated in Figure 2, at pH 4.0–7.0, the adsorption of the Cd^{2+}– or Pb^{2+}–BCBATT complex increased and quantitative recoveries (>95%) were obtained, with the recoveries remaining constant at pH 7.0–8.0. At higher pH values (9.0–10), the recovery values were not quantitative because of the precipitation of hydroxide species.[30,31] Consequently, a pH of 7.0 was chosen as the optimal pH for the phosphate buffer solution in all subsequent studies.

2.2.2. Influence of the BCBATT concentration

The influence of the BCBATT concentration on the efficiency of SPE and the quantitative recovery was tested by varying the volume of BCBATT (1.0 × 10^{-3} mol/L) solution from 0.5 to 5.0 mL. As illustrated in Figure 3, high recoveries of Cd^{2+} and Pb^{2+} ions were achieved for the BCBATT volume of 3.0 mL (3.0 × 10^{-5} mol/L), which was sufficient for metal complexation and was found to be the most effective and optimal volume in the subsequent studies.
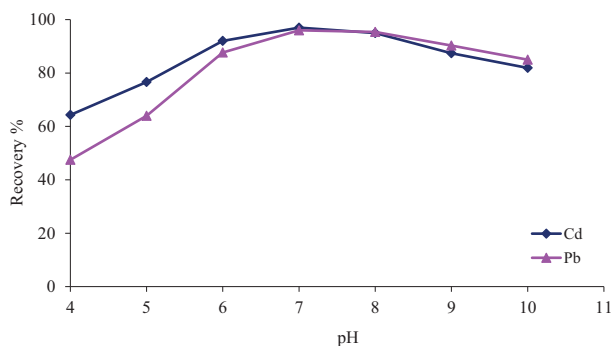
Figure 2. Influence of pH on adsorption of the Cd^{2+}–BCBATT and Pb^{2+}–BCBATT complexes on MWCNTs (N = 3).

Figure 3. Influence of the concentration of BCBATT reagent on the recovery of Cd^{2+} and Pb^{2+} (N = 3).
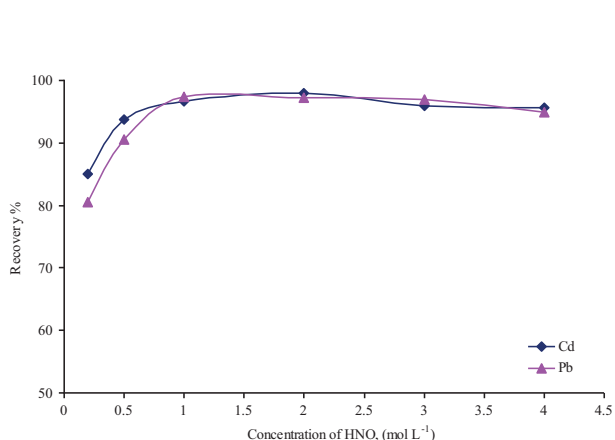
2.2.3. Effect of sample volume

To obtain high recoveries of both analytes, various volumes of the sample in the range from 50 to 300 mL containing 50 μg/L Cd^{2+} or Pb^{2+} were investigated using the proposed SPE procedure. Quantitative recoveries were achieved up to a volume of 200 mL. When using sample volumes greater than 200 mL, the recoveries of Cd^{2+} or Pb^{2+} were decreased. Therefore, 200 mL was the optimal sample volume. Hence, a preconcentration factor of 100 was achieved with 200 mL as the optimal sample volume for both metal ions and the final eluent volume of 2.0 mL.

2.2.4. Influence of eluent

The final stage of SPE is the elution of the metal ions. To obtain a significant enrichment factor and high recovery, different parameters such as type, concentration, and volume of eluting agents were optimized. First, the effect of using HCl, HNO_3, and CH_3COOH as different types of eluent was studied to choose the most selective eluent for the quantitative desorption of Cd^{2+} or Pb^{2+} ions from the solid phase. The results indicated that quantitative recovery values of >95% were achieved with HNO_3. The influence of HNO_3 concentration on the recoveries of both enriched ions was studied by using a variety of concentrations from 0.2 to 4.0 mol/L with the assistance of sonication for 2.0 min at temperatures of 25 °C and 50 °C. Examination of the results presented in Figure 4 shows that the recovery increases until 1.0 mol/L HNO_3 and remains unchanged from 1.0 to 4.0 mol/L HNO_3. Various volumes with the HNO_3 concentration of 2.0 mol/L were used to investigate the influence of the eluent volume with the assistance of sonication. The results indicate that quantitative elution and a significant enrichment factor of Cd^{2+}–BCBATT and Pb^{2+}–BCBATT complexes can be achieved using 2.0 mol/L HNO_3 (2.0 mL), which was thereafter chosen for all subsequent studies (Figure 5). In the proposed preconcentration procedure, the elution step was assisted by ultrasound for extracting the enriched Cd^{2+} or Pb^{2+} ions from MWCNTs at room temperature (25 °C) and to obtain higher quantitative recoveries of the studied analytes (Figure 6). A higher temperature (50 °C) during the elution step does not improve recovery.

2.2.5. Effect of flow rates of sample and eluent solutions

The effect of the sample and eluent solutions' flow rate on the recoveries of the analyte ions Cd^{2+} and Pb^{2+} were examined under the optimum conditions (pH and eluent type) in the range of 1.0–6.0 mL/min. The flow rate of the sample and eluent solutions had no obvious influence on the quantitative recoveries of analytes in

Figure 4. Influence of concentration of HNO_3 on elution of Cd^{2+} and Pb^{2+} (N = 3).
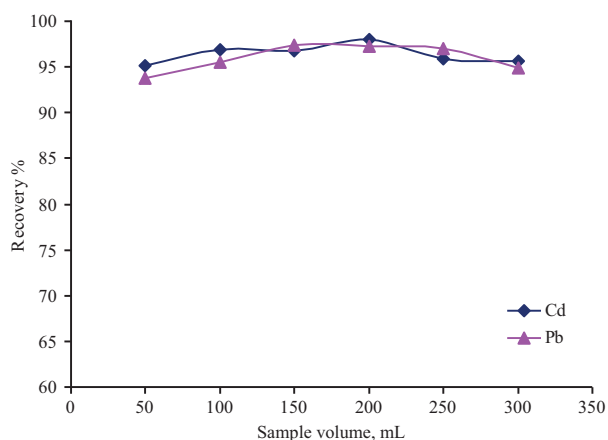
Figure 5. Effects of sample volume on the recoveries of Cd^{2+} and Pb^{2+} (N = 3).
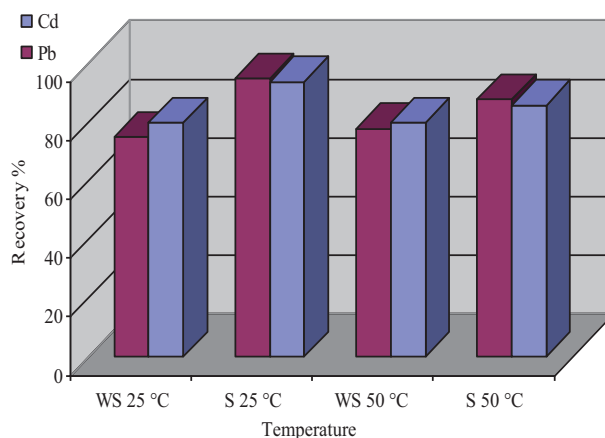
Figure 6. Influence of temperature and sonication on elution of Cd^{2+} and Pb^{2+} ions (S: sonication, WS: without sonication).

the range of 1.0–4.0 and 1.0–3.0 mL/min, respectively. Subsequently, 2.0 mL/min was selected as the flow rate for both sample and eluent solutions.

2.2.6. Influence of interference

The potential influences of the commonly coexisting matrix constituents present in various real environmental samples on the recoveries of Cd^{2+} and Pb^{2+} ions were studied, and the obtained results are provided in Table 2. The tolerance limit is defined as the highest quantity of interfering ions that could be present without creating a relative error higher than $\pm 5\%$ related to the preconcentration and determination of Cd^{2+} and Pb^{2+} ions. An advantage of this method was that the Cd^{2+} and Pb^{2+} ions recovered from the multielement real environmental samples were quantitative at the tolerance levels given in Table 2, and there was no obvious influence of matrix ions on the determination of Cd^{2+} and Pb^{2+} ions under the experimental conditions.

Table 2. Influence of coexisting matrix ions on the recovery of Cd^{2+} and Pb^{2+} ions using BCBATT-impregnated MWCNTs (N = 3; pH 7; eluent volume: 2 mL).

Ion	Added as	Concentration (mg L^{-1})	Recovery (%)^a	
			Cd(II)	Pb(II)
Na	NaCl	5000	95 ± 2	96 ± 2
K	KCl	7000	96 ± 3	97 ± 1
Ca	CaCl$_2$	3000	99 ± 2	103 ± 2
Mg	MgCl$_2$	3000	101 ± 3	95 ± 1
Al	Al(NO$_3$)$_3$.9H$_2$O	500	97 ± 1	98 ± 2
Fe	FeCl$_3$	500	96 ± 3	95 ± 2
Mn	MnSO$_4$. H$_2$O	400	98 ± 3	101 ± 2
Cr	Cr(NO$_3$)$_3$.9H$_2$O	300	96 ± 2	96 ± 1
Co	Co(NO$_3$)$_2$.6H$_2$O	200	96 ± 2	98 ± 3
Cu	Cu(NO$_3$)$_2$.3H$_2$O	100	97 ± 1	95 ± 2
Ni	Ni(NO$_3$)$_2$.6H$_2$O	100	95 ± 2	96 ± 1
Zn	Zn in powder form	100	96 ± 2	102 ± 3

^{a} Mean ± standard deviation.

2.3. Sorption capacity

Sorption capacity is an important factor for evaluation of the adsorbent because it considers the quantity of sorbent required for the quantitative enrichment of Cd^{2+} and Pb^{2+} ions from a certain solution. To estimate the adsorption capacity of the MWCNTs, a batch procedure was performed. An aqueous solution (50 mL) containing 50 mg L^{-1} of Cd^{2+} or Pb^{2+} ions at pH 7.0 was prepared. This solution was added to 100 mg of MWCNT sorbent and then shaken for 5.0 min. The mixture was filtered and the supernatant solution was diluted to 100 mL. FAAS was used to detect both analytes. Adsorption capacity (q) (mg g^{-1}) was calculated using the following equation:

$$q = (C_i - C_f)V/m, \tag{1}$$

where C_i is the initial concentration of an analyte (mg L^{-1}), C_f is the final concentration (mg L^{-1}), m is the mass of the MWCNT adsorbent (g), and V is the volume of sample solution (L).[32-34]

The adsorption capacity of MWCNTs was 8.0 mg/g Cd^{2+} and 8.6 mg/g Pb^{2+}. Furthermore, the MWCNT sorbent was subjected to several loadings with the sample solution and subsequent elution. MWCNTs showed excellent stability and could be used for up to 50 adsorption elution cycles before losing the capability for the recovery of measurable quantities of both analytes.

2.4. Method validation

Using the optimized experimental conditions described above, a satisfactory linear relationship was obtained in the ranges of 1–50 and 1–60 μg/L with correlation coefficients of $R^2 = 0.9996$ and 0.9994 for Cd^{2+} and Pb^{2+}, respectively. The limits of detection (LODs) of the proposed method were 0.2 and 0.3 μg/L, and the limits of quantification (LOQs) were 0.63 and 1.0 μg/L for Cd^{2+} and Pb^{2+}, respectively. A preconcentration factor of

100 for both analytes was obtained as a ratio between the volume of the sample solution (200 mL) and the final volume (2.0 mL) obtained after the elution step. The reliability and precision of the method as the relative standard deviation (RSD%) were investigated by applying six replicate determinations of 30 μg/L of Cd^{2+} or Pb^{2+}, and RSD% values of the recoveries were found to be 3.2% and 2.8% for Cd^{2+} and Pb^{2+}, respectively, which indicates the good precision of the proposed method.

2.5. Analytical applications to environmental samples

We then tested the potential application of the proposed preconcentration method for the identification and separation of the studied analytes in real environmental water (tap, mineral, sea, and waste water) and food (cabbage, spinach, tomato, and hazelnut) samples. To determine the reliability of the method, the samples were spiked with known quantities of metal ions using the standard addition method. The percentages of analyte recovered from the spiked real sample and the RSD% values are presented in Tables 3 and 4. As indicated, the quantitative recoveries for the target analytes were good, in the range of 95%–102% with RSD% of <3.0%. These results show that the method is valid and therefore could be used with real environmental samples to separate, preconcentrate, and determine trace quantities of Cd^{2+} and Pb^{2+} in real samples.

Table 3. The results for the addition-recovery tests for Cd^{2+} and Pb^{2+} ions in water samples using the proposed SPE method (N = 3).

Analyte	Added	Tape water		Mineral water		Sea water		Waste water	
		Found[a]	Recovery	Found	Recovery	Found	Recovery	Found[a]	Recovery
	(μg L^{-1})	(μg L^{-1})	(%)	(μg L^{-1})	(%)	(μg L^{-1})	(%)	(μg L^{-1})	(%)
Cd(II)	0	<LOD	-	<LOD	-	2.2 ± 0.1	-	1.8 ± 01	-
	10	9.8 ± 0.7	98	10.1 ± 0.4	101	11.6 ± 0.2	95	12.1 ± 0.1	102
	20	19.4 ± 0.1	97	20.2 ± 0.3	101	21.4 ± 0.3	96	21.6 ± 0.2	99
	40	40.4 ± 0.2	101	39.2 ± 0.2	98	43.0 ± 0.4	102	41.0 ± 0.2	98
Pb(II)	0	<LOD	-	<LOD	-	1.6 ± 0.06	-	1.2 ± 0.05	-
	10	9.9 ± 0.1	99	9.6 ± 0.2	96	11.1 ± 0.3	96	11.4 ± 0.1	102
	20	19.6 ± 0.2	98	19.0 ± 0.1	95	22.0 ± 0.2	102	20.4 ± 0.2	96
	40	38.8 ± 0.3	97	38.4 ± 0.3	96	39.7 ± 0.4	95	41.6 ± 0.2	101

[a] Mean ± standard deviation.
[b] LOD: Limit of detection.

Additionally, this experimental solid phase extraction method has been used successfully for the estimation of Cd^{2+} and Pb^{2+} content in certified reference materials (CRMs) (TMDA-51.3 fortified water and SRM 1570A spinach leaves). The resulting values of recoveries derived by the developed SPE method were in good agreement with the certified values of the CRMs (Table 5). The application of the proposed SPE procedure to the environmental samples and CRMs indicates that this method shows high accuracy and reliability, is free from interference, and provides validation for the estimation of Cd^{2+} and Pb^{2+} ions at trace levels in real samples.

2.6. Comparison of the proposed SPE method with other SPE studies

A comparison of the developed method with some recent studies on Cd^{2+} and Pb^{2+} ion determination using SPE is provided in Table 6.[28−40] The proposed method shows good sensitivity, high adsorption capacity, lower

Table 4. The addition-recovery results for Cd^{2+} and Pb^{2+} ions in food samples using the proposed SPE method (N = 3).

Analyte	Added ($\mu g\ L^{-1}$)	Cabbage		Spinach		Tomato		Hazelnut	
		Found[a] ($\mu g\ g^{-1}$)	Recovery (%)	Found ($\mu g\ g^{-1}$)	Recovery (%)	Found ($\mu g\ g^{-1}$)	Recovery (%)	Found[a] ($\mu g\ g^{-1}$)	Recovery (%)
Cd(II)	0	<LOD	-	<LOD	-	<LOD	-	<LOD	-
	10	9.5 ± 0.3	95	10.2 ± 0.2	102	9.7 ± 0.2	96	10.0 ± 0.0	100
	20	19.0 ± 0.2	95	19.2 ± 0.4	96	19.6 ± 0.3	97	19.4 ± 0.2	97
	40	39.2 ± 0.5	98	40.8 ± 0.6	102	38.4 ± 0.4	96	38.4 ± 0.4	96
Pb(II)	0	<LOD	-	<LOD	-	<LOD	-	<LOD	-
	10	9.6 ± 0.1	96	9.7 ± 0.1	97	10.2 ± 0.3	102	9.6 ± 0.1	96
	20	19.4 ± 0.3	97	19.0 ± 0.3	95	20.4 ± 0.2	102	19.0 ± 0.3	95
	40	38.8 ± 0.4	97	40.0 ± 0.4	100	40.4 ± 0.4	101	39.2 ± 0.5	98

[a] Mean ± standard deviation.

[b] LOD: Limit of detection.

Table 5. The analysis results for certified reference materials after application of proposed procedure (N = 3).

Analyte	SRM 1570A spinach leaves			TMDA-51.3 fortified water		
	Certified value ($\mu g\ g^{-1}$)	Found[a] ($\mu g\ g^{-1}$)	Recovery, %	Certified value ($\mu g\ L^{-1}$)	Found[a] ($\mu g\ L^{-1}$)	Recovery, % Recovery, %
Cd^{2+}	2.89	2.78 ± 0.14	96	25.8	24 ± 1	95
Pb^{2+}	-	<LOD[b]	-	73.3	71 ± 2	97

[a] Mean ± standard deviation.

[b] LOD: Limit of detection.

LOD and higher PF that could be attributed to the large surface area, and rapid dynamics of extraction, which are the significant features of the developed method, which is comparable to or even better than other SPE methods with or without ligand or chelating agents.

2.7. Conclusions

The proposed method is new, simple, sensitive, effective, inexpensive, and suitable for the estimation of Cd^{2+} and Pb^{2+} ion contents in real food and water samples collected from Saudi Arabia with FAAS. The proposed SPE procedure is based on the use of MWCNTs as sorbents with the assistance of ultrasound, which improves the recovery, combined with a newly synthesized Schiff base (BCBATT) as a chelating reagent, which complexed with Cd^{2+} and Pb^{2+} ions at pH 7.0. The characterization of the ligand and metal complexes was performed by elemental analyses and IR and ^1H NMR spectral studies. Moreover, quantitative recovery, lower LODs, and a satisfactory preconcentration factor can be obtained by applying the proposed approach, which is superior to the other previous SPE methods described in the literature.

3. Experimental
3.1. Apparatus

To determine the analyte metals, an Agilent 55 AA atomic absorption spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA), equipped with a deuterium background correction, cadmium (228.8 nm) and lead (283.2

Table 6. Comparison of the proposed method with some recent SPE studies for the preconcentration of Cd^{2+} and Pb^{2+} ions prior to FAAS determination.

Adsorbent	Medium pH	Eluent (mol L^{-1})	PF/EF[a]	LOD[b] (ng mL^{-1})	Reference
MWCNTs/NBNBAEED	6	HNO$_3$ (3)	Cd^{2+} 60 Pb^{2+} 20	Cd^{2+} 0.25 Pb^{2+} 8.9	28
MWCNTs impregnated with tartrazine	7	HCl(2)	40	Cd^{2+} 0.8 Pb^{2+} 6.6	29
MWCNTs impregnated with TAR	7	CH3COOH (3)	15	Cd^{2+} 2.8 Pb^{2+} 7.2	31
MWCNTs impregnated with BTAO	7	HNO$_3$ (2)	100	Cd^{2+} 0.7 Pb^{2+} 2.6	32
MWCNT/PAN (sonication)	8	HNO$_3$ (2)	50	Cd^{2+} 0.3	33
MWCNTs/quinalizarin	6	HNO$_3$ (2)	100	Cd^{2+} 0.65 Pb^{2+} 0.6	34
MWCNTs modified with TETA	7	HNO$_3$ (3)	113	Cd^{2+} 0.3 Pb^{2+} 3.7	35
MWCNTs/α-benzoin oxime	6.5	HNO$_3$ (2)	50	Cd^{2+} 1.7 Pb^{2+} 5.5	36
Magnetic MWCNTs/APDC	4	HNO$_3$ (2)	-	Cd^{2+} 0.5 Pb^{2+} 0.6	37
ACC/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline	6	HNO$_3$ (3)	50	Cd^{2+} 1.7 Pb^{2+} 9.1	38
ACC/PAN	7	HNO$_3$ (3)	100	Cd^{2+} 1.1 Pb^{2+} 2.8	39
AC modified with TAR	6	HNO$_3$ (3)	143	Cd^{2+} 0.15 Pb^{2+} 2.03	40
MWCNTs/BCBATT/ultrasound-assisted	7	HNO$_3$ (2)	100	Cd^{2+} 0.2 Pb^{2+} 0.3	This work

[a] PF: Preconcentration factor; EF: enrichment factor.
[b] LOD: Limit of detection.
[c] MWCNTs: Multiwalled carbon nanotubes; ACC: activated carbon nanotubes; ACC: activated carbon cloth; AC: activated carbon; NBNBAEED: (E)-N1-(4-nitrobenzylidene)- N2-(2-((E)-4-nitrobenzylideneamino) ethyl) ethane-1,2-diamine; TAR: 4-(2-thiazolylazo)resorcinol; BTAO: 2-(2-benzothiazolylazo) orcinol; PAN: 1-(2-pyridylazo)-2-naphthol; TETA: triethylenetetramine; APDC: ammonium pyrrolidine dithiocarbamate; BCBATT: 5-benzyl-4-[(4-chlororbenzylidene)amine)-4H-1,2,4-triazole-3-thiol.

nm) hollow cathode lamps as radiation sources, and an air-acetylene flame burner, was used. The instrumental and operating conditions were set according to the manufacturer's instructions. An Adwa AD1000 pH-meter (Szeged, Hungary) equipped with a glass electrode was used for the measurement of pH values. An Innovative Ultra sonicator bath (Dwarka, Delhi, India) was used for sonication.

PerkinElmer FTIR 1600 (Waltham, MA, USA) and JEOL-JNM-LA400 spectrometers (Peabody, MA, USA) were used to record the IR and ^{1}H NMR spectra, respectively, of the synthesized BCBATT reagent. A Stuart SMP10 melting point apparatus (Cole-Parmer, Chelmsford, UK) was used to determine the melting point of the newly synthesized BCBATT reagent.

3.2. Chemicals and reagents

The chemicals used were obtained from Merck (Darmstadt, Germany). Deionized/bidistilled water (Millipore Milli-Q system) was used for the preparation of solutions. High-quality HNO_3 (65 m/m%), HCl (37 m/m%), and NH_3 (25 m/m%) solutions were used. Prior to use, all glassware was soaked in diluted HNO_3 solution (1:9 v/v) for cleaning and then rinsed with bidistilled water.

MWCNTs (purity >95%) measuring 10–30 μm in length and 20–30 nm in diameter, with surface area of 300 m^2/g and density of 2.1 g/mL, were obtained from Sigma-Aldrich (Milwaukee, WI, USA). To obtain a homogeneous dispersion before use, the prepared 5.0 mg/mL MWCNT suspension in deionized water was sonicated for 30 min. Polyvinylidene fluoride (PVDF) membrane Millex syringe filters with pore size of 0.45 μm and diameter of 33 mm were obtained from Sigma-Aldrich.
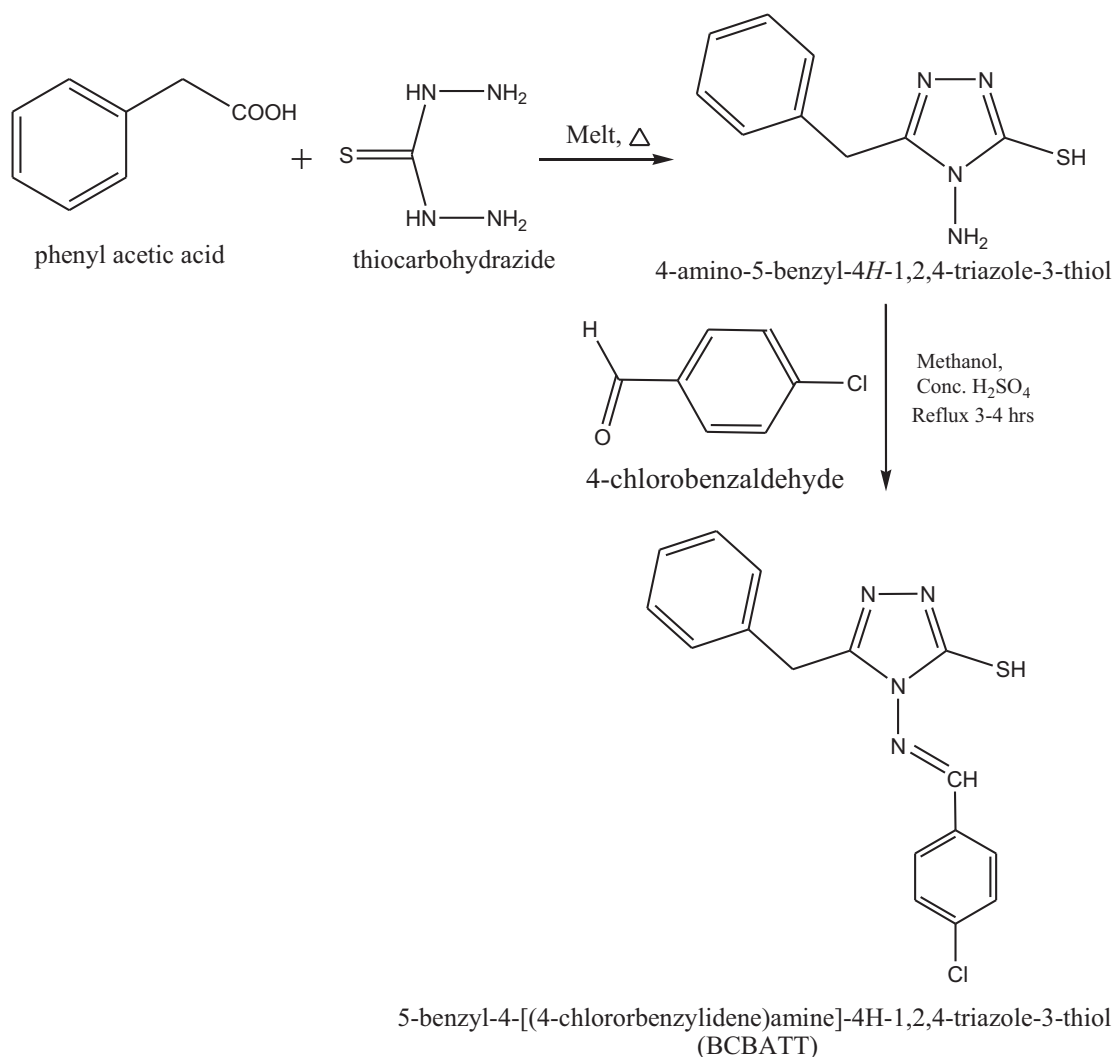
Stock solutions (1000 μg/mL) of the studied Cd^{2+} and Pb^{2+} ions were prepared from nitrate salts of high purity (Fluka Chemie AG, Basel, Switzerland). Diluted standard solutions were prepared by appropriate dilution of aliquots of the stock standard solutions daily with HNO_3 (1.0 mol/L).

To adjust the pH of the solutions, buffer solutions were used. An acetate buffer solution (CH_3COONa/CH_3COOH) at pH 3.75–5.75 was prepared by mixing appropriate volumes of sodium acetate solutions (2.0 mol/L) and acetic acid (2.0 mol/L). Phosphate buffer solutions (NaH_2PO_4/Na_2HPO_4) with pH values of 6.0 and 7.0 were obtained by mixing appropriate volumes of NaH_2PO_4 (1.0 mol/L) and Na_2HPO_4 (1.0 mol/L), respectively. By mixing certain volumes of ammonia (1.0 mol/L) and 1.0 mol/L NH_4Cl (1.0 mol/L) solutions, ammoniacal buffer solutions at pH values between 8.0 and 10 were prepared.[42]

TMDA-51.3 fortified water (National Water Research Institute, Environment Canada, Burlington, Canada) and spinach leaves (SRM 1570A) (National Institute of Standard Technology, Gaithersburg, MD, USA) were used as CRMs to test the accuracy of the developed method.

3.3. Synthesis of BCBATT Schiff base

To a suspension of 4-amino-5-mercapto-3-benzyl-1,2,4-triazole (20 mol) in absolute ethanol, an equimolar amount of p-chlorobenzaldehyde (20 mol) with 3.0 to 4.0 concentrated sulfuric acid drops were added. The reaction mixture was refluxed for 3.0–4.0 h. at 80–90 °C. The obtained precipitate was washed with cold ethanol, filtered, dried in a water bath, and recrystallized from the same solvent and dried under air (58% yields). It had a melting point of 150–152 °C.[43,44] The results of the elemental analysis of the synthesized BCBATT ($C_{16}H_{13}ClN_4S$; M.Wt. 328.82) were as follows (%): C, 58.44; H, 3.98; N, 17.04; S, 9.75 and found (%): C, 58.40; H, 3.95, N, 17.03.; S, 9.72. The synthetic pathway followed for the preparation of 5-benzyl-4-[(4-chlororbenzylidene) amine]-4H-1,2,4-triazole-3-thiol (BCBATT) Schiff base reagent is shown in the Scheme.

phenyl acetic acid   thiocarbohydrazide   4-amino-5-benzyl-4H-1,2,4-triazole-3-thiol

Melt, $\triangle$

4-chlorobenzaldehyde

Methanol,
Conc. H_2SO_4
Reflux 3-4 hrs

5-benzyl-4-[(4-chlororbenzylidene)amine]-4H-1,2,4-triazole-3-thiol
(BCBATT)

Scheme. Synthetic pathway for the preparation of BCBATT Schiff base reagent.

A stock solution (1.0×10^{-3} mol/L) of BCBATT was obtained by dissolving 0.039 g in 10 mL of ethanol in a 100-mL flask, which was topped up with ethanol.

3.4. Preparation of a syringe filter loaded with MWCNTs

An aliquot of 5.0 mL of MWCNT suspension (5.0 mg/mL) was passed through the syringe filter to prepare a filter loaded with MWCNTs and then HNO_3 (2.0 mol/L) solution and deionized water were passed through the filter to clean it. The desired pH values of the filter were adjusted by using buffer solutions before each use. During the elution step, the syringe filter was sonicated in an ultrasonic bath at room temperature.

3.5. Preconcentration procedure

Three milliliters of BCBATT (1.0×10^{-3} mol/L) solution was added to 100 mL of analyzed solutions including Cd^{2+} and Pb^{2+}. Then the pH was adjusted to 7.0 using a phosphate buffer solution. The sample solution was

passed into the syringe filter loaded by MWCNTs at a flow rate of 2.0 mL/min. Afterwards, 2.0 mL of HNO_3 solution (2.0 mol/L) with the flow rate of 2.0 mL/min was used to elute the adsorbed Cd^{2+} and Pb^{2+} ions. Through the elution step, the syringe filter was sonicated in an ultrasonic bath for 2.0 min at room temperature. The concentrations of Cd^{2+} and Pb^{2+} ions in the final eluent solution were estimated using FAAS.

3.6. Applications to real samples

3.6.1. Food samples

The experiment was repeated using different food samples obtained from Mecca city markets, Saudi Arabia. Food samples were dried to a constant weight in an oven at 80 °C. In a Teflon beaker, 10 mL of concentrated HNO_3 (65 m/m%) and 3 mL of H_2O_2 (30 m/m%) were used to digest 1.0 g of dried food sample or SRM 1570A spinach leaves, and the solution was evaporated to near dryness by heating for 2.0 h at 150 °C. Then 10 mL of deionized water was mixed with the samples after evaporation, and the resulting mixtures were filtered through the filter paper. The filtrates were completed to 50 mL with deionized water and stored in polyethylene bottles. The concentrations of Cd^{2+} and Pb^{2+} ions in final solutions were determined using FAAS.

3.6.2. Water samples

The experimental method was successfully applied to the sea, mineral, tap, and waste water samples obtained from Mecca and Jeddah, Saudi Arabia, and stored in polyethylene bottles. A cellulose membrane filter with a 0.45-μm pore size (Millipore) was used to filter the samples prior to acidifying them with HNO_3 (1.0 % v/v) and storing them at 4 °C. H_2O_2 (1.0 % v/v) and HNO_3 (65 % m/m) were used to oxidize the organic content of the water samples. Phosphate buffer solution was added to adjust the sample pH to 7.0. Then the preconcentration SPE procedure was completed as previously described. The same preconcentration SPE procedure was utilized for the CRM (TMDA-51.3 fortified water). The concentrations of Cd^{2+} and Pb^{2+} ions were evaluated by FAAS.

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